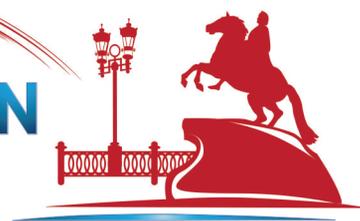




POLYCONDENSATION 2016



Russian
of Academy
of Sciences



A.N. Nesmeyanov Institute of
Organoelement Compounds RAS

INEOS

RSF | Russian
Science
Foundation



Federal
Agency of
Scientific
Organizations

Book of abstracts

Organizers

Aziz M. Muzafarov
Yakov S. Vygodskii

Scientific secretaries

Alexander S. Shaplov
Dmitry A. Sapozhnikov

Moscow - St. Petersburg, Russia
September 11-15, 2016



Sponsored by

The Organizing Committee of the **Polycondensation 2016** gratefully acknowledges the support of:



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A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)

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BUCHI Russia/CIS



Institute of new carbon materials and technologies (ЗАО «ИНУМИТ» - Институт новых углеродных материалов и технологий)

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POLYCONDENSATION 2016

September 11-15, 2016

A.N. Nesmeyanov Institute of Organoelement Compounds Russian academy of sciences (INEOS RAS)

<http://www.ineos.ac.ru/en/>

Moscow – St. Petersburg, Russia

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Forewords

Ernest Maréchal (1931-2016)

Former colleagues and all scientists involved in the field of polycondensation were deeply saddened to learn of the passing of Prof. Ernest Maréchal on January 9th 2016, at the age of eighty-four.

Ernest Maréchal was a graduate of Ecole Normale Supérieure (Cachan, France), with a degree in Physics (Agrégation). He received his Doctorate degree from the University of Paris in 1965, specializing in polymer chemistry, and was immediately appointed full Professor at the University of Rouen, where he created a research group involved in cationic polymerization and polycondensation.

In 1976, he moved to University Pierre-et-Marie-Curie, Paris (UPMC), where he developed extensive research studies on polycondensation catalysis mechanisms, on polymer chemical modification and on the synthesis and applications of a variety of block-copolymers, including polymers with polyamide, polyester, polysiloxane, polyether or polysulfone blocks. He collaborated widely with other eminent scientists in polymer science and established close relationships with the polymer industry. He was behind the discovery and development of thermoplastic elastomers now commercialized by Arkema under the trade name Pebax. His last research works were devoted to pioneering studies on enzymatic catalysis in polyesterification.

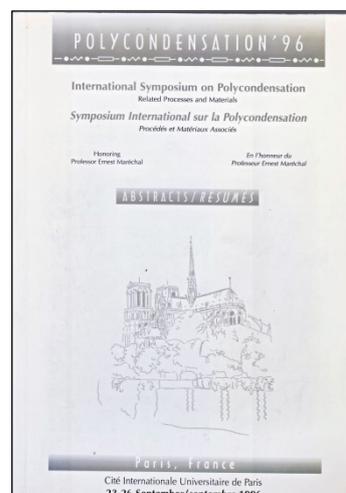
Ernest Maréchal is the author or coauthor of more than 300 research papers and has supervised more than 100 PhD studies. During his career, he acted as head of the Departments of Physical Chemistry and Macromolecular Chemistry of UPMC, President of the Polymer Division of the Société Chimique de France and President of the Molecular and Physical Chemistry Department of CNRS. He was also deeply involved in the activities of IUPAC Polymer Division as a Titular Member and of IUPAC Nomenclature and Terminology Commission. He received several scientific distinctions, among them the Silver Medal of CNRS, the Pierre Sue Great Prize and Lavoisier Medal of the Société Chimique de France.

Ernest was a great figure of polymer science, a leading scientist, a man of culture, full of humour, and a warm and faithful friend who will be sorely missed.

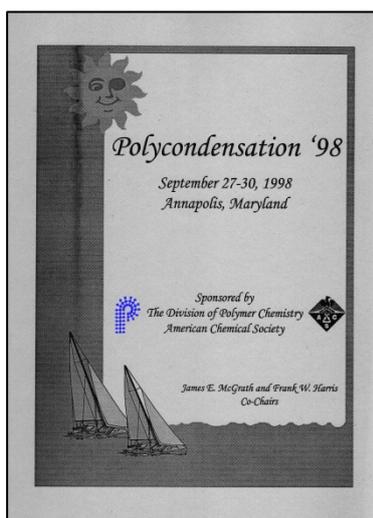
Twenty years ago, in September 1996, the first international congress specifically devoted to polycondensation was organized in his honor on his 65th birthday (Polycondensation 1996, Paris). This gave rise to a continuing series of successful congresses on the same topics, the 11th being held in Moscow and Saint-Petersburg in September 2016. On the next pages we would like to warmly remember these 20 years of the friendly meetings.



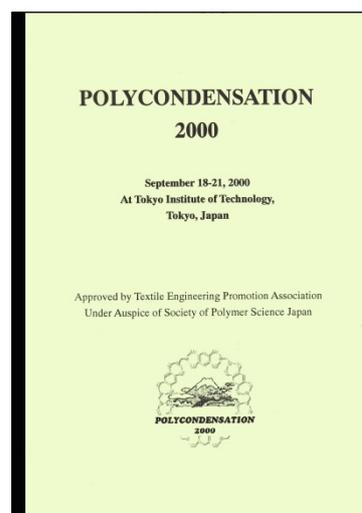
20 years later..



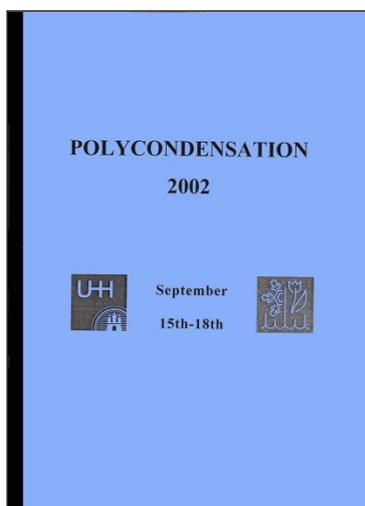
1996
(Paris, France)



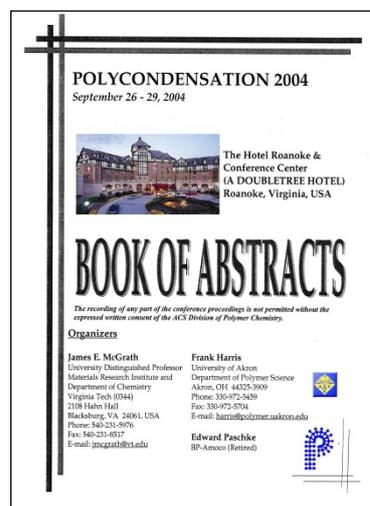
1998
(Annapolis, USA)



2000
(Tokyo, Japan)

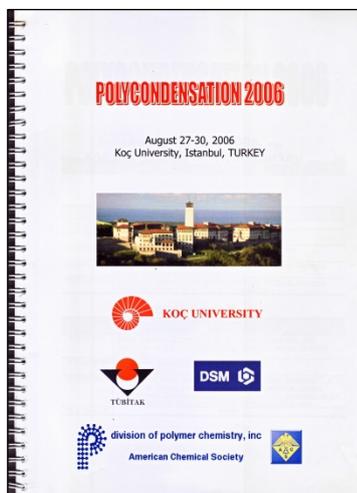


2002
(Hamburg, Germany)

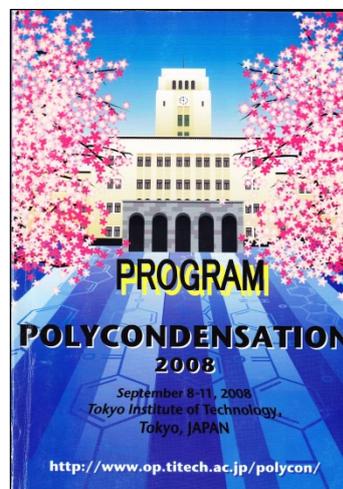


2004
(Roanoke, USA)

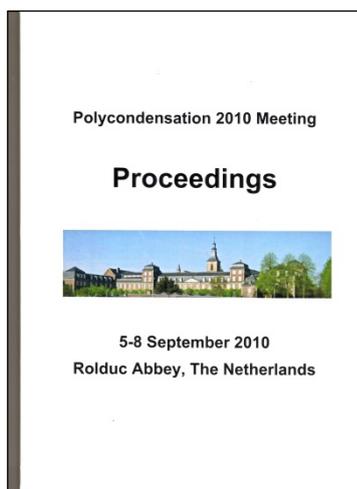
20 years later..



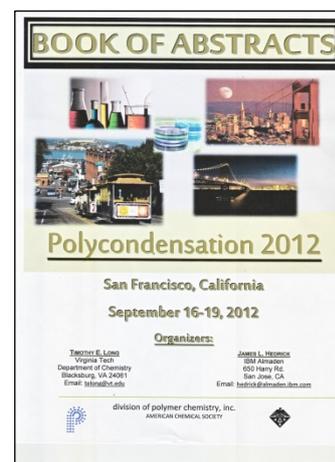
2006
(Istanbul, Turkey)



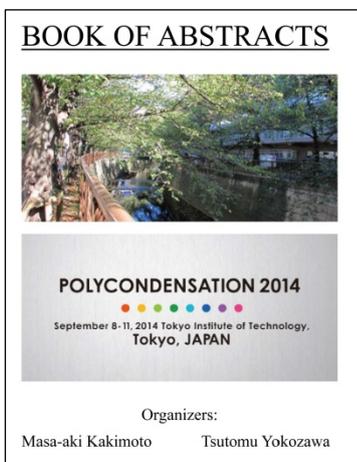
2008
(Tokyo, Japan)



2010
(Kerkrade, Netherlands)



2012
(San Francisco, USA)



2014
(Tokyo, Japan)



2016
(Moscow & St. Petersburg, Russia)

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Organizing Committee

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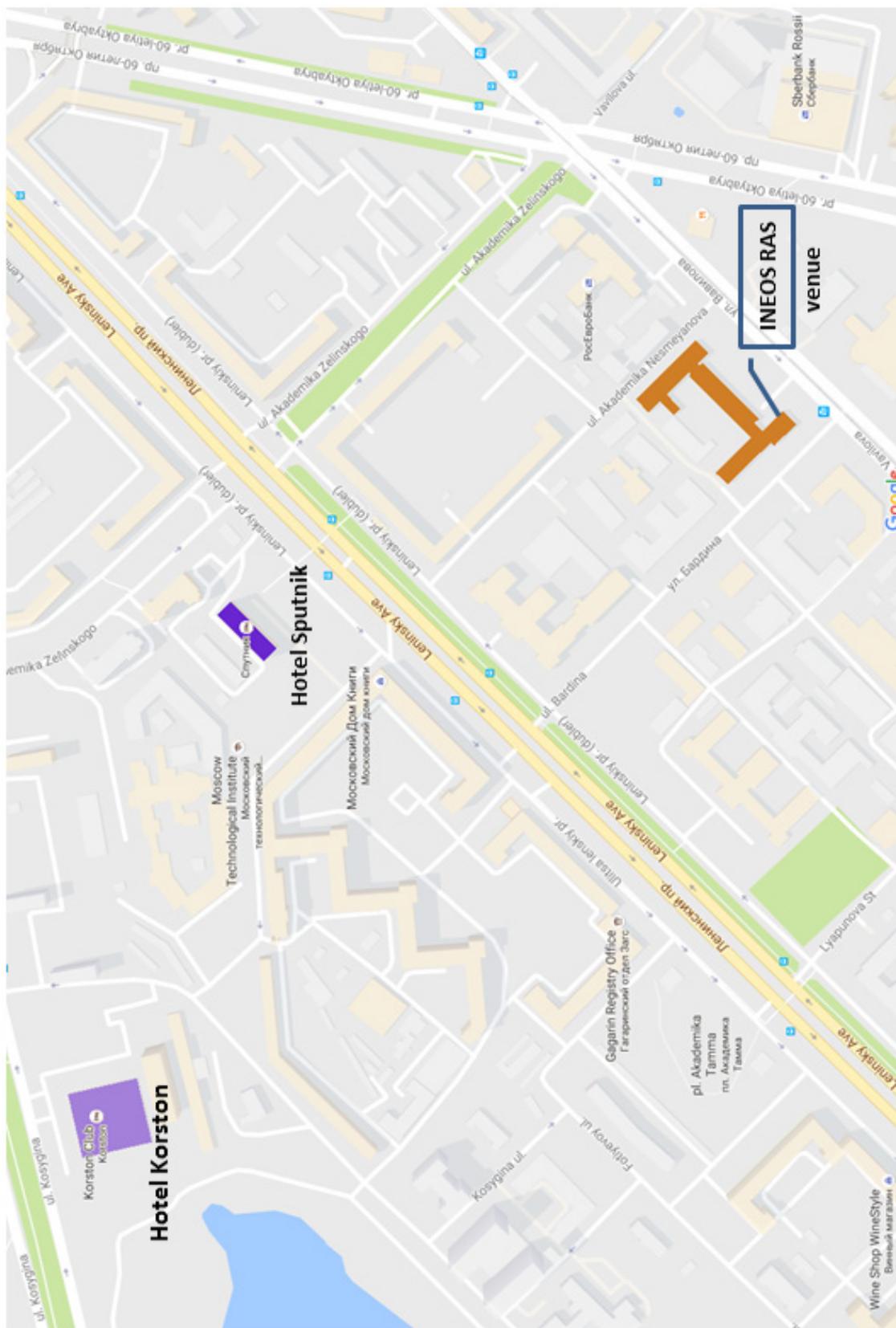
Brigitte Voit (Germany)

Tsutomu Yokozawa (Japan)

General Information

Venue

A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)
Vavilov str. 28, Moscow, Russia during **September, 11 – September, 13**



Congress sessions in St. Petersburg will be held at the Scientists Palace (Vladimir Palace)

Dvortsovaya naberezhnaya 26 (Palace Embankment, 26), St. Petersburg during **September, 14 – September, 15**



Access to the Conference venue

Participants should wear the identification badge collected at the Registration Desk during all conference sessions and events.

Language

The official language is English.

Registration

The POLYCONDENSATION 2016 Registration desk will be opened throughout the whole duration of the congress and will provide the following services:

- On-site registration.
- Handing of badges, conference kits and lunch tickets.
- General information about the conference, accommodation and social program.
- Tickets for the fast train "Sapsan" from Moscow to St. Petersburg (complimentary).
- Tourist information.

Certificate of attendance

Certificates of attendance for all participants will be available in electronic form on request by e-mail (polycon2016@gmail.com).

Для отметки и проставления печати в командировочных удостоверениях просим Российских участников обращаться на стойку регистрации.

Oral Presentations and Audio-Visual

Oral presentations must be in English. Presentations will be given in the Plenary rooms of INEOS RAS in Moscow and of Scientists Palace in St. Petersburg. A computer and LCD projector will be available for your use at the lecture room. There is a possibility to connect the private laptop to the LCD projector via HDMI or COM ports. **All speakers** including invited ones **will have 20 minutes** for presentation and final **5 minutes for questions**. Speakers are strongly recommended to contact the technical staff before the beginning of the session and must hand in their presentation for uploading at least 10 minutes before the beginning of their session or in the late afternoon of the day before, in case of early morning presentations. Please, bring your presentation on a USB flashdrive only. If you require special equipment, please, email your request to polycon2016@gmail.com no later than August 28th and we will do our best to accommodate.

Poster presentations

Poster session will be splitted in two sections: Moscow part and St. Petersburg part. Posters of the Moscow part will be exhibited in the two halls of INEOS RAS (at 3rd and 4th floors), while posters of the St. Petersburg part will be demonstrated in the grand hall of Scientists Palace. All posters must be displayed in English, on a board approximately of **A0 size (vertical arrangement)**. The code number for each poster, as published in the Final Program, will correspond on the label of the display board.

Suggested poster mounting times for Moscow part: 17:00 to 20:00 on Sunday, September, 11th; 10:00 to 17:00 on Monday, September, 12th.

Suggested poster mounting times for St. Petersburg part: 10:00 to 17:00 on Wednesday, September, 14th.

There will be two sessions of Poster presentation, during which at least one of the authors will have to attend:

Moscow session - Monday, September, 12th from 17:10 to 19:10

PM 1 to PM 45

St. Petersburg session - Wednesday, September, 14th from 17:10 to 19:10

PSP 1 to PSP 39

Publishing Opportunities

Authors are invited to submit their contributions presented during POLYCONDENSATION 2016 at the International Journals. The submission will start on September, 15 and will end at December, 31 2016. Details will be given by e-mail and described in the web site (<http://www.polycondensation2016.ac.ru/index.php/en/>) after the end of the congress.

Macromolecular Symposia

Wiley-VCH will publish a volume of *Macromolecular Symposia (Macromol. Symp.)* devoted to papers from Polycondensation 2016 conference. *Macromol. Symp.* presents state-of-the-art research articles in the field of macromolecular chemistry and physics. *Macromol. Symp.* is a member of Macromolecular family journals and relates to high-quality venue for authors (**IF = 0.913**) and an excellent resource for researchers. All submitted contributions are peer-reviewed to ensure a high quality of published manuscripts. Accepted articles will be typeset and published **as online publication** at Wiley Online Library, thereby guaranteeing an immediate international dissemination.

High Performance Polymers journal

SAGE Publications will devote a special issue of the *High Performance Polymers journal (High Perform. Polym.)* to the selected papers from Polycondensation 2016 congress. *High Perform. Polym.* relates to the highly ranked journals (**IF = 1.045**), publishing polymer science and technology. With a principal focus on molecular structure/processability/property relationships of high performance polymers. Applications of particular interest include composite matrices, coatings, adhesives, fibres, films, membranes and active polymers for potential use in sectors such as aerospace, chemicals, energy electronics and transportation. All submitted contributions are peer-reviewed to ensure a high quality of published manuscripts. Accepted articles will be published both **as online and printed forms**.

Coffee breaks (complimentary)

Coffee breaks will be served in the 420 room according to the time schedule.

Lunches (complimentary for foreign participants)

Lunches will be served at the restaurant of Hotel Sputnik (Leninsky prospect, 38) within 10 minutes walking distance from the conference venue according to the time schedule.

Recommended places for lunch for Russian participants:

INEOS RAS canteen (столовая ИНЭОС РАН).

IOС RAS canteen (столовая ИОХ РАН).

Chernomorskaya Rivyera restaurant (Черноморская Ривьера, проспект 60-ия Октября, 8А).

Atrium restaurant (Атриум, Ленинский проспект, 44).

Pizza Amore (Пиццерия Аморэ, Ленинский проспект, 43).

Aozora restaurant (гостиница «Спутник», Ленинский проспект, 38).

Exhibition

During the Polycondensation 2016 Symposium ample space (lobby at the 3rd and 4th floors of INEOS RAS and lobby of the Grand Hall at Scientist Palace) will be dedicated to an exhibition of technical equipments and advertising by Companies. The exhibition will be opened throughout the whole duration of the congress.

Internet Service

Wireless internet connection will be available throughout the conference site at INEOS RAS to all attendants. The WiFi login will be: **polycon2016** password: **polycon2016**

Transfer to St. Petersburg

Attention to all participants: after checking out from your hotel on Tuesday's morning (September, 13) please **DO NOT** leave your luggage at the hotel, instead, please, bring it with you to INEOS RAS. The storage room will be provided. This will facilitate the buses boarding.

- Buses will be available for all conference participants at 18:10 (Tuesday, September, 13) from INEOS RAS venue to Leningradsky Railway station (complimentary).
- The fast train "Sapsan" departs at 19:40 from Leningradsky Railway station in Moscow (Leningrad station, Moscow, Komsomolskaya square, 5/43) and arrives at 23:30 at Moscow Railway station in St. Petersburg (Moscow station, St. Petersburg, Nevsky Prospect, 85).
- Buses will be available for all conference participants to transfer them from Moscow Railway station in St. Petersburg to their hotels in St. Petersburg (complimentary).

Social Program

The Organizing Committee warmly invites you to take part in the social program during your stay in Moscow and St-Petersburg.

Sunday, September 11

The Polycondensation 2016 opening ceremony will be held at INEOS RAS. After the scientific program at 18:30 a Welcome cocktail party will be served at the INEOS's ground floor (complimentary).

Monday, September 12

Moscow boat sightseeing tour is the most relaxing and picturesque tour that Moscow can offer. All participants are invited to Moscow river cruise to see the city center and its main attractions (complimentary for all participants). The busses will depart from INEOS venue at 19:40 and bring the participants to the river pier. After river cruise the busses will be available to bring participants back to their hotels.

Tuesday, September 13

Guided tour to the Tretyakov Art gallery (available free for **accompanying persons**). The details will be served at the Registration Desk.

Thursday, September, 15

Tour with excursion to the amazing Peterhof by Meteor hydrofoil (complimentary for all participants). The busses will depart from Scientist Palace venue at 14:00 and will bring the participants to the river pier. After the tour the busses will be available to bring participants back to their hotels.

Awards

The Conference Organizing Committee on the occasion of 20th Anniversary (the 11th edition) of the Polycondensation Conferencies is proud to establish three Awards. One Award named after Vasiliy Korshak and one Award named after Ernest Maréchal will be assigned to the young scientists. One special Award named after Vasiliy Korshak will be handed to the scientist who has made a special contribution to polycondensation.

The purpose of the Awards is to celebrate the recognition by the scientific community of the scientists who present brilliant and innovative results, making an important contribution in the field of polycondensation.

Conference Timetable

Start	End	September, 11 (Sunday)	September, 12 (Monday)	September, 13 (Tuesday)	September, 14 (Wednesday)	September, 15 (Thursday)
9:00	9:35		Registration			
9:35	10:00		IL 2-03 C. Koning	IL 3-09 T. Matsumoto	IL 4-15 B. Voit	IL 5-21 C. Bielawski
10:00	10:25		IL 2-04 Y. Nabae	IL 3-10 U. Scherf	IL 4-16 K. Kimura	IL 5-22 M. Jikei
10:25	10:50		IL 2-05 R. Tiger	IL 3-11 S. Ando	IL 4-17 A. Yakimansky	IL 5-23 P. Banet
10:50	11:10		Break	Break	Break	Break
11:10	11:35		IL 2-06 T. Kaneko	IL 3-12 D. Mecerreyes	IL 4-18 M. Ueda	OC 5-22 X. Fang
11:35	12:00		IL 2-07 P. Troshin	IL 3-13 A. Lachinov	IL 4-19 T. Yangirov	OC 5-23 B. Zaitsev
12:00	12:25		IL 2-08 Y. Kudryavtsev	IL 3-14 V. Boyko	IL 4-20 A. Didenko	OC 5-24 G. Tu
12:25	13:55		Lunch	Lunch	Lunch	OC 5-25 A. Gubarev
						Analit A. Zhiltsov
						Closing ceremony
13:55	14:20		OC 2-01 Y. Shibasaki	OC 3-08 L. Alexandrova	OC 4-15 A. Sanchez-Sanchez	Lunch
14:20	14:45		OC 2-02 S. Lingier	OC 3-09 E. Potaenkova	OC 4-16 C. Duval	St. Petersburg Excursion
14:45	15:10		OC 2-03 A. Kuznetsov	OC 3-10 I. Blagodatskikh	OC 4-17 S. Morozova	
15:10	15:35		OC 2-04 S. Rimdusit	OC 3-11 C. Colin	OC 4-18 L. Fan	
15:35	15:55	Break	Break	Break		
15:55	16:20	OC 2-05 K. Brigadnov	OC 3-12 S. Chesnokov	OC 4-19 M. Capelot		
16:20	16:45	OC 2-06 A. Hufendiek	OC 3-13 R. Saint-Loup	OC 4-20 G. Summers		
16:45	17:10	OC 2-07 M. Zaytseva	OC 3-14 A. Zhansitov	OC 4-21 L. Jacobs		
17:10	17:30	Opening ceremony A. Muzafarov Y. Vygodskii	Poster session		Poster session	
17:30	17:55	IL 1-01 H. Kricheldorf				
17:55	18:20	IL 1-02 I. Ponomarev				
18:20	19:10	Welcome cocktail party	Moscow Excursion	Transfer to the railway station		
19:30				Train to St. Petersburg		Grand dinner
	20:20					
	22:00					
	23:30					

IL – Invited lectures, OC - Oral contributions.

Scientific Program

Sunday, September 11, 2016

Time		Lecture No.	Title	Speaker	Page
16:20	17:10	<i>Registration</i>			
17:10	17:30	Opening ceremony		A. Muzafarov, Y. Vygodskii	
Sunday Afternoon Session 17:30 – 18:20, Chair A. Muzafarov					
17:30	17:55	IL 1-01	Cyclization and dispersity of polyesters	H. Kricheldorf	27
17:55	18:20	IL 1-02	New trends in polyheteroarylenes synthesis, properties and application	I. Ponomarev	28
18:20	20:20	Welcome cocktail party			

Scientific Program

Monday, September 12, 2016

Time		Lecture No.	Title	Speaker	Page
9:00	9:30	Registration			
Monday V. Korshak's Session 9:30 – 10:50, Chair V. Vasnev					
9:35	10:00	IL 2-03	Novel renewable polyesterimide-based alkyd resins for coating applications	C. Koning	29
10:00	10:25	IL 2-04	Application of aromatic polymers to heterogeneous catalysis	Y. Nabaе	30
10:25	10:50	IL 2-05	Green chemistry of polyurethanes	R. Tiger	31
10:50	11:10	Coffee break			
Monday Morning Session 2 11:10 – 12:25, Chair M. Kakimoto					
11:10	11:35	IL 2-06	Transparent but ultrastrong plastics derived from amino acid	T. Kaneko	32
11:35	12:00	IL 2-07	Low band gap (X-DADAD) _n type copolymers for stable and efficient bulk heterojunction organic solar cells	P. Troshin	33
12:00	12:25	IL 2-08	Modeling of interfacial polycondensation: the kinetics and polymer film structure	Y. Kudryavtsev	34
12:25	13:55	Lunch			
Monday Afternoon Session 1 13:55 – 15:35, Chair D. Mecerreyes					
13:55	14:20	OC 2-01	Segregated block copolymers based on aramide molecule with polyether	Y. Shibasaki	50
14:20	14:45	OC 2-02	Rigid polyesters and polycarbonates from renewable ketal monomers	S. Lingier	51
14:45	15:10	OC 2-03	Control of chain microstructure in catalytic synthesis of copolyimides	A. Kuznetsov	52
15:10	15:35	OC 2-04	Highly filled systems of graphite/graphene in polybenzoxazine for bipolar plate in proton exchange membrane fuel application	S. Rimdusit	53
15:35	15:55	Coffee break			
Monday Afternoon Session 2 15:55 – 17:10, Chair R. Tiger					
15:55	16:20	OC 2-05	Flame retardant epoxy resins modified with epoxyphosphazenes	K. Brigadnov	54
16:20	16:45	OC 2-06	A lignin-derived chemical platform for biobased polymers via ADMET	A. Hufendiek	55
16:45	17:10	OC 2-07	Effect of zinc oxide nanoparticles characteristics epoxy polymer active media	M. Zaytseva	56
17:10	19:10	Poster session			
19:30	22:00	Moscow excursion			

Scientific Program

Tuesday, September 13, 2016

Time		Lecture No.	Title	Speaker	Page
9:00	9:35	<i>Registration</i>			
Tuesday Morning Session 1 9:35 – 10:50, Chair Y. Kudryavtsev					
9:35	10:00	IL 3-09	Highly transparent alicyclic polyimide films fabricated at low temperature	T. Matsumoto	35
10:00	10:25	IL 3-10	Microporous polymer networks made in transition metal-free polycondensation and polyaddition schemes	U. Scherf	36
10:25	10:50	IL 3-11	A comprehensive study on anisotropic thermal expansion behaviors of crystal lattice of aromatic polyimides analyzed by VT-WAXD	S. Ando	37
10:50	11:10	<i>Coffee break</i>			
Tuesday Morning Session 2 11:10 – 12:25, Chair X. Fang					
11:10	11:35	IL 3-12	Innovative redox polymers for electrochemical energy storage	D. Mecerreyes	38
11:35	12:00	IL 3-13	Promising electronic properties of thin polyarylenephthalide films and heterostructures based on them	A. Lachinov	39
12:00	12:25	IL 3-14	Synthesis and properties of some new fluorinated monomers	V. Boyko	40
12:25	13:55	<i>Lunch</i>			
Tuesday Afternoon Session 1 13:55 – 15:35, Chair A. Kuznetsov					
13:55	14:20	OC 3-08	Processable polyimides and polybenzimidazoles: synthesis and their application for gas separation	L. Alexandrova	57
14:20	14:45	OC 3-09	CAGE diamines – perspective monomers for polycondensation polymers	E. Potaenkova	58
14:45	15:10	OC 3-10	Self-polycondensation of telechelic polyvinylalcohol and design of rigid macroporous sorbents for biomedical application	I. Blagodatskikh	59
15:10	15:35	OC 3-11	Synthesis and characterization of new silicone/polyurethane materials	C. Colin	60
15:35	15:55	<i>Coffee break</i>			
Tuesday Afternoon Session 2 15:55 – 17:10, Chair S. Ando					
15:55	16:20	OC 3-12	Composite materials with intertwining carcass structure polyurethane - polydimethacrylate	S. Chesnokov	61
16:20	16:45	OC 3-13	Isosorbide: a biobased building block to improve polycondensate properties	R. Saint-Loup	62
16:45	17:10	OC 3-14	Development of technology of polysulfone production for 3D printing	A. Zhansitov	63
17:30	19:30	Transfer to the railway station			
19:40	23:50	Train to St. Petersburg			

Scientific Program

Wednesday, September 14, 2016

Time		Lecture No.	Title	Speaker	Page
9:00	9:35	<i>Registration</i>			
Wednesday Morning Session 1 9:35 – 10:50, Chair M. Ueda					
9:35	10:00	IL 4-15	Highly aromatic hyperbranched and linear polymers designed for film applications in opto-electronics	B. Voit	41
10:00	10:25	IL 4-16	Conversion of PET to aromatic polymers by using reaction-induced crystallization	K. Kimura	42
10:25	10:50	IL 4-17	Polyimide-based materials for physical and biomedical applications	A. Yakimansky	43
10:50	11:10	<i>Coffee break</i>			
Wednesday Morning Session 2 11:10 – 12:25, Chair A. Tenkovtsev					
11:10	11:35	IL 4-18	Polymer electrolyte membranes based on aromatic polymers with sulfonic acid via long alkyl side chains	M. Ueda	44
11:35	12:00	IL 4-19	Polyarylendiphthalides – a new class of phthalide-type polyheteroarylenes	T. Yangirov	45
12:00	12:25	IL 4-20	Multiblock (segmental) copolyurethaneimides and copolyurethaneamideimides	A. Didenko	46
12:25	13:55	<i>Lunch</i>			
Wednesday Afternoon Session 1 13:55 – 15:35, Chair B. Voit					
13:55	14:20	OC 4-15	Synthesis and characterization of sustainable copolymers PET-CO-PLLA	A. Sanchez-Sanchez	64
14:20	14:45	OC 4-16	Thermal properties of biobased aliphatic polyesters reveal odd-even effect	C. Duval	65
14:45	15:10	OC 4-17	Condensation derived poly(ionic liquid)s	S. Morozova	66
15:10	15:35	OC 4-18	Preparation of fluorinated polyimides with bulky structure and their gas separation performance correlated with microstructure	L. Fan	67
15:35	15:55	<i>Coffee break</i>			
Wednesday Afternoon Session 2 15:55 – 17:10, Chair P. Banet					
15:55	16:20	OC 4-19	Rilsan® HT, the first flexible high temperature polyamide	M. Capelot	68
16:20	16:45	OC 4-20	Engineering polymers mediated by functionalized 1,1-diphenylethylene derivatives: polymer substrates for membrane development	G. Summers	69
16:45	17:10	OC 4-21	Nanomedicine for efficient chemotherapy of brain tumours: From bench to bedside	L. Jacobs	70
17:10	19:10	<i>Poster session</i>			
19:30	22:00	Grand dinner			

Scientific Program

Thursday, September 15, 2016

Time		Lecture No.	Title	Speaker	Page
9:00	9:35	Registration			
Thursday Morning Session 1 9:35 – 10:50, Chair A. Didenko					
9:35	10:00	IL 5-21	Post-polymerization modification through direct C–H functionalization	C. Bielawski	47
10:00	10:25	IL 5-22	Synthesis and healing properties of poly(arylether)-poly(alkylthioether) multiblock copolymers containing disulfide bonds	M. Jikei	48
10:25	10:50	IL 5-23	Solvent-free synthesis of poly(bismaleimide)s	P. Banet	49
10:50	11:10	Coffee break			
Thursday Morning Session 2 11:10 – 12:40, Chair C. Bielawski					
11:10	11:35	OC 5-22	Synthesis and characterization of novel asymmetric polyimides containing phthalimide-naphthalimide moieties	X. Fang	71
11:35	12:00	OC 5-23	Combination of the processes of polymerization and polycondensation type in synthesis, chemical modification and cure of rolivsan thermosetting resins	B. Zaitsev	72
12:00	12:25	OC 5-24	Highly selective coupling reactions toward chlorine-containing electroluminescence polymers	G. Tu	73
12:25	12:50	OC 5-25	Flow birefringence and film birefringence of poly[1,3-bis(3',4'-dicarboxy-phenoxy)benzene 4,4'-bis(4''-N-phenoxy)-diphenylsulfone]imide	A. Gubarev	74
12:50	13:15	Analit	Molecular weight parameters evaluation by means of GPC: advantages of tripple detection based on Shimadzu and PSS equipment	A. Zhiltsov	
13:15	13:30	Closing ceremony			
13:30	14:20	Lunch			
14:20	17:55	St. Petersburg excursion			

Poster Program

Poster session Moscow, Monday, September 12, 2016

Poster no.	Title	Author	Organization	Country
PM 1	Preparation and properties of a polymer containing isocyanurate gradient material based trifunctional polyether	E.S. Afanasyev	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PM 2	Synthesis of new partially crystalline (co)polyimides	A.E. Alexandrova	N.S. Enikolopov Institute of Synthetic Polymeric Materials Russian Academy of Sciences (ISPM RAS)	Russia
PM 3	Organoelement fire resistant coatings for synthetic fibers	A.A. Amelichev	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PM 4	Electron attachment to the phthalide molecule	N.L. Asfandiarov	Institute of Molecule and Crystal Physics, Ufa Research Center of RAS	Russia
PM 5	Laser-induced formation of silver nanoparticles in polybenzimidazole matrix	V.F. Burdukovskii	Baikal Institute of Nature Management SB RAS Buryat State University	Russia
PM 6	Effect of the chemical structure of the photochromic component on the electrical performance of organic memory elements	D.D. Dashitsyrenova	Institute of Problems of Chemical Physics Russian Academy of Sciences (IPCP RAS)	Russia
PM 7	Ferrocene-containing polychalkones as precursors for magnetic nanomaterials	R.A. Dvorikova	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PM 8	Influence of the thickness of nanometer film on the conducting polymer/polymer interface	R.M. Gadiev	Bashkort State Pedagogical University	Russia
PM 9	Synthesis of sequence – ordered copolyarylenphthalide having periodic structure with diphenyloxide and diphenylsulfide links in basic chain	N.G. Gileva	Ufa Institute of Chemistry Russian Academy of Sciences (UIC RAS)	Russia
PM 10	Poly-ether-ether-ketone (PEEK). Influence of residual solvent on the material properties	V.M. Gurenkov	Joint-stock company "Institute of plastics named after Petrov G.S."	Russia
PM 11	The effects of synthesis parameters on the microstructure of hyperbranched polyesters	B.Sh. Hadavand	Department of Resin and Additives, Institute for Color Science and Technology	Iran
PM 12	Flame retardancy and mechanical	S.M. Hong	Center for Materials	Republic of

	properties of polyamide 6 with melamine polyphosphate and ionic liquid surfactant-treated montmorillonite		Architecturing, Korea Institute of Science and Technology	Korea
PM 13	A lignin-derived chemical platform for biobased polymers via ADMET	A. Hufendiek	Ghent University, Polymer Chemistry Research Group	Belgium
PM 14	ESR spectroscopy and cyclic voltammetry as a highly sensitive methods for determination of the intrinsic stability of conjugated polymers	L.N. Inasaridze	Institute of Problems of Chemical Physics Russian Academy of Sciences (IPCP RAS)	Russia
PM 15	Photovoltaic performance of some conventional and innovative fullerene- and polymer-based photoactive materials	O.V. Istomina	Institute of Problems of Chemical Physics Russian Academy of Sciences (IPCP RAS), FOMaterials LTD	Russia
PM 16	Amphiphilic branched copoly lactides	V.V. Istratov	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PM 17	Acrylonitrile-butadiene rubber-modified polybenzoxazine for brake pads application	Ch. Jubsilp	Srinakharinwirot University, Department of Chemical Engineering, Faculty of Engineering	Thailand
PM 18	Hydrolytic polycondensation of organoalkoxysilanes under pressure	A. Kalinina	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS), Enikolopov Institute of Synthetic Polymeric Materials of RAS	Russia
PM 19	Fluorinated binder for microelectronics	S. Kazakov	Joint-stock company "Institute of plastics named after Petrov G.S."	Russia
PM 20	A new anion exchange resin for selective sorption of heavy metal ions	K.Kh. Khakimbatova	Institute of Chemical Sciences named after A.B. Bekturov	Republic of Kazakhstan
PM 21	Green chemistry – a new approaches to the synthesis of redox polymers suitable as sorbents	K.Kh. Khakimbatova	Institute of Chemical Sciences named after A.B. Bekturov	Republic of Kazakhstan
PM 22	Functional composites based on polybenzimidazoles and graphene	B.Ch. Kholkhoeva	Buryat State University, Baikal Institute of Nature Management SB RAS	Russia
PM 23	Branched oligophenylenes with phenylene ethynylene fragments for optoelectronics	I.A. Khotina	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia

PM 24	Cascade hydrolytic polycondensation of organochlorosilanes at non-aqueous media – a new point of view on synthesis of polysiloxanes	A.A. Kondrashova	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS), Moscow technology university	Russia
PM 25	Microporous materials based on the polyphenylene matrix	A.I. Kovalev	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PM 26	High molecular weight processable and thermally stable poly(cyclo)acetals	S. Lingier	Ghent University	Belgium
PM 27	Influence of inductive and steric effect under the polycondensation aryl(hydroxy)cyclotetrasiloxane isomers leading to the formation of the stereoregular cycloliner polyorganosilsesquioxanes in the presence of layered-architecture	N.N. Makarova	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PM 28	Through-space electronic interactions in the design of novel acceptor materials with reduced electron affinity for fullerene/polymer solar cells	A.V. Mumyatov	Institute for Problems of Chemical Physics Russian Academy of Sciences (IPCP RAS)	Russia
PM 29	New approach to use thin polymer film as a detector of phase transition in metals	I.R. Nabiullin	M. Aknulla Bashkir State Pedagogical University	Russia
PM 30	Improved photovoltaic performance of organic thin-film solar cells (OSCs) with Urchin-like gold nanoparticles (UL-AuNPs)	A. Pangdam	Niigata University, Graduate School of Science and Technology	Japan
PM 31	Polymer gradient materials based on poly(epoxy isocyanurate) networks: chemical structure and its influence on the properties	M.D. Petunova	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PM 32	Tuning the optoelectronic and photovoltaic properties of conjugated polymers (-X-DADAD-)n by using different acceptor (A) units	F.A. Prudnov	Institute for Problems of Chemical Physics Russian Academy of Sciences (IPCP RAS)	Russia
PM 33	Synthesis and applications of poly(N-phenylenebenzimidazoles)	D.Y. Razorenov	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PM 34	Synthesis and properties of new poly(arylene thiophenes)	E.N. Rodlovskaya	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia

PM 35	Effect of polymers chemical structure on the membrane characteristics	I.A.Ronova	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PM 36	Effect of ionic liquids with thiocyanate anion on epoxy-rubber composition curing rheokinetics	O.I. Sidorov	FSUE "FCDT "Soyuz"	Russia
PM 37	Carbon nanofiber paper based on heterocyclic polymers for high temperature polymer electrolyte membrane fuel cells	K.M. Skupov	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PM 38	High performance polymer/ fullerene solar cells processed from environment-friendly non-halogenated solvent	D.K. Susarova	Institute for Problems of Chemical Physics, Russian Academy of Sciences (ICPC RAS)	Russia
PM 39	Novel TTBTBTT-based copolymers for organic solar cells designed using Suzuki and Stille polycondensation reactions	D.K. Susarova	Institute for Problems of Chemical Physics, Russian Academy of Sciences (ICPC RAS)	Russia
PM 40	Electrolyte membrane based on silica-containing copolymer for lithium batteries	M.B. Umerzakova	Institute of Chemical Sciences	Republic of Kazakhstan
PM 41	Synthesis of reactive oligoimides by thermichemical cyclization in the presence of alkyltriethoxysilane-trialkylamine	A.V. Ustimov	N.S. Enikolopov Institute of Synthetic Polymeric Materials Russian Academy of Sciences (ISPM RAS)	Russia
PM 42	Cryopolycondensation of poly(dimethylsiloxane) with tetraethoxysilane in the medium of moderately-frozen benzene	O.O. Vasilieva	Moscow Technological University (MIREA)	Russia
PM 43	Synthesis of polyurethanes in macroporous polymer matrix	V.V. Yudin	G.A. Razuvaev Institute of Organometallic Chemistry Russian Academy of Sciences (IOMC RAS)	Russia
PM 44	The influence of oxygen on the charge carriers transport in thin films of poly(difenylphenalide)	A.R. Yusupov	M. Akmullah Bashkir State Pedagogical University	Russia
PM 45	Poly(3-hydroxybutyrate) and its blends with polyethylene glycol – high potential materials for tissue engineering	V.A. Zhuikov	A.N. Bach Institute of Biochemistry Russian Academy of Sciences (INBI RAS) Lomonosov Moscow State University	Russia
PM 46	Synthesis of bisphenols containing pendant furyl group based on chemicals derived from lignocellulose and their utilization for preparation of clickable aromatic polyesters	S.S. Kuhire	CSIR-National Chemical Laboratory	India

Poster Program

Poster session St. Petersburg, Wednesday, September 14, 2016

Poster no.	Title	Author	Organization	Country
PSP 1	Synthesis and investigation of aromatic (co)polyamides and their application in the optical fibre technology	B.A. Bayminov	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PSP 2	Development of a new masterbatch system containing chain extenders for poly(ethylene terephthalate)	D. Berg	DWI – Leibniz-Institute for Interactive Materials e. V. , Institute for Technical and Macromolecular Chemistry (ITMC), RWTH Aachen University	Germany
PSP 3	Controllable surface imprinting on silica-gel via Atom Transfer Radical Polymerization for S-1-(1-naphthyl) ethylamine recognition	N.Bing	Shanghai Polytechnic University, School of environmental and materials engineering	China
PSP 4	Renewable citrimides as building block for polyesters	P. Buijsen	DSM Coating Resins	Netherlands
PSP 5	Synthesis and properties of transparent polyimides derived from dianhydrides containing cyclohexane unit	G. Chen	Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences	China
PSP 6	Dilute solution properties of polyetherimide via hydrodynamics study	A.S. Gubarev	St. Petersburg State University	Russia
PSP 7	Preparation and characterization of transparent polyimide hybrid films with low thermal expansion coefficient	M. He	Institute of Chemistry Chinese Academy of Sciences, Laboratory of Advanced Polymer Materials	China
PSP 8	Microwave synthesis of the polyfluorenes. OLEDs with stable blue electroluminescence	D.M. Ilgach	Institute of Macromolecular Compounds Russian Academy of Sciences (IMC RAS)	Russia
PSP 9	Biobased monomers from the furanic platform in polyesters	N. Jaquel	Roquette Frères, Polymer Chemistry Department	France
PSP 10	Surface properties of pyridylphenylene dendrimers	I.Yu. Krasnova	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PSP 11	Multicenter polyester initiators for preparation of graft copolymers with oligo(2-ethyl-2-oxazoline) side chains.	M.P. Kurlykin	Institute of Macromolecular Compounds Russian	Russia

			Academy of Sciences (IMC RAS)	
PSP 12	The hydrodynamic properties of hyperbranched pyridylphenylene polymer solutions	E.V. Lebedeva	St. Petersburg State University	Russia
PSP 13	Amphiphilic diblock copolymers based on poly(3-hexylthiophene)	B. Lee	Korea Advanced Institute of Science and Technology, Department of Chemistry	Korea
PSP 14	Optimization of the macromolecular design for enhancing of bulk conductivity and electrochemical stability of poly(ionic liquid)s	E.I. Lozinskaya	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PSP 15	Thermoreversible conversion between macrocycle and linear oligomers	T. Matsumoto	Life Sciences & Sustainable Chem., Tokyo Polytechnic University	Japan
PSP 16	Different macromolecular architectures of poly(phthalimide-co-naphthalimide)s by controlling relative reactivity of monomers	N. Mushtaq	Ningbo Key Laboratory of Polymer Materials, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences	China
PSP 17	Molecular dynamics simulations of uniaxial deformation of thermoplastic polyimides	V.M. Nazarychev	Institute of Macromolecular Compounds Russian Academy of Sciences (IMC RAS)	Russia
PSP 18	Conductive properties of a polystyrene composite films with covalently linked graphene oxide	M.N. Nikolaeva	Institute of Macromolecular Compounds Russian Academy of Sciences (IMC RAS)	Russia
PSP 19	Surface and morphological investigation of synthesized nanostructured ridges from electrospun polyvinyl alcohol – egg albumin blend using atomic force microscopy	J.M. Ramis	Technological Institute of the Philippines, Department of Chemical Engineering	Philippines
PSP 20	Novel polyurethane flexible foam/modified iron oxide nanocomposites	M. R. Naimi-Jamal	Iran University of Science and Technology, Department of Chemistry, Research Laboratory of Green Organic Synthesis and Polymers	Iran
PSP 21	Synthesis of conjugated polymers by Stille coupling of semifluorinated thiophenes	S. Stein	Leibniz Institute of Polymer Research Dresden	Germany
PSP 22	Synthesis and using of organo soluble (co)polyimides in optical fibres coatings production	D.A. Sapozhnikov	A.N. Nesmeyanov Institute of Organoelement Compounds Russian	Russia

			Academy of Sciences (INEOS RAS)	
PSP 23	Hyperbranched polypyridylphenylenes: synthesis and templating of metal nanoparticles	E.S. Serkova	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PSP 24	Grafting of 1,2,3-triazolium-based poly(ionic liquid)s on ionic polyimide as an approach for conductive and flexible films	A.S. Shaplov	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PSP 25	Bisphenol-A-formaldehyde sols: preparation, structure and properties	E.E. Sheveleva	N.D. Zelinsky Institute of Organic Chemistry Russian Academy of Sciences	Russia
PSP 26	Structure of lactide-based block copolymers in solution revealed by Small-Angle X-Ray scattering	E.V. Shtykova	A.V. Shubnikov Institute of Crystallography Russian Academy of Sciences (CRYS RAS) Moscow State University	Russia
PSP 27	The structure and properties of the hybrid film materials on the basis of the heterocyclic polymers and MQ-resins	V.M. Svetlichnyi	Institute of Macromolecular Compounds Russian Academy of Sciences (IMC RAS)	Russia
PSP 28	Silica precursor hyperbranched polyethoxysiloxane (PEOS) as PP additive	M. Swaton-Höckels	DWI – Leibniz-Institute for Interactive Materials e. V. and Institute for Technical, Macromolecular Chemistry (ITMC), RWTH Aachen University	Germany
PSP 29	Synthesis of hyperbranched and star-shape polyimides in catalytic medium	A.Yu. Tsegelskaya	N.S. Enikolopov Institute of Synthetic Polymeric Materials Russian Academy of Sciences (ISPM RAS)	Russia
PSP 30	Copolyamides with luminophore anthrazoline groups in the backbone	I.A. Valieva	Institute of Macromolecular Compounds Russian Academy of Sciences (IMC RAS)	Russia
PSP 31	Thermal transportation properties for composite containing mixed alumina and graphene	W. Yu	School of Environmental and Materials Engineering	China
PSP 32	Effect of graphene nanoplatelet on the dielectric property of PVDF/PMMA blends	D. Yang	School of Environmental and Materials Engineering	China
PSP 33	“Head-to head” polyarylenedipthalides of polyphenylene series as structural isomers of polyarylenepthalides	T.A. Yangirov	Ufa Institute of Chemistry	Russia

PSP 34	Polyamide reinforcing by modified single-walled carbon nanotubes as the protective coatings for optical fibre	O.N. Zabegaeva	A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)	Russia
PSP 35	Novel polycondensation method of improving high-temperature properties of rolivsan microheterogeneous copolymers modified by inserting epoxy and imide bridges between spherical microdomains	B.A. Zaitsev	Institute of Macromolecular Compounds Russian Academy of Sciences (IMC RAS)	Russia
PSP 36	Polyimides and sulfonated polyimides based on 1,1-diphenylethylene derivatives: polymer substrates for new proton exchange membranes	G. Summers	University of South Africa, Department of Chemistry	Republic of South Africa
PSP 37	Nanoparticle-bound doxorubicin for chemotherapy of glioblastoma	S. Gelperina	Drugs Technology Ltd., Nanosystem Ltd.	Russia
PSP 38	Synthesis and characterization of DOPO-containing biobased polyesters and copolyesters	A. Korwitz	Leibniz Institute of Polymer Research Dresden	Germany
PSP 39	Tailored design of polyurethane coatings from PET recycling for applying in corrosion protection	I.E. Alaa	Central Metallurgical Research & Development Institute (CMRDI)	Egypt
PSP 40	Synthesis and properties of new copolymers with biquinoline units in the main chain and metal-polymer complexes based on	N.S. Guliy	Institute of Macromolecular Compounds Russian Academy of Sciences (IMC RAS)	Russia
PSP 41	Surface properties and chemical structure of polyethersulfone films treated by direct current discharge	M. Piskarev	N.S. Enikolopov Institute of Synthetic Polymeric Materials Russian Academy of Sciences (ISPM RAS)	Russia
PSP 42	Structural modification of polyimides for various applications	A.S. Yegorov	Federal State Unitary Enterprise «State Scientific Research Institute of Chemical Reagents and High Purity Chemical Substances» (FSUE "IREA")	Russia

Cyclization and dispersity of polyesters

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Starting out from Flory's most probable distribution concept [1], correct and incorrect evaluations of SEC measurements are discussed. Using the correct mode, polyesters prepared by irreversible and reversible polycondensation methods were studied. Polyesters of α,ω -alkanediols and isophthalic acid or polyesters of diphenols and sebacic acid were prepared by three different irreversible polycondensation methods [2,3]. Formation of cyclic oligo and polyesters was monitored by MALDI-TOF mass spectrometry and dispersities were measured by SEC. The results are compared with the theories of Flory [1] and Odian [4].

Equilibrated polyesters were prepared by reversible polycondensation of ethyl 6-hydroxycaproate or by alcohol-initiated ring-opening polymerization of ϵ -caprolactone. Various catalysts were compared. The influence of dilution and of di- or multifunctional initiators was evaluated. Furthermore, equilibrated polylactides were prepared from L- or meso-lactide at 120, 160 and 180°C. A fast even-odd equilibration was discovered in addition to reversible cyclization and intermolecular transesterification. The influence of these different equilibration mechanisms on the dispersity was investigated. The preparative and theoretical consequences are discussed.

References

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- [3] Kricheldorf, H.R.; Weidner, S.M.; *Macromol. Chem. Phys.* **2016**, accepted.
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New trends in polyheteroarylenes synthesis, properties and application

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Polyheteroarylenes are heterocyclic high-performance polymers and consist of fused aromatic and heterocyclic rings. They are very important polymer family, which can be used as thermally and chemically stable, heat-, and fire-resistant materials (films, fibers, membranes, nanostructured products etc.). Among them, polyimides (PI) and polybenzimidazoles (PBI) are widespread for electrotechnics, electronics, aerospace, separation, electrochemical technologies and many other applications.

Over a period of sixty years INEOS RAS is known throughout the world for the pioneering work at the junction of the polymer, organic and inorganic chemistry, studies of the processes of polymer formation as well as structure—property relations. It brought about the chemistry of polymers with organoelement molecular chains and opened the routes to novel classes of linear and network polymers. New materials with valuable thermal, catalytic, sorptional and electro-physical properties, thermostable composites and membranes for electrochemical devices have been made up on the basis of these polymers.

Recent results obtained by Laboratory for Heterocyclic Polymer Synthesis will be reported in prospective lecture [1-3].

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Application of aromatic polymers to heterogeneous catalysis

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This paper describes the synthesis of aromatic polymer materials such as of polyimide nano-particles, hyperbranched poly(ether sulfone) and hyperbranched poly(ether ketone), and their application to catalysis as illustrated in Figure 1.

One major problem for polymer electrolyte membrane fuel cells in commercial applications is the cost and scarcity of platinum, which is used as the cathode catalyst, and the development of Pt-free cathode catalysts is strongly desired. We have explored the synthesis of a carbon-based catalyst from polyimide nano-particles. Polyimide is a thermo resistive polymer and the morphology of precursor can be retained even after the carbonization; therefore, finer morphology can be expected. The obtained carbo-based catalyst shows a quite promising fuel cell performance. [1,2]

In the meantime, polyimide nano-particles can be utilized as a support for heterogeneous catalysts. We have been investigating the catalysis of aromatic hyperbranched polymers such as hyperbranched poly(ether sulfone) [3] and poly(ether ketone) [4], and such hyperbranched polymer can be covalently immobilized onto the polyimide and carbon nano-particles. [5] Such materials have been demonstrated as heterogeneous catalysts for several chemical reactions.

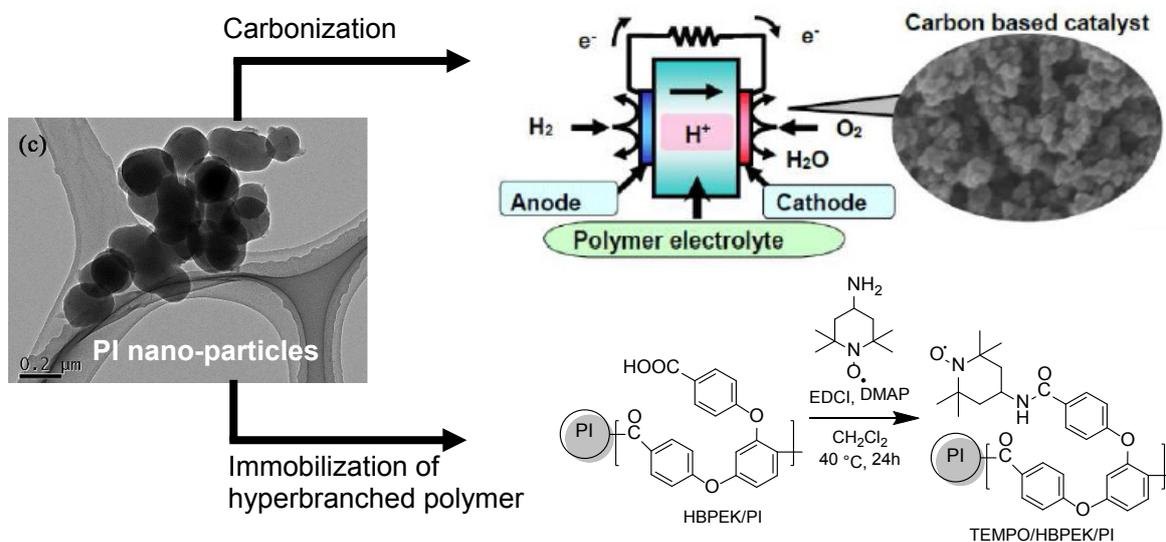


Fig. 1. Application of polyimide nano-particles to catalysis

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The studies for fuel cells and hyperbranched polymers are respectively funded by NEDO and KAKENHI.

Green chemistry of polyurethanes

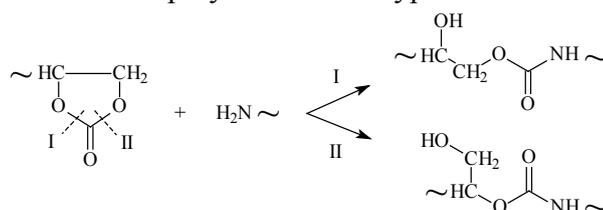
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Classical synthesis of polyurethanes is based on the reactions of di- or polyisocyanates with di- or polyols. Industrial production of polyurethanes exists almost without any changes 80 years yet though the process is not irreproachable from the ecological point of view because of isocyanates are extremely toxic monomers and they are prepared from primary amines by the way of their reaction with phosgene which is battle toxic substance as known. That is the main reason why alternative routes for synthesis of polyurethanes are being developed in present time.

Some problems of Green Chemistry of polyurethanes are discussed in the report. There are the reactions of non-isocyanate polyurethanes preparation by the interaction of cyclocarbonates with primary amines, catalytic fixation CO₂ as the method of synthesis of cyclocarbonates, structure and reactivity of cyclocarbonate containing oligomers based on triglycerides of plant oils as renewable raw materials for new polyurethanes.

Ring opening of cyclic carbonate groups via their reaction with an amine results to polyurethanes containing primary or secondary hydroxyl groups that opens the opportunities for the corresponding modification of polymers of this type:



Modern representatives about the mechanism of urethane formation without isocyanates are based on kinetic and quantum chemical studies of model reactions. It is shown that the reaction can proceed through the one- or multistage paths involving one or two amine molecules. The second amine molecule plays the role of the catalyst of the process, resulting in a substantial decrease in the activation energy of the reaction. The relative contributions of these routes to the observed reaction rate depend on the amine concentration, temperature and the nature of the solvent. Activation energies of the reaction between of ethylene carbonate and one and two molecules of n-butyl amine are equal 14.0 and 3.7 kcal/mole in dioxane and are 7.0 or 2.5 kcal/mole in n-butanol, respectively.

The mechanism of the reaction CO₂ with epoxides with formation of cyclocarbonates in the presence of different catalysts is discussed in the report. The results are based on quantum chemical studies of the model reactions. The experimental results on preparation and structural investigation of cyclocarbonate containing oligomers via catalytic reaction of carbon dioxide with epoxidized soybean oil as renewable raw material for new urethanes are presented. It is shown by mass-spectrometric method that the oligomers, which are triglycerides of epoxide- and cyclocarbonate-containing derivatives of natural carboxylic acids, are characterized by an extremely wide composition and functionality distribution, reflecting almost the entire set of components contained in plant raw material. The presence of 25 types of triglycerides of unsaturated (oleic, linoleic, linolenic) and saturated (stearic and palmitic) carboxylic acids in various combinations in oligomers has been found. The functionality distribution of oligomers regarding to epoxy and cyclocarbonate groups and problems of the use of plant raw materials for the production of non-isocyanate polyurethanes are discussed.

This work was supported by Russian Foundation for Basic Researches (RFBR), grant no. 14-03-00026.

Transparent but ultrastrong plastics derived from amino acid

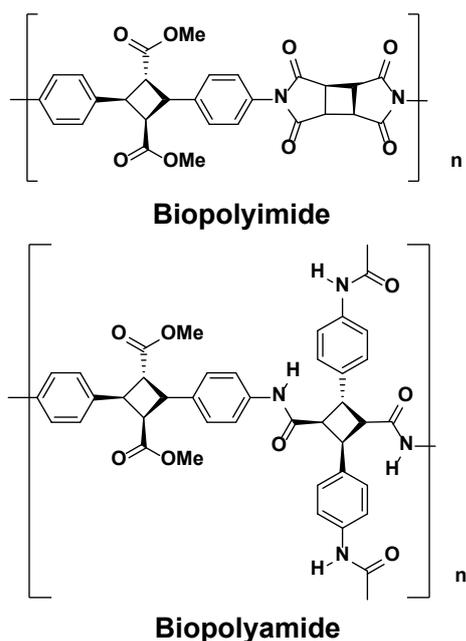
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Scheme 1. Representative structure of biopolyimide and biopolyamide prepared here from amino acid

Weight-saving of industrial materials is indispensable for establishment of green-sustainable societies. Alternation of plastics from hard and heavy materials such as metals and glasses is very effective on lightening. Most plastics, however, have lower thermal and mechanical performances than the heavy materials. Especially, transparent plastics such as polycarbonates and polymethylmethacrylate are expected to alternate glass materials but their thermomechanical performances were too low to apply in wide fields of electronics and optics. Conventional bioplastics, a series of aliphatic polyesters, such as polyhydroxyalkanoates and poly(lactic acid) showed high transparency but low mechanical performances, either. Actually most of strong plastics are partially crystallized to reduce the transparency. In order to solve the dilemma, we have tried to prepare new amorphous bioplastics comprising rigid aromatic backbones. Here we report 4-aminocinnamic acid (4ACA) which was bioavailable by a microorganismal engineering. The photodimer of 4ACA was prepared via [2+2] cycloaddition, which is a kind of biological dianilines. The dianilines were indispensable for preparation of the aromatic polyamide and polyimide but generally were very difficult to produce by a direct method of fermentation. The biodianilines were polymerized with diacids to produce aromatic polyamides and with tetraacid dianhydrides to produce aromatic polyimides. Especially the polyimides derived from the photodimer and cyclobutanetetra-carboxylic dianhydrides showed a good thermomechanical performance, and additionally showed a high transparency [1]. Besides we synthesized acetylated 4ACA photodimer as a bio-derived diacid, and then the diacid was polycondensed with the dianilines to produce new biopolyamides with truxillamide backbone comprising rigid phenylenes and their connecting cyclobutanes. Cyclobutanes sandwiched by two phenylene rings can behave as a molecular spring and rigid structure as a result of tautomerization, The molecular spring produced ultra-strong and transparent polyamides having higher mechanical strength than heavy materials such as glasses [2].

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This work was made under a partial financial support from Grant-in-Aid for Scientific Research (B) (15H03864)

Low band gap (X-DADAD)_n type copolymers for stable and efficient bulk heterojunction organic solar cells

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Organic solar cells based on conjugated polymers demonstrated efficiencies approaching 8-10%. Unfortunately, the best-performing materials undergo rapid photochemical degradation. On the contrary, long operation lifetimes (7-15 years) have been projected for some less efficient polymers possessing robust chemical structures, e.g. PCDTBT.

In the present talk we will present our strategy of designing PCDTBT-like polymers with narrowed band gaps using alternating DADAD architectures as building blocks (D – electron donor such as thiophene, while A is an acceptor like benzothiadiazole or benzoxadiazole) [1-3]. Synthesized polymers demonstrated diverse optoelectronic and photovoltaic characteristics. The best materials showed solar cell efficiencies approaching 7% in combination with long-term operation stability. Higher performances of 10-11% are feasible for single junction devices due optimal band gaps (1.60-1.65 eV) and deep-lying HOMO energy levels (~ -5.5 eV) of the designed materials.

The developed polymers enabled fabrication of larger area solar cells under ambient conditions in air using slot die coating, which is a roll-to-roll compatible film deposition technology [4]. The power conversion efficiency of the coated devices exceeded 6%.

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Modeling of interfacial polycondensation: the kinetics and polymer film structure

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Heterogeneous polymerization of condensation monomers is widely used for in situ fabrication of micro- and nanocapsules and membranes and nowadays is being adapted to 3D printing. Here we report on the modeling of linear (A_2B_2) and branched (A_3B_2) interfacial polycondensation (IP) focusing on the reaction kinetics and characteristics of the polymer product.

Regardless of the comonomer reactivity and miscibility, the kinetics in an initially bilayer melt passes from the reaction to diffusion control. The polymer composed of immiscible monomers precipitates at the interface forming a film. In linear IP, the film is nearly uniform and the reaction proceeds in a narrow zone, which expands much slower than the whole film. It leads to a convective flow of macromolecules expelled from the reactive zone to the film periphery, which we call the chemical extrusion effect. This concept is used to predict the degree of polymerization (DP) and end-group distribution within the film in close agreement with the simulations [1]. Increasing the comonomer immiscibility leads to thinner and more uniform films with the higher average DP. The final product is considerably more polydisperse than expected for the homogeneous polycondensation.

Crosslinking in the case of branched IP drastically changes the mechanism of polymer film development. Branched macromolecules undergo gelation within the crossover period from the reaction to diffusion controlled kinetics. Comparison with the linear IP shows similar conversion rates but very different product characteristics. The simulations demonstrate that the chemical extrusion effect is suppressed and polycondensation proceeds like in a homogeneous system until the gel point is attained. Later on the crosslinked polymer films become markedly heterogeneous in density, with a dense core and loose shell regardless of the comonomer interactions. In contrast to the linear IP, their average DP grows with the comonomer miscibility and end groups are mostly trapped deeply in the film core [2].

Our results shed new light on the details of interfacial polycondensation processes and demonstrate high potential of molecular simulations in this field.

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This work was supported by the Russian Academy of Sciences (Program IV.5.3).

Highly transparent alicyclic polyimide films fabricated at low temperature

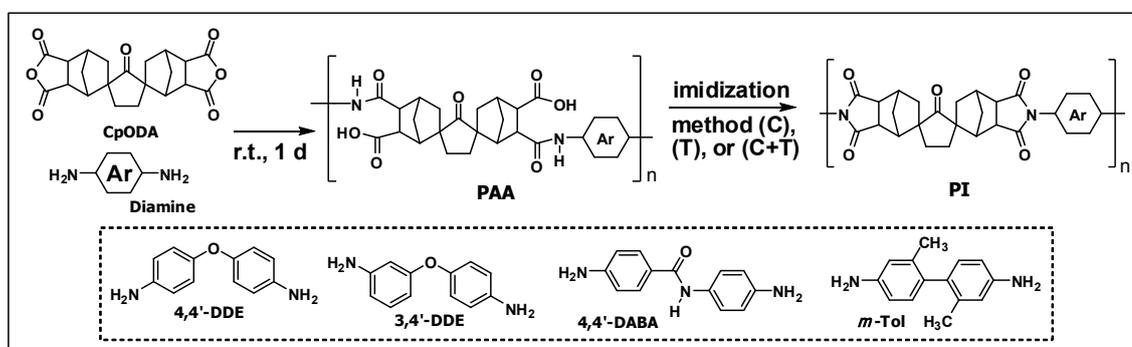
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Alicyclic polyimides having polyalicyclic structure have much attention because of their high-temperature stability and high transparency. In this presentation, we will report two novel approaches, a combined chemical and thermal imidization method “(C+T)” and a precipitation chemical imidization method “(C)” as a low temperature film-fabrication technique for hardly soluble alicyclic polyimides with high T_g. In addition the conventional thermal imidization “(T)” was also done for comparison. The synthetic route of polyimides, the chemical structures of monomers, and their abbreviations are shown in **Scheme 1**.



Scheme 1. The synthetic route of polyimide and the abbreviations of monomers

The alicyclic dianhydride having cyclopentanone bis-spiroornbornane structure (CpODA) was polycondensated with aromatic diamines at r. t. Poly(amic acid)s (PAAs) possessed an inherent viscosity (η_{inh}) range of 1.5-0.5 dL/g. The PAAs were imidized by three methods as described above using the same PAA lot. As can be seen from **Table 1**, all the polyimide films possess excellent thermal stability. It is noteworthy that the CTE values of PI(CpODA+4,4'-DABA) films are almost same as copper foil. The polyimide films exhibit $\lambda_{cut-off}$ s (wavelength at 1 % transmittance in UV-vis spectrum) shorter than 336 nm, and the T_{vis} (averaged transmittance in the visible region (400-780 nm)) of each polyimide film is over 85%. Especially, the films fabricated by a (C) and a (C+T) methods have outstanding optical properties (T_{vis}: 89-86 %, $\lambda_{cut-off}$: 278-334 nm).

Table 1. Thermal and optical properties of the CpODA-based alicyclic polyimide films

method	diamine	T5(°C)	Td(°C)	Tg(°C)	CTE(ppm/K)	T _{vis} (%)	$\lambda_{cut-off}$ (nm)
C	<i>m</i> -Tol	456	475	345	38	89	285
C	3,4'-DDE	478	488	329	48	88	268
C+T	4,4'-DABA	472	495	>400	24	86	334
C+T	3,4'-DDE	472	488	331	54	88	278
T	4,4'-DABA	481	501	>400	17	84	337
T	3,4'-DDE	467	483	333	57	85	289
T	4,4'-DDE	468	488	354	49	86	290

T5, Td: 5 %-wt loss and decomposition temperatures CTE: coefficient of thermal expansion

Microporous polymer networks made in transition metal-free polycondensation and polyaddition schemes

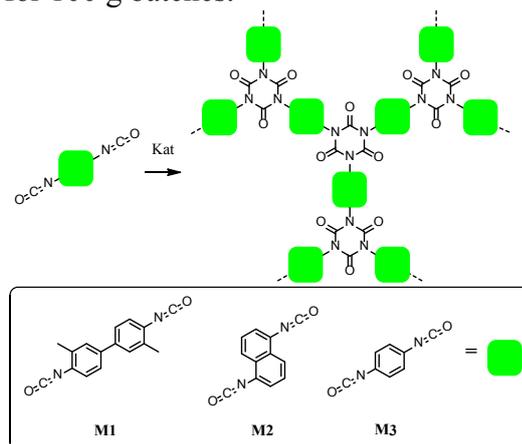
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Several types of microporous polymer networks (MPNs) have been made in (transition) metal-free polycondensation and polyaddition schemes. Our examples include the cyclotrimerization of bisindanone-type monomers [1], the polyhydroxymethylation of biscarbazolyfluorenones and related monomers [2,3] as well as the cyclotrimerization of diisocyanates [4].

All products showed high S_{BET} surface areas in the range of 1500-2200 m^2/g , hydrogen uptakes up to 1.7% (at 77 K) and a promising application potential for the removal of lipophilic contaminations in water. Some of the methods allow for the production of compact and mechanically stable monoliths [4]. For the diisocyanate cyclotrimerization, the up-scaling potential was demonstrated for 100 g batches.



Scheme 1. Chemical structures of commercially available diisocyanates used as well as of the resulting aromatic polymer networks in the cyclotrimerization of diisocyanates [4]



Fig. 1. Photograph of a diisocyanate-based microporous polymer monolith [4]

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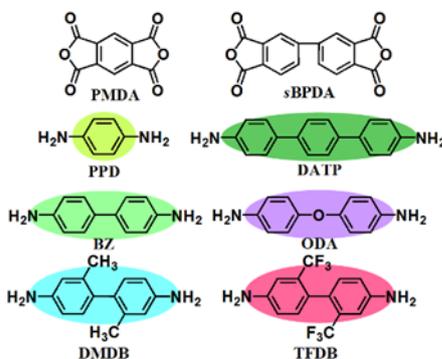
A comprehensive study on anisotropic thermal expansion behaviors of crystal lattice of aromatic polyimides analyzed by VT-WAXD

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To gain insight into the anisotropic thermal expansion behaviors of aromatic polymers and to obtain design principles for new materials exhibiting low thermal expansion as well as high thermal and mechanical stability, highly crystalline μm -sized particles of thirteen kinds of aromatic polyimides (PIs) were synthesized, and their coefficients of linear (CTE) and volumetric (CVE) thermal expansion of crystal lattices were precisely analyzed by variable temperature synchrotron wide-angle X-ray diffraction (VT-WAXD). The CTEs and CVEs of PIs having flexible main chains have been reported by Brillhart et al. [1]. PI particles were prepared by heating of NMP solutions of poly(amic acid) at 200°C for 2 h, followed by annealing of precipitated particles at 400°C for 2 h. The particle morphology was sheaf or coral type, similar to polymer spherulites. Transmission VT-WAXD profiles were measured at BL40B2 beamline at JASRI/SPring-8 and 11C beamline at Photon Factory/KEK in the temperature range of 50–350°C. Diffraction peaks observed in the profiles were assigned according to literature, and relative thermal expansion estimated from d -spacing were plotted against temperature. The CTEs along c -axis are small for all the PIs, though negative CTEs were observed for PIs having a bent linkage or bulky side groups ($-\text{CF}_3$). Moreover, the CVE of PMDA/TFDB is the largest despite its rigid-rod structure. The CVEs of rigid-rod PIs without side chains (PMDA/PPD, /BZ, /DATP) increase with increasing the phenyl rings at the diamine moieties. This could be associated with rotational motion of the phenyl rings. PIs having bulky side groups (PMDA/DMDB, /TFDB) exhibit nearly isotropic thermal expansion along a - and b -axes, whereas highly anisotropic expansion was observed for a PI having a bent ether linkage (PMDA/ODA) with an extraordinarily negative CTE along the a -axis (-44.2 ppm/K). This could be due to vigorous librational motion along the b -axis associated with ‘flip-flop’ of phenyl rings at the diamine moiety, which also induces a negative CTE along the c -axis. These experimental findings are beneficial for designing and developing novel thermally stable polymers exhibiting very low CTEs and CVEs.



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Innovative redox polymers for electrochemical energy storage

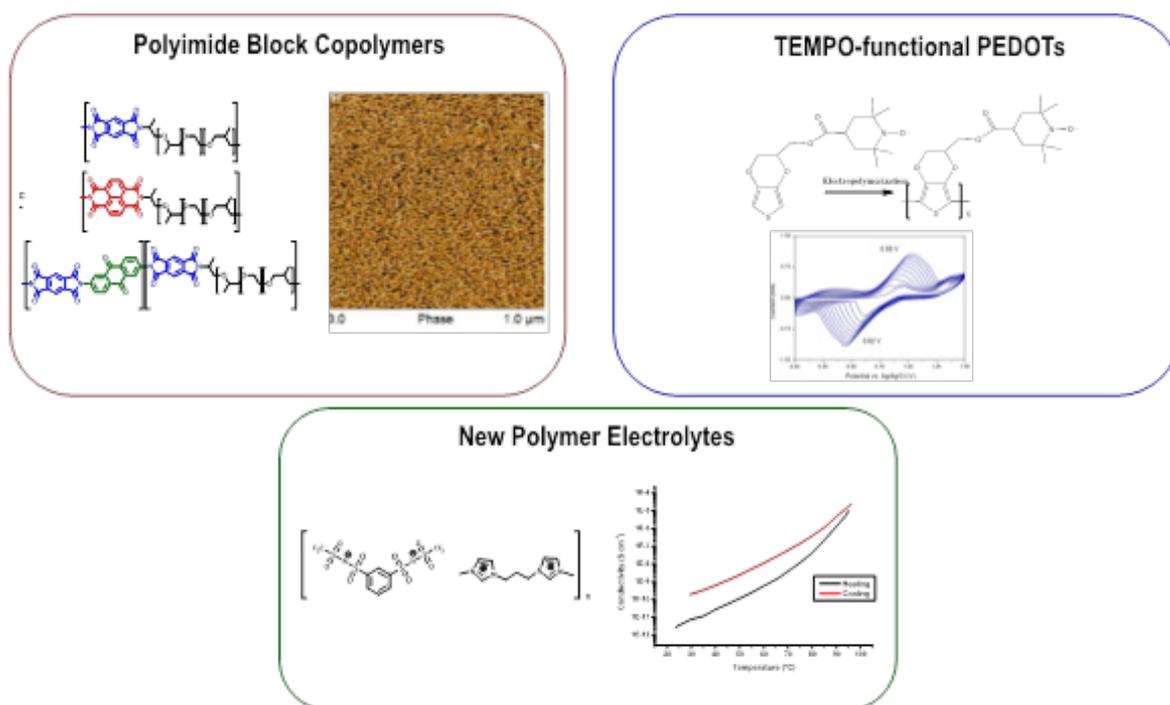
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Polymers with redox properties are electroactive macromolecules containing localized sites or groups that can be oxidized (loss of electrons) and reduced (gain of electrons). Redox polymers are mainly investigated for its application in energy technologies such as batteries, supercapacitors and emerging areas such as nanomedicine.¹

In this presentation we will review our recent activities in the synthesis of innovative redox polymers by polycondensation. Innovative redox polymers can be used to increase the performance of new battery technologies as redox active cathodic material, polymer electrolyte or polymeric binders. Some examples include, the synthesis of new redox polymers such as polyimide block copolymers, TEMPO-functional poly(3,4-dioxythiophene), PEDOT/lignin biohybrids. The application of these polymers in different types of batteries (Li, Li-S) or supercapacitors will be finally shown.



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Promising electronic properties of thin polyarylenephthalide films and heterostructures based on them

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Thin polyarylenephthalides films demonstrate unique electronic properties essentially differ from volume properties. Its can become the high conductive materials under the abnormal low external influences such as pressure, magnetic field and others. The difference from main stream of conductive polymers is in absence of π -electron conjugation in the polyarylenephthalides. It is the insulator materials with a wide band gap. The formation metal like conductivity into thin films of nonconjugated polymers is a special talk which will be discussed in the review. Another theme is the possible mechanisms of the abnormally high conductivity. There are two approaches both molecular transformation and energy level transformations, we would like to present. Very important aspect the influence of molecule structure to polymer thin film conductivity is discussed in the paper.

Combine two factors both the high level conductivity and low level external influences needed for operation conductivity are a good condition for different applications of these polymer materials. The paper consist discussion on possible application the organic materials in follow fields: spintronics, physical and chemical sensors, sensor elements for nondestructive control of metal details and construction, as memristors, source of electrons, transistors and quantum dimension devices.

Synthesis and properties of some new fluorinated monomers

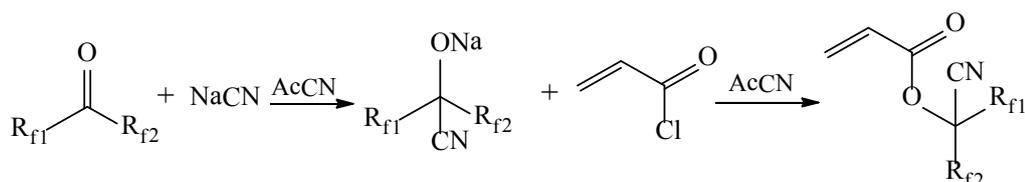
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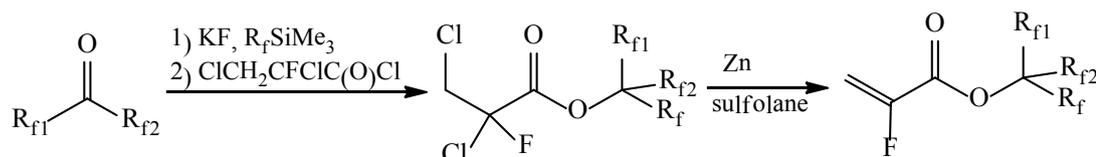
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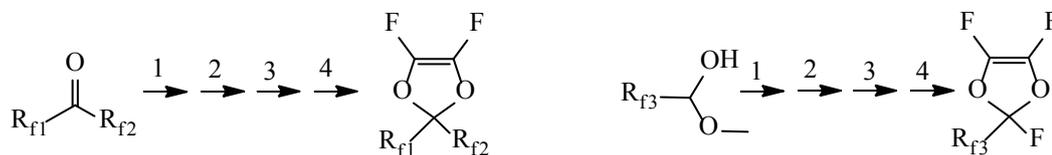
A number of cyanoperfluoro- and cyanochlorineperfluoro-alkylacrylates with halogenation grade equal to 66.6% were prepared from polyfluorogalogenation ketones.



Group of tertiary polyfluorinated ether alpha-fluoroacrylic acid type $\text{CH}_2=\text{CF}-\text{CO}_2-\text{C}(\text{R}_1)(\text{R}_2)(\text{R}_f)$ which contains degree of halogenation more than 80% were prepared

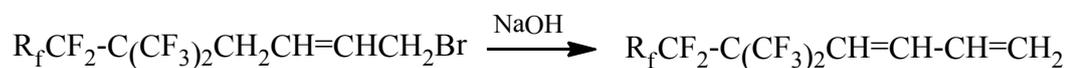


We developed the methods of synthesis for different fluorinated dioxoles from commercially available ketones and hemiacetals.



1) $\text{HOCH}_2\text{CH}_2\text{Cl} + \text{Na}_2\text{CO}_3$; 2) Cl_2 ; 3) SbF_3 ; 4) Zn

Group of butadienes containing polyfluorinated tertiary substituent were synthesized.



$\text{R}_f = \text{F}; \text{C}_2\text{F}_5$

Highly aromatic hyperbranched and linear polymers designed for film applications in opto-electronics

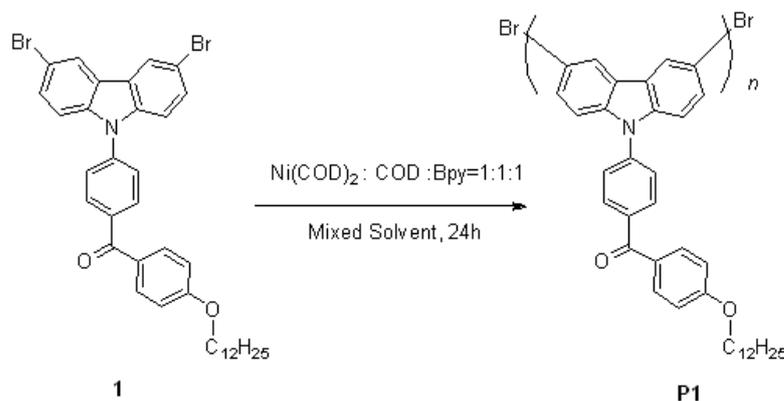
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The microelectronics industry and especially the organic/flexible electronics industry continue to demand new innovative polymeric materials. Besides the active (conducting and semiconducting) polymers, also the insulating materials in between, the dielectrics, as well as materials with special optoelectronic properties are highly important since they determine significantly the final performance of the device. In the area of insulating materials high performance hyperbranched (hb) polymers (e.g. hb polyphenylenes, hb-PPh) offer significant potential in the application as gate dielectric material which can be adopted for high performance OFETs by design-matching with the respective semiconducting material. The branching provides the highly needed solubility and allows solution processing or even processing by printing techniques. For multilayer device preparation, we also developed suitable crosslinking strategies which can be thermally or photochemically induced.[1] Furthermore, hyper-branched polyvinylsulfides through thiol-yne addition of B₃+A₂ monomers [2] proved to be excellent candidates for high refractive index (HRI) materials well suited for 1D planar all-polymer photonic crystals and efficient light out-coupling from OLEDs [2,3]. Polymers with RI as high as 1.79 have been achieved when using a naphthalene-based B₃ monomer and benzene-1,4-dithiol or naphthalene dithiol as A₂. Furthermore, crosslinkable linear polycarbazoles with benzophenone substituents show excellent *Thermally Activated Delayed Fluorescent* (TADF) properties.



Scheme TADF polycarbazole P1

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Conversion of PET to aromatic polymers by using reaction-induced crystallization

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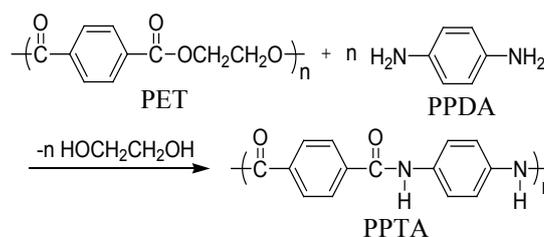
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Poly(ethylene terephthalate) (PET) has been widely used in our daily life. Synthesis of value-added materials from wasted PET is of importance as an effective upgrade recycling system to construct the future recycling-based society. Aromatic polyamides are well known as high-performance materials, and poly(1,4-phenylene terephthalamide) (PPTA) is a representative among them. The conversion of PPTA from PET had been previously examined by ester-amide exchange reaction in the melt phase or solution phase. [1,2] In these studies, the content of 1,4-phenylene terephthalamide (PTA) moiety in synthesized polymers was limited to at most 60 % owing to the intractability of PPTA. In this study, the conversion of PET to PPTA was examined as shown in Scheme by using reaction-induced crystallization to overcome the above limitation.

PET ($M_w = 2.8 \times 10^4$, acid value = 4.11×10^{-5} mol/g) and dibenzyltoluene mixture were placed into a cylindrical vessel, and the mixture was heated up to polymerization temperature. Concentration of PET was 5 wt%. When the PET was entirely dissolved, PPDA was added under stirring, and then the reaction was continued without stirring. Precipitated products were collected by filtration. Reactions were carried out at 320°C for 12 h by the addition of PPDA equimolar to the ester linkage in PET ($M = [\text{Amino group of PPDA}] / [\text{Ester linkage of PET}] = 1.0$). Precipitates were obtained with the yield of 62% and the content of PTA moiety (χ_{PTA}) was 92 mol%. Oligomers rich in the PTA moiety formed by ester-amide exchange reaction were precipitated to



Scheme 1 Preparation of PPTA from PET *via* ester-amide exchange reaction

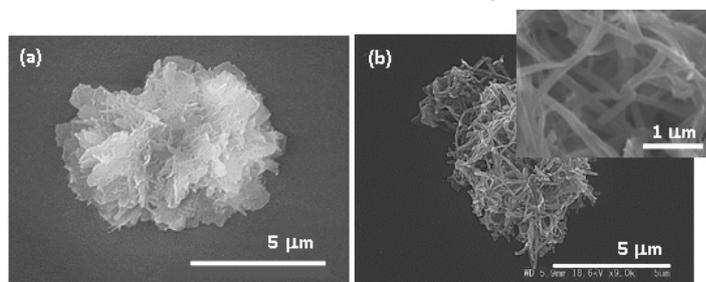


Fig. 1 Morphology of precipitated PPTA crystals

form the crystals owing to the decrease in the solubility. However, the χ_{PTA} value did not reached to 100 mol%. The reaction was next carried out in the slight excess of PPDA for 24 h. PPTA was formed as precipitated crystals at 350°C for 12 h at M of 1.3 and at 320°C at M of 1.7-2.0 with the yield of 75-92%. The obtained PPTA precipitates possessed high crystallinity, and they were plate-like and needle-like crystals as shown in Fig. 1. The small amount of PET moiety left in the oligomers was excluded by the ester-amide exchange reaction during crystal growth. M_w of PPTA crystals prepared at 350°C at M of 1.3 was 1.02×10^4 . High molecular weight PPTA can be prepared under non-stoichiometric condition by using crystallization in the heterogeneous system. Poly(benzimidazole) was also synthesized from PET.

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Polyimide-based materials for physical and biomedical applications

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A series of OH- and COOH-functionalized polyimides were synthesized. OH-containing azo-chromophores with bulky substituents, preventing an undesirable centrosymmetric aggregation of chromophores, were covalently attached to the synthesized polyimides via Mitsunobu reactions. These structural features of the chromophores made it possible to enhance the second-order NLO-properties of the synthesized chromophore-containing polyimides and to achieve the values of the second harmonic generation coefficient $d_{33} = 32\text{-}60$ pm/V.

Regular polyimide brushes PI-g-PMMA, PI-g-PMAA, and PI-g-PDMAEMA with a polyimide (PI) backbone and polymethylmethacrylate (PMMA), polymethacrylic acid (PMAA), and poly(N,N-dimethylamino-2-ethyl methacrylate) (PDMAEMA) side chains are synthesized via ATRP “grafting from” approach.

It is shown that rather well-performing pervaporation membranes may be prepared from PI-g-PMMA polyimide brushes with the pervaporation separation index $\text{PSI} > 70000$ for separation of water-isopropanol mixtures. Membranes prepared of blends of PI-g-PMMA with poly(*m*-phenylene-isophthalamide) are highly productive and selective in pervaporation separation of methanol-hexane mixtures.

The complexation of porphyrazines with PI-g-PMAA gives water soluble biocompatible nanoparticles, possessing a bright red emission. The nanoparticles were shown to be internalized and accumulated in the tumor cells on the nuclear membrane and nucleus (Fig. 1a). Cell investigations confirmed a high photodynamic activity of the nanoparticles. Whole-body fluorescent imaging experiments on mice bearing metastatic colorectal carcinoma showed the selective nanoparticle accumulation in a model tumor (Fig. 1b).



Fig. 1. (a) Intracellular localization of the porphyrazine photosensitizer incorporated into PI-g-PMAA nanoparticles: 1 – nucleus, 2 – nuclear membrane. (b) Whole-body fluorescence imaging (left – before, right – 3 hours after injection of PI-g-PMAA/porphyrazine complex aqueous solution).

Studies of the behavior of PI-g-PDMAEMA polyimide brushes in aqueous solutions by the dynamic light scattering method showed that they are pH- and thermally responsive, their lower critical solution temperature depending on pH value.

The synthesized amphiphilic polyimide brushes PI-g-PDMAEMA were successfully used as nanocontainer templates for preparing in situ and stabilizing Ag^0 nanoparticles (~10 nm) in water without any external reducing agents.

This work was supported by the Russian Science Foundation (RSF), grant no. 14-13-00200.

Polymer electrolyte membranes based on aromatic polymers with sulfonic acid via long alkyl side chains.

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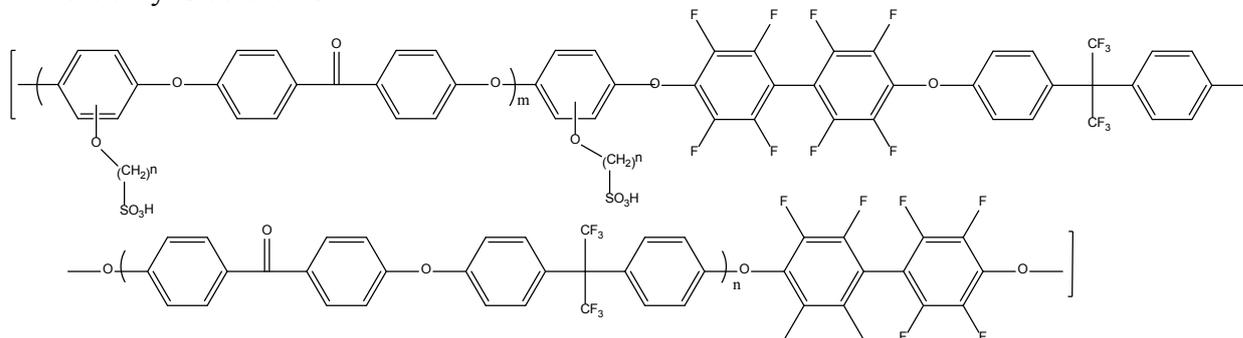
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The polymer electrolyte membrane fuel cells (PEMFCs) have received a great interest as a clean and efficient technology for power generation, in which the polymer electrolyte membranes (PEMs) play an important role as a proton conductive role as well as the separator of the anode and cathode. Numerous sulfonated aromatic hydrocarbon polymers have been reported as an alternative of perfluorinated PEMs. The proton conductivity of aromatic PEMs is inferior to that of perfluorinated PEMs under low relative humidity (RH) probably due to less connectivity of proton paths. In this presentation, we introduce our recent studies on development of PEMs containing alkylsulfonated side chains to remedy this problem.^{1,2,3}

Here we show one report on the development of PEM based on the multiblock and graft concepts together, to design a series of multiblock poly(phenylene ether ketone)s with long flexible alkyl side chains.



A series of multiblock poly(phenylene ether ketone)s with pendant alkylsulfonic acids were prepared and evaluated as proton exchange membranes for fuel cells.

The long block length was largely responsible for the high water-retention capacity of polymer under low RH conditions, which resulted in higher proton conductivity. Compared to previously reported membranes for PEMs, the membranes exhibited better proton conductive behaviors, although having a much lower IEC level of 1.13–1.41 mequiv. g⁻¹, suggesting the involvement of aggregated ion channels in facilitating proton transport.

Membranes exhibited promising fuel cell performance. In particular, high power densities of 0.768, 0.626 and 0.410 Wcm⁻² under 80%, 50% and 30% RH, respectively, were obtained which were higher than those of Nafion.

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Polyarylenedipthalides – a new class of phthalide-type polyheteroarylenes

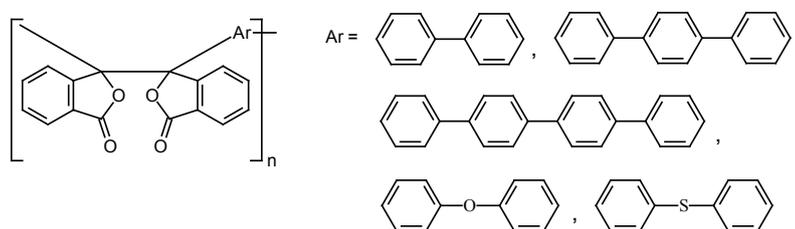
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In all known phthalide containing polymers (polyesters, polyamides, polyimides, polyarylenephthalides etc.) phthalide group regularly interchanges with aromatic (heteroaromatic) fragments of the main chain (**Ar**) and is linked with them through its nodal quaternary carbon atom by C(sp³)-C(sp²) bond [1, 2]. In the polyheteroarylenes of new type with **Ar** regularly alternate not one isolated phthalide group but two adjacent ones linked with each other by C(sp³)-C'(sp³) single bond.



Scheme 1.

For obtaining the polyarylenedipthalides (PADP) with increased sp³-hybridized carbon content we used two approaches that are based on the reaction of dehalogenation of *o*-diketo-carboxylic pseudo-acids chlorides and of *p*-halogen substituted 3,3'-diarylphthalides. Polycondensation of the pseudo-acids chlorides proceeds by “head-to-head” type and leads to random polymers formation.

For obtaining the stereospecific polyarylenedipthalides we used diastereoisomeric *p*-bromo-3,3'-diarylphthalides (meso- and (±) racemic) as chiral monomers that attach themselves to the growing polymer chain by “tail-to-tail” type entirely keeping chiral centres configuration.

Heterotactic PADP obtained from racemic dipthalides (M_w=5000-70000) have a good solubility in the main classes of organic solvents while as syndiotactic PADP synthesized from meso-dipthalides are soluble only in concentrated sulfuric acid. PADP of polyphenylene series are characterized by bright photoluminescence. The obtained polymers begin softening and decomposition at ≈ 350⁰C. Degradation of PADP in the inert atmosphere and in the air is followed by the thermochromism in ultraviolet visible and (at the deep carbonizing stages) by formation of foamed coke with increased content of diamond-like carbon that possesses a high hardness (≥8 by Mohs scale).

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Multiblock (segmental) copolyurethaneimides and copolyurethaneamidoimides

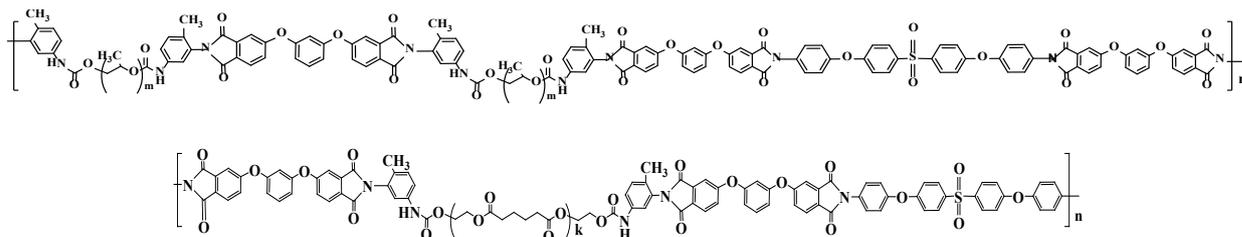
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Our report considers the chemical structure - properties correlation in the family of newly synthesized multiblock (segmental) copolyurethane imides and copolyurethane amidoimides. Scheme of the synthesis of the polymers involves reactions of isocyanate terminated polyethers (polyesters) with both aromatic tetracarboxylic acid dianhydrides or 4-chloreformyle phtalic anhydride (for example 1,2). Than derived macromonomers having terminal anhydride or chloreanhydride groups reacts with aromatic diamines to give the desired products. In the result, the studied polymers contain urethaneimide (urethaneamidoimide) hard segment and a flexible polyether (ester) segment in the base unit. There is a microphase separation in block copolymers synthesized. The formula of one of synthesized copolymers is given below.



The content of aromatic and aliphatic in the copolymers were varied by altering of reactive functional groups. We investigated the thermal stability and mechanical properties of copolymers synthesized in static and dynamic modes, the glass transition temperature and melting transition temperature. The glass transition temperatures of the copolymers are in the negative Celsius temperature region. There are regions of practical module independence from temperature (plateau of rubber like elasticity) on the curves of dynamic mechanical analysis. Thus we have shown that polymers synthesized have the properties of elastomers.

Nano-particles of tungsten disulfide (WS₂) were used to prepare nanocomposites. The introduction of functional fillers (as plasticizer) has led to a significant change in the properties of the synthesized copolymers.

At temperatures higher than 200°C, the polymers and nanocomposites pass to the flowing state, which is indicated by the rheological tests of the polymers synthesized, the polymer melts being a non-Newtonian fluid without supramolecular structures in the temperature range from 210 to 260°C. The possibility of using melt technologies (injection molding) made it possible to obtain moldings. Thus we have shown that polymers synthesized are processed like thermoplastics.

All of this can be attributed to the polymers synthesized a new generation of thermoplastic elastomers (thermoelastoplasts).

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Post-polymerization modification through direct C–H functionalization

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Post-polymerization modification is a powerful method for tailoring the structures and properties displayed by many polymeric materials. In some cases, such methodology may be the only route to a targeted polymer, particularly when a monomer is unavailable or inert toward conventional polymerization techniques. Most post-polymerization modifications utilize functional groups that are present in the side chains or end groups of a polymer. As such, pre-functionalized monomers are often required. Another strategy for the post-polymerization modification of polymeric materials is the direct functionalization of C–H bonds. Despite being inert, C–H bonds are omnipresent which renders them attractive targets for chemical modification.

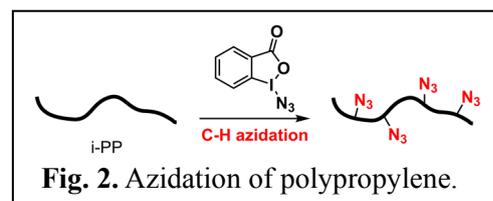
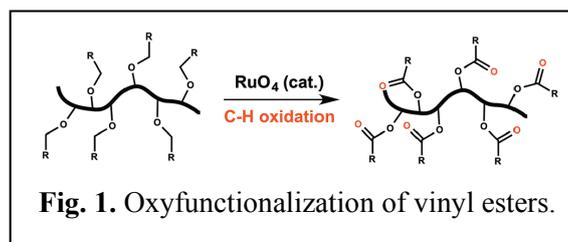
In this presentation, a ruthenium catalyzed C–H oxyfunctionalization of various polymers under mild conditions will be described (see Fig. 1). The methodology facilitated the conversion of poly(vinyl ether)s into their respective poly(vinyl ester)s and poly(vinyl ether-*co*-vinyl ester) in good yields [1], and facilitated the synthesis of high molecular weight poly(propenyl ester)s and other polymers which typically require extremely high pressures to synthesize. The aforementioned methodology was also used to convert poly(ethylene glycol) (PEG) to poly(ethylene glycol-*co*-glycolic acid) with minimal chain degradation. The introduction of the hydrolytically labile ester groups into the PEG backbone is expected to increase the biodegradability of the respective copolymer and facilitate the use of high molecular weight derivatives in biomedical applications.

Finally, the C–H azidation of isotactic polypropylene (PP) using a stable precursor will be described (see Fig. 2). The azido-functionalized PP was further modified using azide-alkyne cycloaddition chemistry to afford a range of grafted polypropylene-based copolymers. The presentation will conclude with some perspectives on incorporating useful functional groups into common polyolefin feedstocks to broaden their utility and potentially facilitate the realization of new classes of polymeric materials.

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This work was supported by the Camille Dreyfus Teacher-Scholar Awards Program, the US Army Research Office (W911NF-09-1-0446 and W911NF-09-1-0456) and the National Science Foundation (CHE-1266323). CWB is grateful to the IBS (IBS-R019-D1) and the BK21 Plus Program funded by the Ministry of Education and the National Research Foundation of Korea for their support.



Synthesis and healing properties of poly(arylether)-poly(alkylthioether) multiblock copolymers containing disulfide bonds

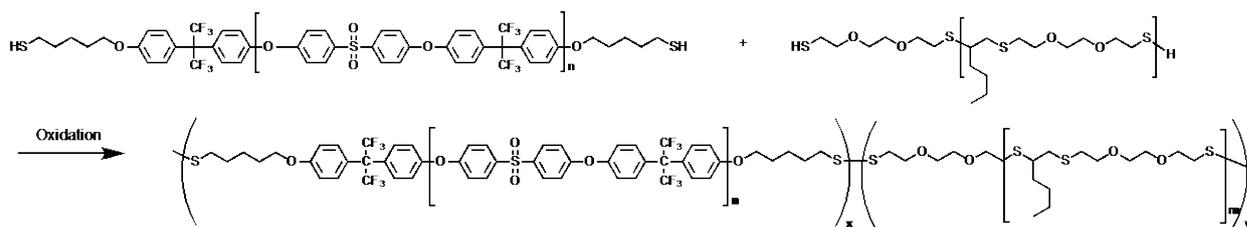
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Multiblock copolymers composed of soft and hard segments show unique elastic properties, which are known as thermoplastic elastomers. The soft segments are low-T_g oligomers and contribute soft and elastic properties. The hard segments are high-T_g oligomers and play a role of physical crosslinkings. Disulfide bonds are one of the dynamic covalent bonds, which can be reversibly cleaved and formed by external stimuli.[1] Self-healing properties under mild external stimuli can be expected if disulfide bonds are introduced into the soft segments in multiblock copolymers. In this study, we have investigated the synthesis and healing properties of the multiblock copolymers composed of poly(arylether) and poly(alkylthioether) containing disulfide bonds.

Thiol-terminated poly(arylether sulfone) oligomers (PES) as hard segments were synthesized from 2,2-bis(4-hydroxyphenyl)hexafluoropropane and difluorodiphenyl sulfone as starting compounds. Thiol-terminated poly(alkylthioether)s (PTE) as soft segments were synthesized from 1-hexyne and 3,6-dioxa-1,8-octanedithiol via photo-initiated thiol-yne reaction.[2] Both of thiol-terminated oligomers were oxidatively coupled to form the multiblock copolymers via disulfide bonds. The resulting polymers showed the microphase separation of PES (hard) and PTE (soft) domains. Tensile test of the multiblock copolymers resulted in the large elongation at break over 500 % and low moduli in the range 3-5 MPa. As a healing test, the test pieces were completely cut in half and then manually recombined. The recombined samples were heated at 100°C for 20 min on a hot plate. The elongation at break was recovered up to 88 %, which implies that the multiblock copolymers are self-healable. The healing efficiency highly depended on the amount of disulfide bonds in the multiblock copolymers. The relationship between the structure of the multiblock copolymers and self-healing efficiency will be discussed.



Scheme 1. Synthesis of Poly(arylether sulfone) (PES) and Poly(alkylthioether) (PTE) Multiblock Copolymers via Oxidative Coupling Reaction.

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Solvent-free synthesis of poly(bismaleimide)s

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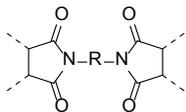
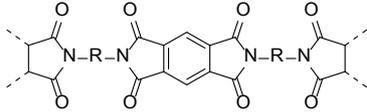
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Due to their wide operating temperature range (-269 to 400 °C), their dielectric strength, and their mechanical stability up to 200 °C, polyimide based materials appears as the most suitable materials for the protection of semi-conductor components [1]. However, such polymers are difficult to process because they cannot be thermoformed and their synthesis requires the use of a toxic and high boiling point organic solvent [2]. In order to circumvent these issues, new bismaleimides liquid at room temperature have been developed in order to carry out the solvent-free synthesis of poly(bismaleimide)s.

In this study, the synthesis and characterization of four new liquid bismaleimides will be thus described. Two of them were obtained by condensation reaction between maleic anhydride with diamines with a spacer R either fully hydrocarbonated or containing polydimethylsiloxane units. For the other two, a pyromellitic unit has been added in both previous structures. The bismaleimides monomers were synthesized with a crude yield varying from 75 to 95 %, and their structure has been confirmed by ¹H NMR and ATR-FTIR. According to the nature of the spacer R, their viscosity varies between 8 and 800 Pa.s at 25 °C.

Then, the polymerization conditions of these original monomers have been optimized leading to the formation of materials without the use of any solvent. The resulting materials are homogeneous, brown and transparent. Their soluble fractions, quantified by solid-liquid extraction with dichloromethane for 72 h, vary between 5 and 40 % according to the spacer R nature and the presence of pyromellitic unit.

Table 1. Properties of the synthesized poly(bismaleimide)s

General structures	Soluble fractions (wt%)	Water contact angle (°)	Temperature at 5 wt% loss (°C)	Glass transition temperature(s) (°C)	Storage modulus at 200 °C (MPa)
	5 to 10	90 to 110	340 to 375	95 -105 and 0	1 to 20
	25 to 40	~90 to 115	350 to 390	45 -105 and -25	0,1 to 1

Their cross-linking density depends on the same structural parameters. Thus, the materials present either elastomeric behavior or thermoset one according to their chemical composition. Their different physico-chemical properties will be discussed as a function of the chemical structure of the synthesized poly(bismaleimide)s.

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Segregated block copolymers based on aramide molecule with polyether

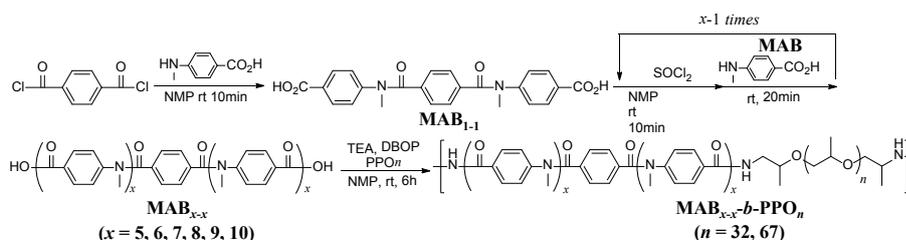
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Recently, we have prepared a series of poly(*N*-alkyl benzamide) by the direct condensation polymerization of *p*-(*N*-alkylamino)benzoic acids, and the structures and packing of the PABA_{*n*} polymers have been elucidated; PABA₁, PABA_{*n*} where *n* = 3, 4, and 5, and PABA₁₇ possess crystalline structures in monoclinic, orthorhombic, and hexagonal packing lattices, respectively (Figure 1).[1] We also have demonstrated a simple and highly efficient convergent approach without protection and deprotection steps for the synthesis of aromatic polyamide dendrimers using thionyl chloride.[2] By combining these techniques, we expected that the poly(amide ether) having uniform length of the hard segments could be designed and readily prepared (Scheme 1).



Scheme 1 Synthesis of the aramid molecules ($x = 5 \sim 10$), and the copolymerization with PPO_{*y*}.

The detailed structure of the prepared copolymers were well characterized with ¹H NMR spectroscopy. Figure 1 depicts the DMA curves and the Tan δ vs temperature relationship of the copolymers. For the poly(MAB₆₋₆)-*b*-PPO₃₀, the storage modulus (*E'*) started to decrease around -50 °C, and sharply dropped around 30 °C. The polymer having longer HS, poly(MAB₈₋₈)-*b*-PPO₃₀ also started to decrease the *E'* around -50 °C, and the second *E'* drop was observed around 50 °C. In contrast, the polymers having longer SS such as poly(MAB₆₋₆)-*b*-PPO₆₇, poly(MAB₇₋₇)-*b*-PPO₆₇, poly(MAB₈₋₈)-*b*-PPO₆₇, and poly(MAB₉₋₉)-*b*-PPO₆₇ all show more clear *E'* drop at lower temperature of -60 °C. These data clearly suggest the phase-separated structure within the films.

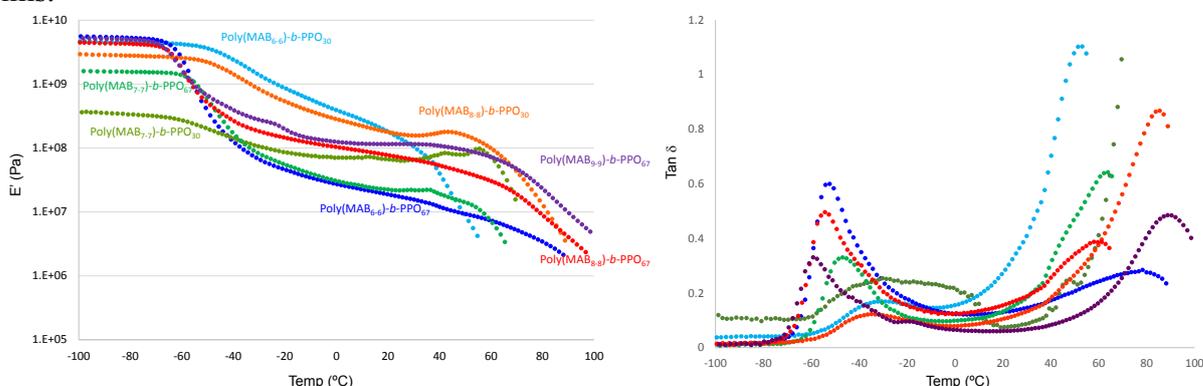


Figure 1. DMA analysis of MAB_{*x-x*}-*b*-PPO block copolymers

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Rigid polyesters and polycarbonates from renewable ketal monomers

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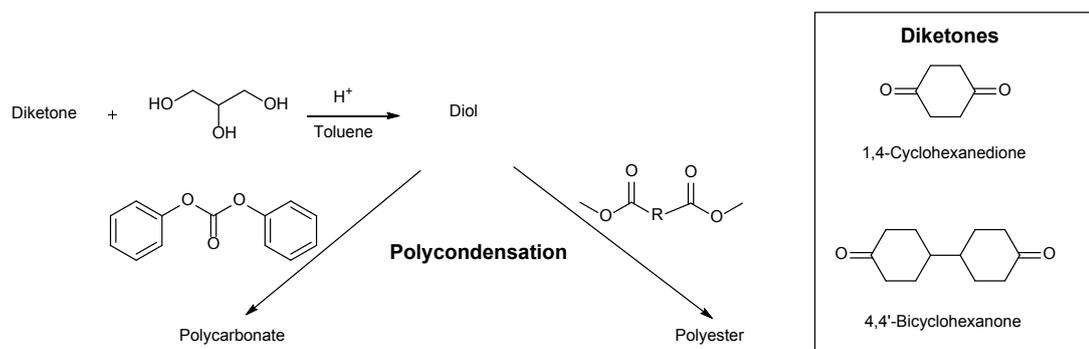
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Research in the area of polymers obtained from polycondensations is shifting from the use of crude oil based monomers to renewable monomers [1]. An important feature asked from renewable polymeric structures, is a higher rigidity while maintaining processability. In this context, much research is devoted to renewable alternatives for terephthalic acid in polyesters and bisphenol A in polycarbonates. Following this approach, a drop-in strategy is possible on an industrial level, which avoids extreme investments [2]. Next to this, price and accessibility of the monomers play an as important role as the resulting properties of the polymer.

In this work, rigid new diols were synthesized from glycerol, which is a renewable and cheap bulk chemical and a byproduct in the biodiesel production [3]. The rigidity of the new monomers was realized by reacting glycerol with various diketones to form cyclic ketal containing diols, thereby providing an alternative to the conventionally used aromatic structures. Next, polycarbonates were synthesized with diphenyl carbonate. Thus, more renewable and less toxic diols, providing alternatives to bisphenol A in the polycarbonate synthesis, are presented. These new diols were also combined with several diesters in order to obtain renewable polyesters with good thermal properties. Initially, a procedure for both polymerizations was explored. Subsequently, extensive chemical, thermal and mechanical analysis was performed on the synthesized polymers in order to allocate them to possible applications.



Scheme 1. Overview of the synthesis of glycerol based diols and their use in polycondensation reactions to polycarbonates and polyesters.

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Control of chain microstructure in catalytic synthesis of copolyimides

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Review of authors' results of systematic research into mechanism of the one-pot catalytic synthesis of binary multiblock copolyimides (CPIs) with the controlled block length. Synthesis of the high molecular weight CPIs is carried out by the one-pot high temperature polycondensation of two diamines (comonomers) and tetracarboxylic acids dianhydride (intermonomer) or vice versa, using molten benzoic acid as catalytic solvent, at 140°C. Parameters of CPIs chain microstructure (chain microheterogeneity coefficient K_m , average blocks length) were determined by NMR ^{13}C . It is established, that slow intermonomer addition to the mixture of two comonomers in BA results in formation of multiblock CPIs, whereas in a case of the one-shot loading, a random copolymer is formed [1, 2]. Such a behavior typical for "ideal interpolycondensation" is unusual if one takes into account reversible character of transient amido acid formation. To explain such a behavior, detail kinetic analysis of CPIs formation in BA was executed. Mathematic model of CPIs formation was developed adoptable for any reactants loading character [3]. Standard mathematical software (for numeric integration of differential equations) and experimental data on the kinetics model reactions were used in K_m calculations. Good agreement between theoretical and experimental K_m values was found. In a case of the comonomers pair 2,3,5,6-tetrafluoro-p-phenylene diamine – 4,4'-oxydianiline (TFPDA-ODA), it was found that even in a case of great difference in diamines basicity (4 units of $\text{p}K_b$), a block length in CPI is not more than 4-5 comonomer units, which value corresponds to the effective comonomers reactivity ratio in BA of about 1:10. Such a rather small difference in reactivity is much less than expected one for reaction of acylation of TFPDA and ODA in amic solvents. It can be explained by that not acylation but imidization (low sensitive reaction to chemical structure) is the true rate-determining reaction in imide cycle formation in molten BA. Because of low equilibrium constant of amido acid formation and strong catalysis of this stage by BA, the process of PIs and CPIs chain growth in BA run as a one-step irreversible reaction (imidization) with very fast pre-equilibrium. In other words, acylation step becomes almost negligible, though it has some influence on the absolute value of effective comonomer reactivity. Using the mathematical model developed, it is possible to predict the molecular weight, overall rate of chain growth and an average block length of CPIs at any conversion of synthesis in BA, for any combination of comonomers and any regime of intermonomer or intermonomer/comonomer loading.

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Highly filled systems of graphite/graphene in polybenzoxazine for bipolar plate in proton exchange membrane fuel application

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In this work, we compare properties of highly filled systems based on graphite filled polybenzoxazine, graphene-filled polybenzoxazine and the filled systems of mixed graphite/graphene in polybenzoxazine. These highly filled systems show potential use as high performance bipolar plates in proton exchange membrane fuel cell (PEMFC). The relatively large particle size of graphite used was found to provide very high loading of the graphite (i.e. 80 wt%) in BA-a polybenzoxazine resulting in relatively high thermal conductivity value up to 10.2 W/mK. In the case of graphene filled polybenzoxazine, the maximum graphene content was determined to be about 60 wt% therefore a lower thermal conductivity value of about 8.0 W/m K was obtained. The outstanding properties of graphene filled polybenzoxazine were observed in their electrical conductivity and mechanical properties which were found to show greater values than graphite filled polybenzoxazine comparing at the same filler content as a result of a much higher aspect ratio of the graphene compared to the graphite. Consequently, the mixed filler systems of graphite/graphene in polybenzoxazine was formulated. The property characterization suggested that an addition of small amount of graphene filler can systematically enhance mechanical properties of the graphite filled composites. It was also observed that thermal conductivity values of the graphite/graphene filled polybenzoxazine was significantly improved with the value as high as 14.5 W/mK at 83 wt% of the carbon filler (graphene 7.5% and graphite 75.5%) as a result of tremendous amount of conductive filler network with less phonon scattering in the network.

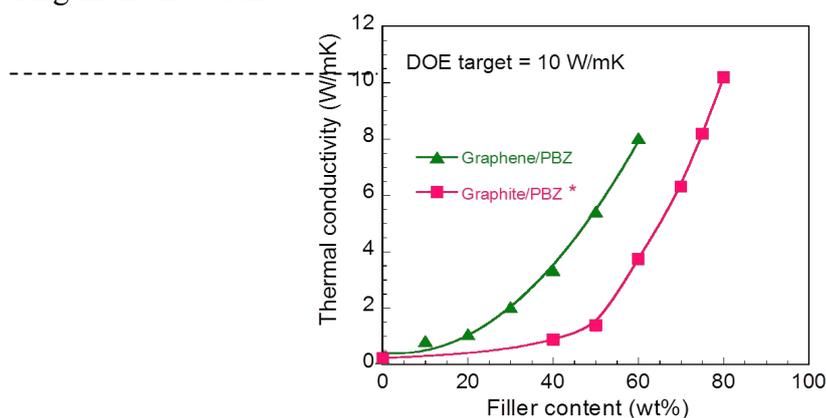


Fig. 1. Thermal conductivity of graphite (■) and graphene (▲) filled polybenzoxazines.

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Flame retardant epoxy resins modified with epoxyphosphazenes

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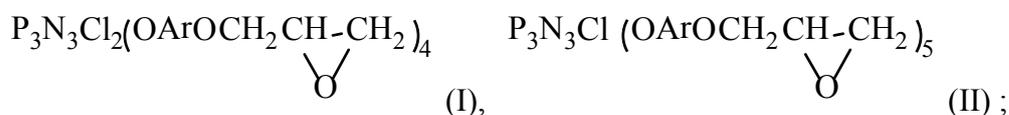
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Fire resistance of organic polymers can be enhanced by incorporation of phosphorus and halogen atoms into the macromolecules, or by using of flame retardants, containing those atoms.

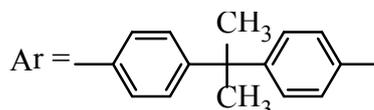
Two component phosphorus-nitrogen-containing epoxy resins were synthesis (scheme 1) in order to obtain oligomers containing different quantities of nitrogen and phosphorus, and, as a result with adjustable parameters of fire resistance.

In present work we investigat joint polycondensation of hexachlorocyclotriphosphazene (HCP), diphenilolpropane (DPP) and epichlorohydrine (EHD), which was used as a reagent and a solvent [1]. To eliminate the possibility of gel formation caused by polyfunctionality of HCP during polycondensation, variable excess of the DPP was used. Whereby epoxyphosphazene I and II was synthesized, also organic epoxy resin ED was obtained.

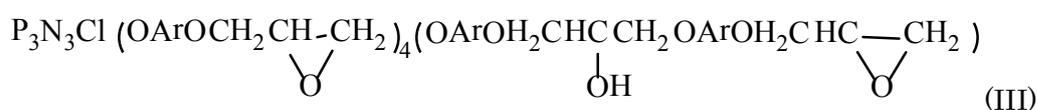
Epoxyphosphazene synthesized with the molar ratio HCP:DPP from 1:6 to 1:16 mostly consist of tetra- (I) and pentasubstituted (II) derivatives:



where:



According to MALDI-mass spectra of the EP fraction a minor amount of type III oligomer with $m/z = 1872$ present in the polycondensation products additionally to the compounds I and II.



According to the GPC and the content of the phosphorus, chlorine and epoxy groups in oligomers content of the EP fraction in the resulting mixture was calculated.

The LOI values of the phosphazene containing epoxy resins cured by isomethyltetrahydrophthalic anhydride shown their increased fire resistance, especially at elevated levels of EP fractions.

Phosphazene containing epoxy resins were tested protective and dielectric coatings, molding compaunds, binders for filled plastics and adhesives. They demonstrate an appropriate or higher level of properties in comparison with organic epoxy oligomers and also provide enhanced fire resistance.

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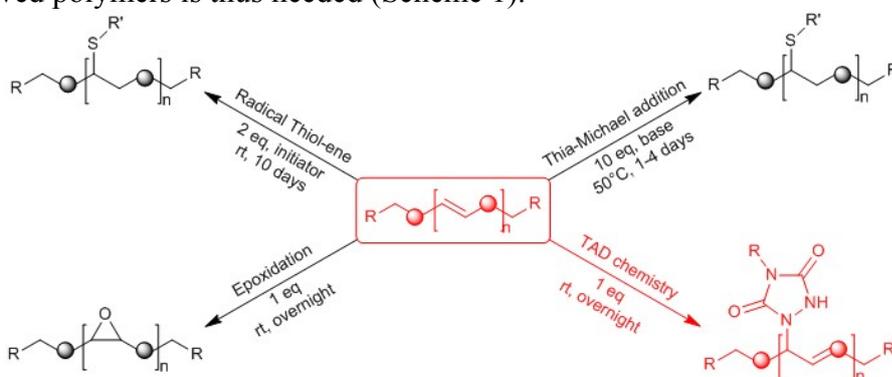
TAD-chemistry and ADMET-polymers: a sustainable alliance

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Acyclic diene metathesis (ADMET) has been known since the nineties, but the impact of the resulting polymers on the field of green chemistry, was certainly not anticipated. To open ways to tailor-made materials in the future, post-functionalisation methods of the available unsaturations are necessary. From 1992 until now, some functionalisation methods have been described, with varying degrees of success [1],[2],[3]. Harsh conditions, multiple equivalents, long reaction times and/or low yields make the proposed reactions less interesting for industrial applications. A robust, additive-free, atom efficient and orthogonal procedure for the functionalisation of ADMET derived polymers is thus needed (Scheme 1).



Scheme 1. Overview of the possible post-polymerisation functionalisation methods.

We propose the use of triazolinediones as a functionalisation method for ADMET polymers. 1,2,4-Triazoline-3,5-dione (TAD) [4],[5] exhibits a high reactivity toward both conjugated dienes and isolated alkenes in a Diels-Alder or an Alder-ene reaction, respectively. These reactions reliably give a specific reaction outcome with olefinic reaction partners in almost any setting. On top of this, the reactions can be monitored visually, as all triazolinediones show a strong absorption in the visible light spectrum.

In this work, we demonstrated the successful post-functionalisation of ADMET derived polymers utilizing TAD chemistry. Post-functionalisation was performed in a quick and quantitative manner, on bio-based ADMET polymers with several polymer backbones and with a variety of TAD compounds. It was shown that the glass transition temperature of the polymers could be tuned by the degree of functionalisation. In a last step, the functionalized polymers were cross-linked by a bivalent TAD compound to obtain functionalized thermoset materials.

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Effect of zinc oxide nanoparticles characteristics epoxy polymer active media

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A promising direction in quantum electronics is providing tunable lasers based on polymer active media, generating radiation in the visible region of the spectrum.

In this regard, relevant research is aimed at improving the characteristics of polymeric active media.

The aim of the work was to study the effect of zinc oxide nanoparticles on the spectral and lasing characteristics epoxy polymeric active media.

Polymeric active media were created by the activation of the epoxy polymer dye phenalemine 512 (P512) and the doping of zinc oxide nanoparticles. Epoxy resins were obtained by curing epoxy oligomer by isomethyltetrahydrophthalic anhydride with dimethylbenzylamine catalyst for curing. P512 does not form chemical bonds with the epoxy resin, and forms a solid solution of the dye in the polymer. Zinc oxide nanoparticles were prepared by direct precipitation. Zinc acetate served as a precursor, sodium hydroxide as precipitant, isopropanol as environ. Zinc oxide nanoparticles are spherical in shape with a size 7 ± 1.5 nm. The solution containing the zinc oxide nanoparticles combined with epoxy oligomer, whereupon isopropanol was removed by evaporation.

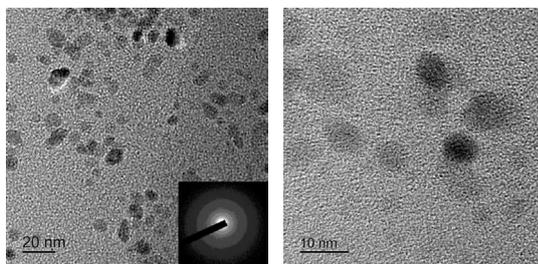


Fig. 1 – TEM microphotograph ZnO nanoparticles

Pumping of epoxy polymer active media carried out by radiation with a wavelength of 532 nm. Lasing wavelengths (λ_r) and the efficiency (COP) generation were 607 nm and 604 nm, and 21% and 5% with P512 at a concentration in the epoxy polymer active media 0.2% and 0.4% respectively. Doping epoxy polymer active media by the zinc oxide nanoparticles in an amount of 0.01% resulted to a change in the characteristics of the epoxy polymer active media. λ_r was 600 nm and 609 nm, and the generation efficiency was 20% and 7.5% at the P512 at a concentration of 0.2% and 0.4% respectively. This generation has been increasing, the narrowing of the emission band evidenced it.

Thus, conducted research shows the prospects of improving the characteristics of epoxy polymer active media by presence of P512 and zinc oxide nanoparticles.

Processable polyimides and polybenzimidazoles: synthesis and their application for gas separation

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Polymer membranes are considered as effective technology for the separation of gaseous mixtures and aromatic polyimides (PIs) are known as one of the most promising potential candidates as gas-separation membranes because of their reasonable permeability and high selectivity for CO₂/CH₄ and O₂/N₂ gas pairs together with the excellent thermo-oxidative and mechanical properties [1]. Use of monomers, diaminas or dianhydrides, with bulky pedant groups allows not only to improve the polymer processability but also to increase the fractional free volume and thus results in better gas permeability [2]. Hereby we would like to report the synthesis and properties of the rigid-rod PIs based on 4-4'-Diaminotriphenylmethane (DA-TPM) and its derivatives. Introduction of the pedant phenyl ring into the polymer backbone improved significantly their solubility without sacrificing the high thermal stability [3]. PIs obtained by one-step synthesis showed good mechanical properties and additionally much better gas transport properties (higher permeability and selectivity) in comparison with PIs synthesized with commercially available 4-4'-Diaminodiphenylmethane [4]. The best TPM-6FDA membrane showed the ideal selectivity $\alpha = 17.2$ and 28.9 for O₂/N₂ and CO₂/CH₄ correspondingly. Additionally, polybenzimidazoles (PBIs), another type of rigid-rod polymers with superb thermo-oxidative, chemical and dimensional stability, based on a common tetramine (3,3-diaminobenzidine) have been synthesized and their gas separation properties will also be discussed.

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CAGE diamines – perspective monomers for polycondensation polymers

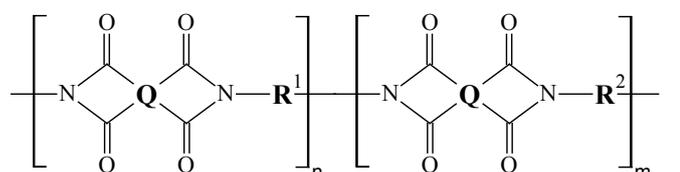
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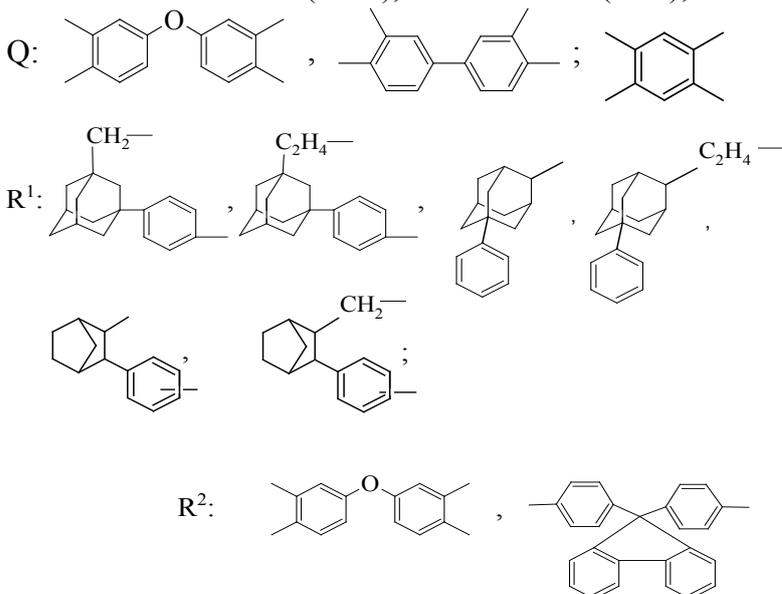
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Polyimides are used in various branches of industry, primarily as thermally resistant dielectric materials. One of the ways to improve the technical characteristics of such polymers, and expand the scope of their practical use is an introduction to the structure of the polymers the alicyclic fragments.

We obtained polyimides based on dianhydrides of aromatic tetracarboxylic acids and a series of cage diamines by single-stage high-temperature polycyclisation in solution method and two-stage method:



where $n = 0 \div 100\%$ (. mol), $m = 0 \div 100\%$ (mol.);



Obtained polyimides have fairly high thermo oxidative stability: $t_{5\%} 380 \div 500$ °C depending on the structure of the polymer. According to hydrolytic stability, majority of the polymers significantly surpass those of fully aromatic polyimides. It should be noted, that high hydrolytic stability is ensured only in the presence of aliphatic bridges separating the amino group and the cage fragment.

Basic electrical properties of the alicyclic polyimides were studied and it was shown that they are highly thermally resistant dielectrics with low dielectric constant value, which is especially important for microelectronic products.

It should be noted, that the way to produce the bicyclic diamines includes a small amount of steps relatively while the working characteristics of obtained polymers are saved on a fairly high level.

Self-polycondensation of telechelec polyvinylalcohol and design of rigid macroporous sorbents for biomedical application

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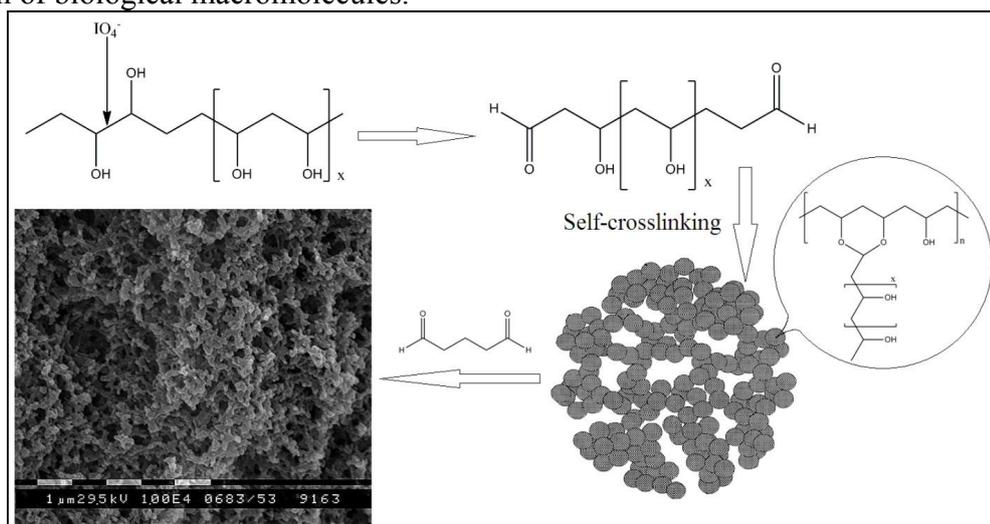
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A novel method for poly(vinylalcohol)-based macroporous matrix (MP-PVA) preparation in aqueous media without usage of an outer porogens has been elaborated [1]. The method includes selective PVA oxidative cleavage at 1,2-diol fragments and self-polycondensation (self-crosslinking) of generated telechelic oligomers followed by crosslinking with an excess of glutaraldehyde (GA) (scheme 1).

MP-PVA represents a highly crosslinked matrix that is non-swellable in water and common organic solvents and has a high pore volume and pore surface and contains reactive aldehyde groups. Surface topography of MP-PVA has revealed its heterogeneous globule-like structure with open macropores of about 100–300 nm in diameter and large pores of about several microns. Dynamic light scattering study has elucidated the phase separation during the self-crosslinking step as the main factor responsible for macroporous structure generation. This two-phase structure of polymer solution is fixed by further crosslinking with GA.

The prepared matrix has been successively applied as the parent platform for boronate affinity separation and quantification of glycated and non-glycated haemoglobin in human blood of diabetics patients. The reactive aldehyde-groups containing MP-PVA matrix may be promising for design of new macroporous sorbents and monoliths for affinity ligands immobilization and separation of biological macromolecules.



Scheme 1. The scheme of macroporous PVA preparation.

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Synthesis and characterization of new silicone/polyurethane materials

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Materials based on polyurethane and silicone are already independently used for many various applications. However, each of them has its own limits. Indeed, on one hand, polyurethane materials have very good mechanical properties thanks to hydrogen interactions, but they are not stable at high temperature. On another hand, silicone based materials exhibit high thermal stability, they are highly hydrophobic and chemically inert. However, they are much sensitive to mechanical stress (mainly choc) than polyurethane materials. To overcome drawbacks of these two materials, they have been combined to provide new materials with the strengths of both units without their weaknesses^{1,2}.

In this work, new Silicone/Polyurethane (Si/PU) materials have been synthesized by solvent-free condensation between different functionalized oligomers with different terminal group (A and B) and molecular weight. The different parameters of synthesis (curing time and temperature, reactive proportion, ...) have been optimized to obtain homogenous Si/PU materials with different compositions (Table 1). Degradation temperatures, thermomechanical properties, hardness and thermal ageing were measured for each material.

Finally, to improve their properties, Si/PU materials have been also filled. The effects of chemical nature of fillers (carbon black, calcium carbonate and a modified silica) and their weight proportions (varying from 5 to 30 wt.%) were investigated. A thermal ageing study shows that the presence of fillers in materials allows reducing until 20% of weight loss after 1000 h at 150°C.

Table 1. Properties of synthesized Si/PU materials

%Siloxane/%PU	Hardness (Shore A)	Degradation Temperature at 5 wt% loss (°C)	Storage modulus at 25 °C (MPa)	Weight loss after 1000h at 150°C (%)
6,0 ^c	30	245	0,5	42
6,1 ^d	30	280	1,6	27
11,3 ^c	30	265	-	<i>In progress</i>
13,2 ^c	-	280	<0,01	-

^c: terminal group A; ^d: terminal group B

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Composite materials with intertwining carcass structure polyurethane - polydimethacrylate

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Despite the diversity of nano- and micro-structured composite materials (CM), and methods for their formation, there are a number of problems whose solution requires to complication of the organization level of the reinforcing components. One way to improve the strength of reinforced CM is using the formation of composites with interconnected extended nano- and micro-sized reinforcing elements instead of using just nanoparticles or reinforcing fibers. The ability to set the final geometry of the product during the CM formation is also important. To solve these problems, we offer the following method of CM obtaining. At first, the formation of the porous polymeric monolith scaffold, in which the open related pores with a given size uniformly distributed in bulk, is realized by photopolymerization method. On the next step, the polymerization reaction, leading to the formation of two 3-dimensional mutually wretched polymeric scaffolds, is conducted in the volume of porous structure. Earlier, we synthesized polymer monoliths with open related pore system via photopolymerization of compositions based on oligocarbonatedimethacrylate OCM-2 [1]. Pore sizes in the resulting polymers are in the range of 10^2 - 10^4 nm, and that allows using these porous polymers as matrices for conducting the secondary polymerization in them. Polymerizing in the pore volume system should have a sufficiently low viscosity to penetrate into pores; curing should not be accompanied by the release of low molecular weight products; process should have low shrinkage to reduce stress on the pore walls. Accordingly, the polyisocyanate - polyol system was used as the composition for secondary polymerization. So, the porous polymer matrices based on dimethacrylates OCM-2, MDP-2 and TGM-3 were synthesized, and the polyurethane-forming composition were introduced in these matrices. PM-200 (a mixture of diphenyl methane diisocyanate with the functionality of 2.6 - 2.7), polyols Laprol 502, Laprol 503 and provided by Ltd. «Covestro» Desmodur 44V20L and Desmophen 28HS98 were used as the components of the composition. The compositions for photopolymerizable mixtures allowing to obtain the porous polymer matrix having an average pore diameter from 0.4 to 20 microns were found. The methods of introduction of polyisocyanate - polyol mixtures in such porous matrices and CM production were developed. The structure of the surface layers of the received CM was investigated by AFM, SEM and optical microscopy.

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Isosorbide: a biobased building block to improve polycondensate properties

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Isosorbide or 1,4-3,6 dianhydrohexitol, derived from starch and more precisely from sorbitol, is one of the chemical intermediates of interest in the field of thermoplastic materials and for curable resins application. Hence, isosorbide found its place as a monomer suitable for polycondensates synthesis [1] like polyesters, polycarbonates and thermoplastic polyurethanes. Concerning aliphatic [2] or semi-aromatic polyesters [3], the addition of isosorbide increases glass transition temperature, opening to this new polymer several usual applications of amorphous polymers. The properties of other thermoplastics like polycarbonates [4] or TPU can as well be improved by the incorporation of isosorbide. The preparation of poly (ethylene-co-isosorbide) terephthalate with different ratios of isosorbide will be particularly detailed. The structure – properties relationship will permit a focus on the synthesis of polyesters with semi-crystalline or amorphous structures. The influence of isosorbide on the polymerization, on the processing of the resulting polyester as well as the modification of the final properties will be enlightened.

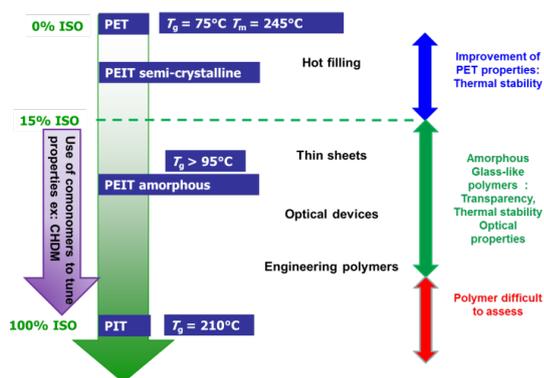


Fig. 1. Properties and main application fields of PET with different isosorbide contents.

In polycarbonate, isosorbide is much more than just a solution for Bisphenol A replacement. Hence, Isosorbide containing polycarbonates present significantly increased properties like mechanical strength, heat resistance and optical properties with resulting properties between usual Polycarbonate and PMMA.

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Development of technology of polysulfone production for 3D printing

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Currently, for obtaining products from polymeric materials, it is gaining more and more popularity so-called additive manufacturing or 3D-printing. Unlike traditional polymer processing techniques (extrusion, injection molding) new technology allows production of objects of any geometry and the degree of difficulty, on the basis of the digital model.

High-tech formation of working details with complex configurations with the use of 3D technology sets high standards to polymeric materials in terms of their consumer characteristics and processability. Most polymeric materials currently used in additive technology is not suitable for obtaining high and responsible products by the 3D printing. Perspective for these purposes are polyethersulfones. However, the use of high performance polymers in 3D-printing is limited to a number of complex problems which solution requires a certain technological advance. Research in the field of features of application of polymeric materials in additive technology is very limited and includes mostly ABS plastic and polylactide.

The report discusses the results of experimental studies on the development of high-tech processes of polysulfones of different chemical structure and technology of 3D printing by layering molten polymer strand .

On the basis of the laws identified in the studies, optimized technology for producing polysulfones of different chemical structure, by improving each of the process steps that make up the entire production of polymer synthesis cycle of the class and, as been found, contributing to the final set of material properties for 3D printing, describing its quality and stability properties.

The regularities of cross-linking and thermal degradation polysulfones of different chemical structure at processing temperatures and 3D printing, depending on the structure of the reaction medium and methods of blocking end groups. The influence of technological modes of 3D-printing by layering molten polymer strands on the physico-mechanical properties of polysulfones.

Identified regularities can become the foundation of a new type of science-based directional development of polymeric materials for additive technologies with predictable properties and determine the main ways of development for this new field of polymer chemistry.

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Synthesis and characterization of sustainable copolymers pet-co-*plla*

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Most plastics are produced from the processing of fossil fuels and their contribution to the depletion of these resources together with the environmental impact of their extraction are under question. Poly(ethylene terephthalate) or PET is a high consumption material with many applications in packaging and textile industry owing to its excellent physical and chemical properties. Due to its increasing consumption and non-biodegradability, PET waste disposal has created serious environmental and economic concerns. An interesting option for the treatment of PET is chemical recycling. Recently, Hedrick and coworkers were able to form monomers as feedstock for a variety of valued materials from PET recycling [1].

On the other hand, the production and use of biodegradable plastics will increase by 65% between 2012 and 2017, according to the Bioplastics European Association [2]. The poly (lactic acid) or PLA, is a biobased and biodegradable polyester that is mainly used for packaging, textile, agriculture and bio-medical applications. PLA is produced from feedstocks derived from biological or renewable resources. The increasing demand for biodegradable plastics must be accompanied by academic research to optimize their formulation and processing for developing durable grades with better performance. In this work, new polymers were obtained by combining a biodegradable polyester with recycled material, following a sustainable approach. Copolymers (PET-co-PLLA) were synthesized linking monomers derived from recycled PET with PLLA (obtained by ROP), where copolymers with diverse compositions were made and exhibited different properties. Structural and morphological characterization of the novel polymers prepared were performed. The thermal properties of these materials were also studied. Moreover, the polymers were synthesized trying to follow the green chemistry pocket guide [3].

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Thermal properties of biobased aliphatic polyesters reveal odd-even effect

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In this study, new aliphatic polyesters have been synthesized from 1,4-butanediol and long aliphatic diacids (from 13 to 18 carbons) by a direct esterification process. The polycondensation was found to be much more efficient compared to classical procedures reported in literature and lead to high molecular weight polymers (30 000 -55 000 g/mol).

The thermal characterization of the polyesters displayed melting points between 46 to 85°C and crystallization temperatures from 28 to 74°C and also featured a good thermal stability (350-400°C).

The differential scanning calorimetry analysis highlighted “odd-even” effect on the melting and crystallization temperatures (Figure 1), and pointed out higher temperatures for polyesters incorporating an even number of methylene in the repeating units.

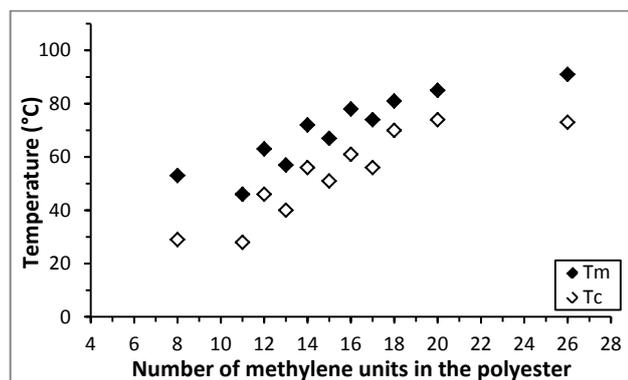


Fig. 1. Evolution of melting and crystallization temperatures with number of methylene units in the polyester

This behavior has already been reported so far [1,2] and is generally attributed to different alignments of carbonyl group [3]. Nevertheless, more studies have to be done to get further insights on this odd-even effect. In this context, we propose to realize computational modeling of polyesters having an odd and even number of methylene units to elucidate polymer chains organization.

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Polycondensation ionic liquids

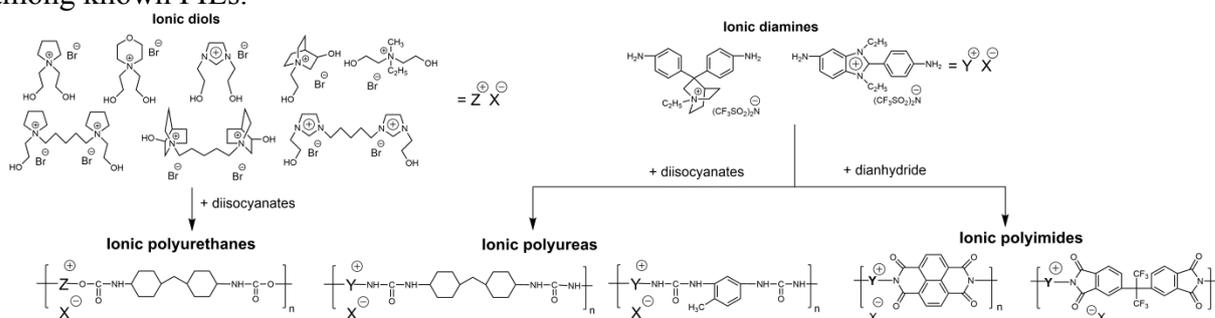
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Polymeric ionic liquids (PILs) combine all the unique properties of ionic liquids (IL) - and the ability of high molecular compounds to form films and membranes. The possibility of controlling the properties of PILs by varying the structure of cation and anion determines their utilization as unique materials for lithium batteries, CO₂ sorbents, gas separation membranes, etc. The majority of PILs is synthesized by polymerization, while the condensation analogues are poorly known [1]. Thus, the purpose of this study was the formation of new type of condensation derived PILs with valuable properties: high thermal stability, improved mechanical strength, high gas permeability, etc.

Various methods for the preparation of new PILs were applied: polycondensation of ionic diamines and diols with the corresponding neutral monomers or modification of neutral condensation polymers. The novel ionic polyurethanes, polyureas and polyimides were synthesized. The obtained ionic polyurethanes were studied for the CO₂ sorption. It was shown that polyurethanes with the BF₄ anion have the highest CO₂ sorption (22.1 mg / g, 273 K, 1 bar) among known PILs.



Scheme 1.

The novel PILs with improved hydrophobicity (with water-wettability angle equal to 94°) and enhanced hydrolytic stability were prepared by quaternization of the neutral polyimides (PIs). The membranes formed from ionic PIs were characterized by the highest CO₂ permeability among PILs - 28.9 Barrer (20°C, 100 kPa). The filling of the films with ILs (up to 50 wt.%) allowed to increase the permeability of CO₂ (up to 85.2 Barrer) and the selectivity of gas separation ($\alpha_{\text{CO}_2/\text{N}_2}$ up to 34) [2]. The composite films based on ionic PIs and carbon black were successfully used as new cathode materials for Li batteries, demonstrating an average specific capacity up to 75 mA·h/g during 100 cycles of charge/discharge at a rate of C/5 and 25°C.

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Preparation of fluorinated polyimides with bulky structure and their gas separation performance correlated with microstructure

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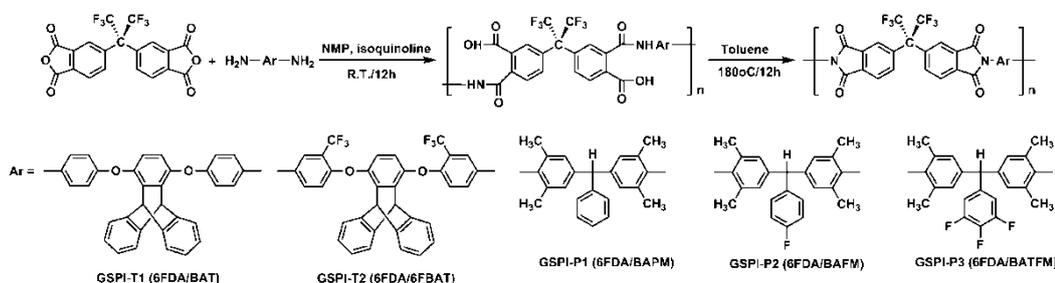
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Aromatic polyimides are one of the most attractive materials for gas separation due to their excellent properties, *e.g.*, excellent thermal stability, good mechanical properties, outstanding chemical resistance, and high gas selectivity. They are especially suitable for using in some extreme situations, such as, high temperature, high pressure, or existence of harsh substances [1]. However, conventional polyimide membranes possess low gas permeability on account of the strong attractive force between intra/inter-molecules, which also lead to poor processability. In the past decades, many attempts have been made to enhance the gas permeability of polyimide membranes under the premise of maintaining their inherent good gas selectivity [2]. Fluorinated polyimides containing 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) have been identified as materials exhibiting both high gas permeability and selectivity [3]. In addition, introduction of bulky moieties into the polymer backbone, to disturb the chain packaging and consequently increase the free volume, is also an efficient way to improve the permeability of polyimide membranes.

In this research, aiming at development the polyimide membranes with enhanced gas permeability, the fluorinated polyimides with high fractional free volume were prepared from 6FDA and novel aromatic diamines with bulky triptycene and pendent phenyl moieties as shown in Scheme 1. These polymers showed excellent solubility, high thermal stabilities and outstanding mechanical properties. The correlation of gas separation performance with the microstructure of these polyimide membranes was investigated. The results indicated that the gas permeability of these membranes is strongly depended on their free volume and also affected by fluorine content. The GSPI-P membranes revealed much higher permeability coefficients than the GSPI-T membranes combined with good selectivity. The larger fractional free volume of GSPI-P membranes is directly associated with their higher gas permeability, even though they gave narrower d-spacing than GSPI-T membranes. Moreover, the GSPI-P membranes also provided good selectivity for CO₂/CH₄ and CO₂/N₂ gas pairs because their appropriate cavity size is favorable to separate the CO₂ from the other gases.



Scheme 1. Synthesis of fluorinated polyimides with triptycene moieties and pendent phenyl moieties

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Rilsan® HT, the first flexible high temperature polyamide

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Designing lighter materials would help to decrease vehicles weight and therefore allow for reduction in fuel consumption.

To that end, ARKEMA recently developed Rilsan® HT, an entirely new thermoplastic polymer, which is a breakthrough for the automotive industry, as it is able to replace metal and rubber in tubes for high temperature under-the-hood applications. It is indeed the first polyamide to combine high temperature resistance with flexibility.

Rilsan® HT is synthesized by polycondensation from renewable (non-fossil) materials, among which one is a relatively newly commercially available monomer.

In this presentation, we would like to emphasize some of the technical challenges ARKEMA, as an industrial, had to overcome to bring such a new polymer to the marketplace. Focus will be laid on the design, synthesis and formulation of this new polyamide at labscale but also on the upscaling at the industrial scale. In particular, the consequences of using a newly commercially available monomer on the industrial synthesis will be discussed.

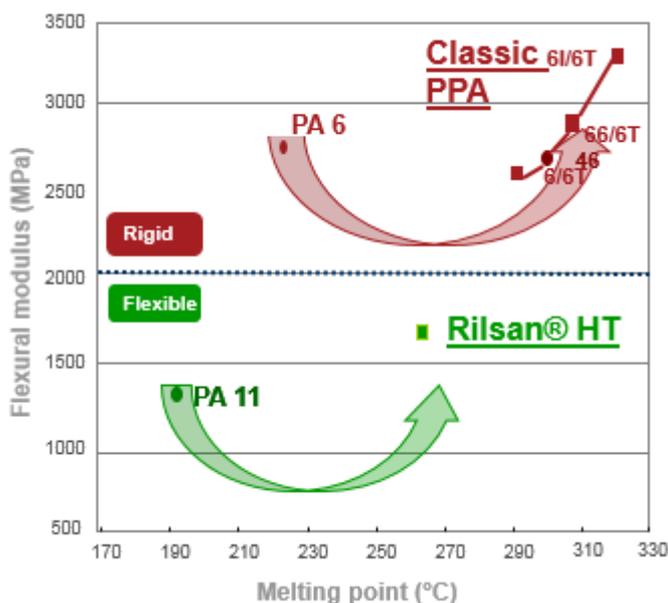


Fig. 1. Rilsan® HT: a new polyamide bridging the gap between long-chain PA and classical polyphthalamides

Engineering polymers mediated by functionalized 1,1-diphenylethylene derivatives: polymer substrates for membrane development

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The current research involves the utilization of symmetrically functionalized 1,1-diphenylethylene derivatives as monomers in step growth polymerization methods to form well defined engineering polymers [1].

The use of appropriate symmetrically disubstituted 1,1-diphenylethylene derivatives as monomers in step growth polymerization processes affords a series of new poly(ether ether sulfone), poly(ether ether ketone) and polyimide derivatives. For example, the utilization of 1,1-bis(4-hydroxyphenyl)ethylene and 1,1-bis(4-*t*-butyldimethylsiloxyphenyl)ethylene as monomers in nucleophilic displacement polycondensation reactions with 4,4'-difluorodiphenylsulfone and different bisphenols forms a series of new polysulfone derivatives [1]. Furthermore, a series of new PEEK derivatives were prepared by the cesium fluoride catalyzed polymerization of 4,4'-difluorobenzophenone with 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane and 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene in different mole ratios of monomers to afford well-defined PEEK derivatives with the introduction of the 1,1-diphenylethylene unit along the polymer backbone. Similarly, a series of new aromatic polyimide derivatives were prepared by step growth polymerization methods by the polycondensation reactions of 4,4'-oxydiphthalic anhydride with different mole percentage ratios of 2,2-bis[4-(4-aminophenoxy)phenyl]propane and 1,1-bis(4-aminophenyl)ethylene as monomer precursors. The intermediate polyamic acids were subjected to a thermal imidization process to provide the corresponding polyimide derivatives.

The resultant 1,1-diphenylethylene based engineering polymer derivatives were subjected to post polymerization sulfonation reactions via the thiol-ene click reaction with sulfonating agents to form the corresponding sulfonated polymers with the sulfonate group pendant to the polymer backbone.

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Nanomedicine for efficient chemotherapy of brain tumours: From bench to bedside

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Brain tumours, and especially glioblastomas, belong to the most aggressive human cancers associated with a very unfavorable prognosis for the patients. Treatments of choice are neurosurgery and radiotherapy, while the contribution of chemotherapy is only modest, which is largely due to the ineffective drug delivery to the brain limited by the blood–brain barrier (BBB). Thus poor brain uptake of doxorubicin (DOX) is perhaps the main reason why this potentially active anti-tumour antibiotic is not used for the chemotherapy of glioblastoma.

The nanoparticle-based formulation of doxorubicin (working name “Nanodox”) is a novel drug candidate against glioblastoma based on brain delivery by poly (lactide-co-glycolide) (PLGA NPs) nanoparticles. Nanodox is being developed by R-Pharm Group (Russia) through its research-oriented subsidiary - Drugs Technology LLC.

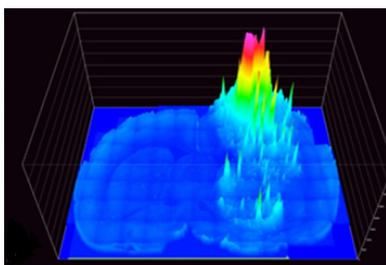


Fig. 1. Enhanced accumulation of the surface-modified PLGA nanoparticles in the intracranial C6 glioma in rats

This drug delivery product is designed with the consideration of the specific features of the BBB. The PLGA NPs appear to be the carriers of choice that combine many advantages of other delivery systems, such as a potential for selective targeting and an opportunity to tailor particles with the desired characteristics offered by the versatility of polymer chemistry. The PLGA NPs coated with a specific surfactant represent a self-assembling delivery system acquiring biological vectors from the blood, which enables their passage across the BBB and doxorubicin delivery to the tumour inside the brain. This ability of the PLGA NPs to deliver drugs that are not BBB permeable by simple intravenous infusion is representing a major breakthrough. The technology is a result of the fruitful long-term collaboration

between Russian and German scientists [1]. The laboratory technique was successfully optimized, scaled-up, and transferred to industry (pilot production).

Extensive preclinical studies confirmed the efficacy of Nanodox and demonstrated its favorable toxicological profile. The most important finding was the reduction of DOX cardiotoxicity (reduced cardiac and testicular toxicity, as compared to the free drug) that could be explained by the altered biodistribution of the nanoparticle-bound drug.

A Phase I dose escalation study of the nanoparticle-bound doxorubicin in patients with advanced solid tumours (including GBM) is currently on-going in Russia. The drug is well tolerated and does not cause any dose-limiting toxicity (DLT) adverse effects at the dose levels studied so-far. Overall this technology holds great promise for the treatment of severe CNS diseases such as glioblastomas.

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The project is supported by the Russian State Program “Pharma 2020”.

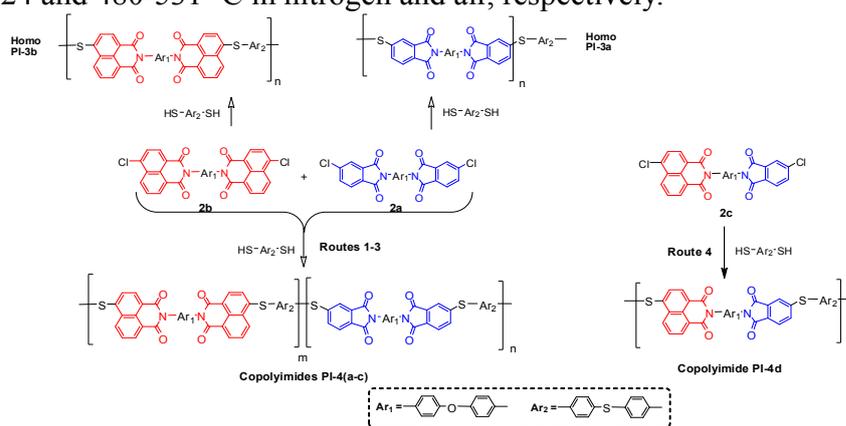
Synthesis and characterization of novel asymmetric polyimides containing phthalimide-naphthalimide moieties

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Aromatic polyimides (PIs) represent an important class of high performance polymer materials in various applications such as gas separation membranes, composite matrices, and high-temperature adhesives and coatings. In comparison, polyphthalimides possess better melt/solution processability, while polynaphthalimides display better thermal properties, hydrolytic stability and fire resistance [1]. Recently, we are more interested in the polyimides containing asymmetric both phthalimide and naphthalimide units in the main chain [2-3]. Firstly, we reported the polyimides derived from two asymmetric diamines containing naphthalimide moiety, which resulted into high T_g (311-421 °C), good solubility in polar solvents, and excellent thermal stability ($T_{5\%}$ of 435-563 °C) of PIs. In continuation, we investigated and integrated the excellent properties of naphthalimide and phthalimide by synthesizing different molecular architectures (homo, random, gradient type and block) polymers by aromatic nucleophilic substitution polymerization. Three different bischloro-imide monomers [bischlorophthalimide **2a**, bischloronaphthalimide **2b**, bischloro (naphthalimide-phthalimide) **2c**] were prepared and reacted with 4,4'-thiobisbenzenethiol by different synthetic routes, to synthesize homo **3a-b**, block **4a** and random (**4c-d**) copolyimides (Scheme 1). For studying molecular architecture of polymers, the relative reactivity of bischloro-imide monomers (**2a-b**) was examined by gas chromatography mass spectrometry (GC-MS) using model compounds *N*-phenyl-4-chloro-1,8-naphthalimide and *N*-phenyl-4-chlorophthalimide. In comparison with homopolyimides **3a-b**, naphthalimide-phthalimide based copolyimides **4b-d** demonstrated good solubility in aprotic solvents and better mechanical properties. These polymers exhibited high glass transition temperature (T_g) of 198-319 °C and good thermal stability based on 5% weight loss temperature ($T_{5\%}$) of 492-524 and 480-531 °C in nitrogen and air, respectively.



Scheme 1. Synthesis of homo **3a-b** and copolyimides **4a-d** by different synthetic routes

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Combination of the processes of polymerization and polycondensation type in synthesis, chemical modification and cure of rolivsan thermosetting resins

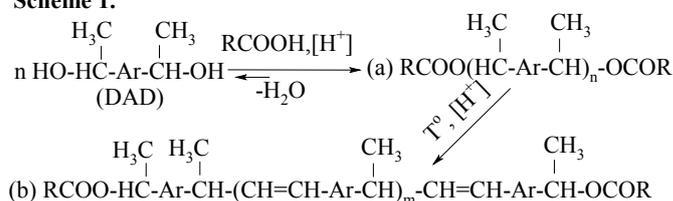
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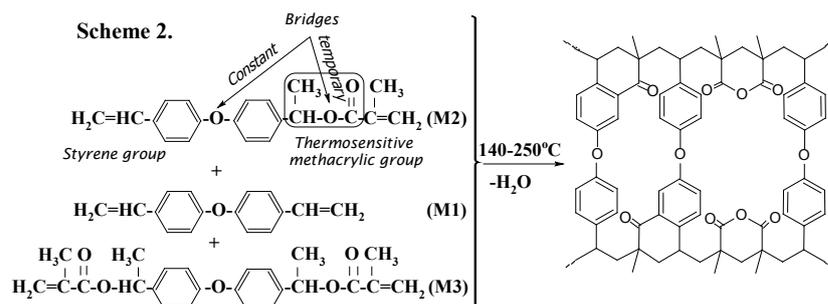
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The development of rolivsan resins (ROLs) introduces a new structure-forming tool into the chemistry of heat resistant polymers, namely, (α -hydroxyethyl)phenylene group as a part of di-*sec.* aromatic diols (DAD). ROLs are formed in the series of consecutive-parallel reactions including: (a) co(poly)condensation of DAD and unsaturated carboxylic (e.g., methacrylic) acids

Scheme 1.

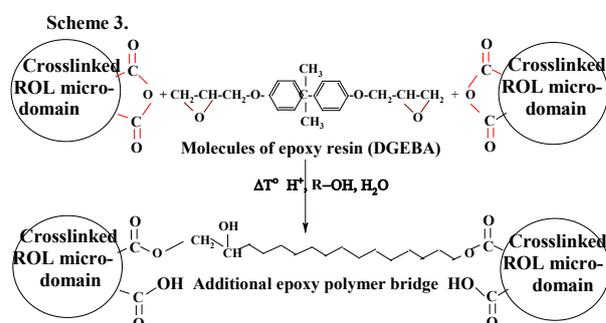


(RCOOH) leading to the formation of oligoethers with methacrylate end groups, (b) proton-transfer polyaddition of (di)vinylaromatics and (di)methacrylates of DAD resulting in the formation of unsaturated oligomers with methacrylate end groups (Scheme 1) [1,2].(Di)vinyl-



aromatics and (di)methacrylates of ROLs participate in radical crosslinking and form densely crosslinked microdomains at 140-170°C. Increase in temperature leads to acid-catalyzed splitting of thermosensitive methacrylate

bridges and subsequent cyclocondensation reactions of the neighboring reactive units that results in the formation of α -methylene tetralone and methacrylic anhydride units. The final microheterogeneous ROLs' copolymers are highly crosslinked microdomains with pending anhydride units weakly bound to each other by defective polymer interlayers (Scheme 2) [1]. A novel chemical method for impro-



ving high-temperature properties of ROLs' thermo-setting resins based on development of microheterogeneous model of the formation of crosslinked ROLs-epoxy and ROLs-diamine blends has been proposed [3]. The method provides additional crosslinking of the microdomains by reactions with modifiers, such as epoxies or aromatic diamines. High-temperature properties of ROLs co-cured with of aromatic diamines (8 \pm 2 wt.%) (via bulk

(poly)reactions of radical crosslinking, acylation, and oxidative polymerization) can be substantially improved compared to the cured neat ROLs.

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Highly selective coupling reactions toward chlorine-containing electroluminescence polymers

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The chlorine-containing organic conjugated molecules are drawing more and more attention recently because of the potential as strong competitors for optoelectronic materials.^[1] To the best of our knowledge, there are still few reported chlorine-bearing aryl materials, because of the synthetic difficulties. To acquire chlorine-functionalized organic materials, a post-chlorine-functionalization method has been reported.^[2] However, controlling the chlorine ratio and chlorine position during the post chlorine processing is extremely difficult and almost impossible. As such, the development of more efficient approaches for the preparation of chlorine-bearing molecules is highly desirable for the field of material chemistry. Here, high selectivity and yield from aryl-aryl coupling reactions between chlorine-containing aromatic bromides and organotin/organoboron reagents are reported.^[1, 3] The reactivity of the chlorine can be completely restrained by employing the optimized Palladium catalysts, which makes it possible for application in preparation of the chlorine-bearing molecules. Then, a series of high molecular weight conjugated copolymers with chlorine on the backbones are straight forward synthesized under the optimized Stille/Suzuki couplings. The resulting chlorine-bearing copolymers show large Stokes shift, low self-absorption and deep LUMO level. And the HOMO level of the materials can be finely tuned by using different donor moieties to realize efficient hole injection and deep red to NIR fluorescence. Based on this, deep red to NIR emission is obtained with good brightness and external quantum efficiency by using the chlorine-containing polymers as the emitter.^[1, 3, 4]

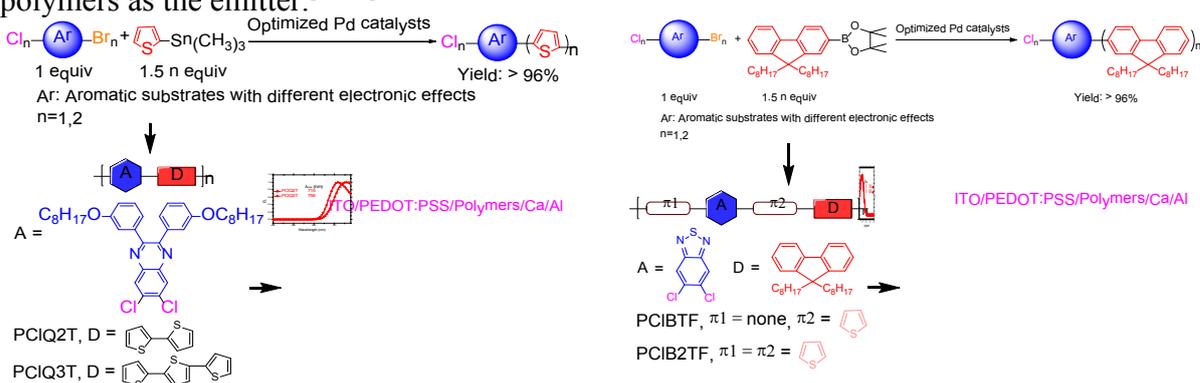


Fig. 1 Highly selective Stille coupling reactions (left) and Suzuki coupling reactions (right) toward chlorine-containing electroluminescence polymers

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Flow Birefringence and Film Birefringence of Poly[1,3-bis(3',4-dicarboxyphenoxy)benzene 4,4'-bis(4''-N-phenoxy)-diphenylsulfone]imide

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Polyheteroarylenes (PHAs) are polymers possessing different types of heterocycles in the main chain. They show good mechanical properties, may be used at high temperatures and exhibit considerable interchain interaction energies [1-4]. The optimal chain rigidity of PHAs may be tuned by varying the chemical structure of heterocycles entering a monomer and using various bridge elements between the cycles. Thereby it becomes possible to use PHAs as a basis for preparing polymeric materials with required properties. However, a substantial drawback of commercial PHAs is their poor processability due to their insolubility in organic solvents. This is why the development of thermally and chemically stable polyheteroarylenes soluble in organic solvents is a high priority task of modern polymer science.

One of the approaches to the synthesis of polyetherimides (PEIs) was performed earlier for resolving the task of PHAs solubility in organic solvents [5]. It included the polycondensation of multinuclear dianhydrides of tetracarboxylic acids and diamines in solutions of an amide solvent (such as N-methyl-2-pyrrolidone) followed by thermal imidization (in a solution or solid state) of the resulting poly(amic acid). The synthesized PEI samples have been characterized by methods of molecular hydrodynamics. This in turn allowed to proceed to determination of birefringence effects of synthesized polyetherimides both in solutions and in films.

The study of polymer films and membranes is of the particular importance from both points of view fundamental knowledge and practical applications considering that in most cases the unique features of polymer films and membranes are specified by their interface properties. The phenomenological theory developed by Cherkasov–Vitovskaya–Bushin [6] allows to separate structural β_M (inherent specific anisotropy of a monomer unit) and orientation S_0 (order parameter) contributions to the value of spontaneous birefringence B :

$$\frac{\Delta B}{\Delta H} = -\frac{\pi \cdot N_A \cdot \rho}{\lambda} \cdot \left(\frac{(n^2 + 2)^2}{9n^3} \right) \cdot \beta_M \cdot S_0,$$

where H – a film thickness, N_A – the Avogadro constant, ρ – a film density, λ – wavelength, n – refractive index. The polyetherimide films were prepared in a wide range of the thicknesses and studied by means of inclined polarised beam method. The acquired experimental data satisfied the predictions of Cherkasov–Vitovskaya–Bushin theory. The value of orientational order of PEIs was determined and compared with the data found for other polymer systems [7].

Acknowledgment: GMP thanks SPb University for partial financial support: research grant 11.38.267.2014.

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Preparation and properties of a polymer containing isocyanurate gradient material based trifunctional polyether

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Functionally gradient-modulus materials (FGM) are complicated composites consisting of two or more components which mixed so that their contents gradually change in a predetermined direction. Thus, FGM can possess desirable properties of each component. In recent years, many studies on FGM was written, which were oriented more at lower molecular weight materials such as ceramics, metals and other inorganic materials [1-4], but only a small number of studies was devoted to the polymer gradient-modulus materials (PGM) [5,6].

We have studied the conditions for preparation of solid PGM based on the aliphatic trifunctional polyether Laprol 5003 (Voranol 4711) and 2,4-toluenediisocyanate using a chain extender 1,4-butanediol. Previously urethane prepolymer was prepared, which was compiled on the basis of potting compounds. PGM is obtained on semi-automatic sealing laboratory installation, which allows control the speed of injecting precursors; as a result the same material has a different internal chemical structure in a given direction (Fig. 1).

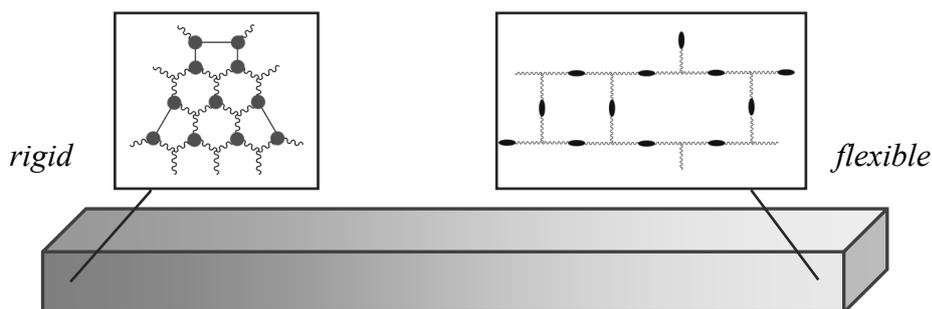


Figure 1. Schematic presentation of PGM and its chemical structure.

After the heat treatment of the material the samples were cut over the same distance (1 cm) for different tests. The measurement results of the modulus of elasticity during uniaxial compression showed that it varies along the length of the sample from 19 to 410 MPa, i.e. a smooth transition from rigid rubber to the low modulus plastic takes place. According to thermo-mechanical analysis, the heat resistance increases gradually from 210 to 330°C as we distance from the elastic analysis zones, due to the increasing content of isocyanurate rigid fragments in the polymer network.

Thus, we obtained a polymer gradient-modulus material in which the elastic part is formed of polyurethane structure, and rigid – polyurethaneisocyanurate one. The dependencies of physical and mechanical properties vs. the sample length, and hence the composition were shown.

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Synthesis of new partially crystalline (co)polyimides

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It is known that aromatic polyimides possess the complex of unique properties such as excellent mechanical properties, chemical, radiational and photostability, etc. combined with wide operating temperature range - from cryogenic up to $-300\text{ }^{\circ}\text{C}$. Poor processability of many PIs caused by high efficient rigidity of polymer chain is a factor limiting PI's application area. Improvement of processability of PIs can be achieved by introduction of two hinge oxygen atoms into repeating unit. Ultem^R 1000 (Sabic Innovative Plastics) polyetherimide (PEI) is an example of this approach in design of PI's polymer chain. Ultem^R 1000 has amorphous morphology with $T_g = 217\text{ }^{\circ}\text{C}$ and the temperature of beginning the weight loss retains of about $450\text{ }^{\circ}\text{C}$. Such a difference makes it possible melt processing of this polymer by extrusion and injection molding.

However, upper exploitation temperature of Ultem^R 1000 is limited by the T_g . Introduction of harder fragments into the PEI chain leads to increase T_g (Extrem^R UH, Sabic IP) but has a negative impact on the melt processability of polymer due to high the melt viscosity. An alternative approach is to build a chain of from structural elements providing the ability to crystallize due to certain the "flexible- hard" balance. In the latter case, the upper exploitation temperature would be limited by melting point of crystalline phase which is usually $100\text{-}170\text{ }^{\circ}\text{C}$ higher than T_g . Polyetheretherketon is most known an example of such approach in design of polyheteroarylene chain. In a series of polyimides, the melt processable polymers capable to form crystalline phase, occur very rarely (LARC CPI^R, (NASA)). In present research, series of (co)polyimides, based on aromatic diamine or their mixtures with aliphatic diamines and aromatic tetracarboxylic acid dianhydride with melting temperature T_m $360\text{-}370\text{ }^{\circ}\text{C}$ were synthesized and characterized. The (co)polyimides were prepared by the method the one-stage high temperature catalytic polycondensation in molten benzoic acid [1]. The properties of synthesized PI were investigated by the method IR- spectroscopy, DSC, TMA, TGA, etc.

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Organoelement fire resistant coatings for synthetic fibers

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Most of fibrous cellulosic materials are characterized as highly flammable and have an increased speed of flame propagation. Previous studies showed that in order to reduce the combustibility of such fibers it is expedient to use phosphorus nitrogen-containing retardants.

This work presents a method of receiving fire resistant phosphorus nitrogen-containing organosiloxane coatings on the surface of cellulosic fibers by means of layered molecular assembly with the use dodecaethoxy(decaaminopropyl)decasiloxane and nitrilotrimethylenephosphonic acid. It is shown that such a three-layered coating provides an increasing of oxygen index from 20 to 47%.

The aim of the work is the investigation of the possibility of using cellulosic fibers as flame retardants for phosphorus nitrogen-containing organosiloxane coatings, covalently bonded with fibers surface.

The availability of aminomethylene phosphonic groups on the coating surface was confirmed by the X-ray photoelectron spectroscopy.

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Electron attachment to the phthalide molecule

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Phthalide, the monomeric unit of conductive polymer thin films, is investigated by means of Electron Transmission Spectroscopy, Negative Ion Mass Spectrometry, and DFT quantum chemical calculations. Formation of gas-phase long-lived molecular anions of phthalide is observed around 0.7 eV, and is ascribed to cleavage of a C-O bond of the pentacyclic ring of the parent molecular anion to give a vibrationally excited (electronically more stable) open-ring molecular anion. The energy of the transition state for ring opening of the parent negative ion is calculated to be 0.65 eV above the ground state of the neutral molecule. The energy (2.64 eV) evaluated for the corresponding transition state in the neutral molecule is much higher, so that the process of electron detachment from the anion must lead to a neutral molecule with its initial pentacyclic structure. The average lifetime of the molecular negative ions formed at an electron energy of 0.75 eV and 80 °C is measured to be about 100 μs. The known switching effect of thin phthalide films could stem from the presence of a similar open/closed transition state also in the polymer.

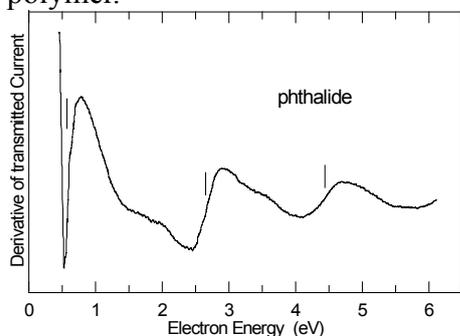


Fig 1. ET spectrum of phthalide molecule.

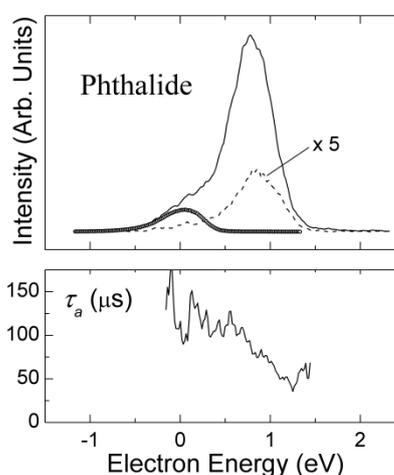


Fig. 2. *Upper panel:* current of molecular negative ions (solid line), signal of the corresponding neutral component (dashed line), and SF_6^- current (thick line) as a function of incident electron energy. *Lower panel:* electron detachment time (τ_a) from molecular negative ions as a function of incident electron energy. The temperature of the collision cell was 80 °C. $\tau_a(\text{SF}_6^-)$ was measured to be 140 μs under the present conditions.

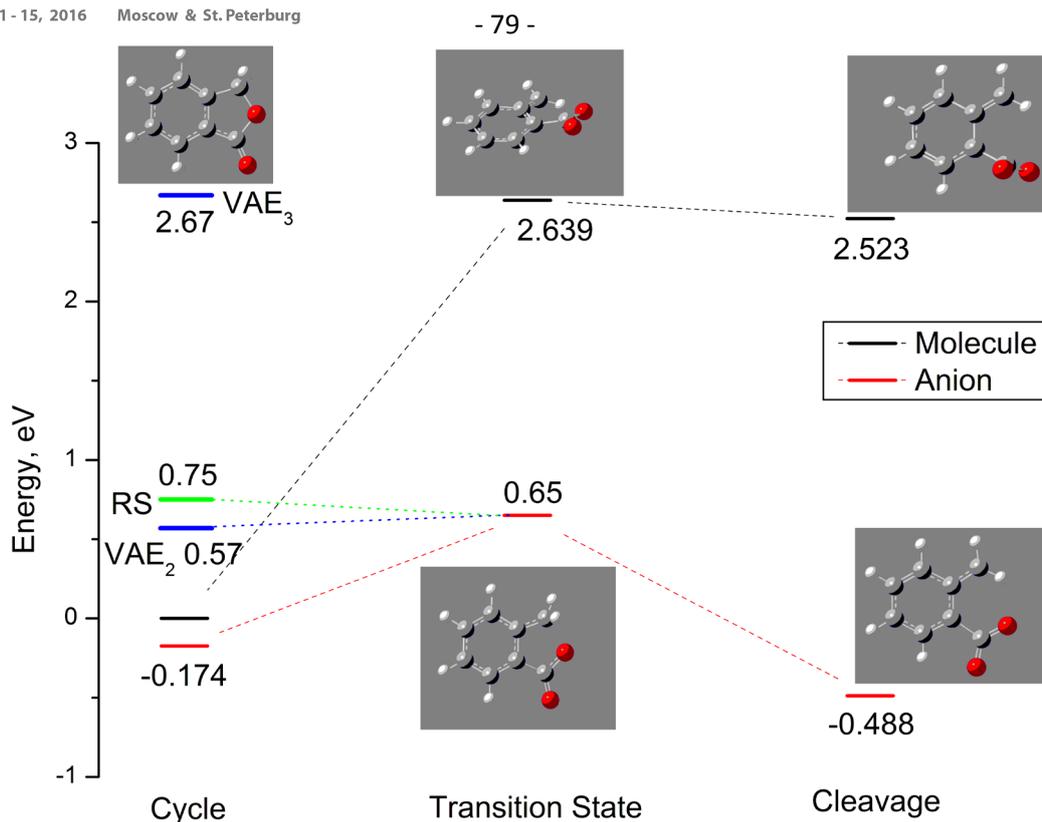


Fig. 3. Energy diagram of cyclic (left); transition state (middle); and cleavage structure of the molecule and anion of phthalide.

Formation of gas-phase long-lived molecular anions of phthalide around 0.7 eV takes place through cleavage of a C-O bond of the pentacyclic ring of the parent molecular anion to give a vibrationally excited (electronically more stable) open-ring molecular anion. The energy of the transition state for ring opening of the parent negative ion is calculated to be 0.65 eV above the neutral ground state of the molecule. The energy (2.64 eV) evaluated for the corresponding transition state in the neutral molecule is much higher, so that the process of electron detachment from the anion must lead to a neutral molecule with its initial pentacyclic structure. The average lifetime of the molecular negative ions formed at an electron energy of 0.75 eV and 80 °C is measured to be about 100 μ s. The known switching effect of thin phthalide films could stem from the presence of a similar open/closed transition state also in the polymer.

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Laser-induced formation of silver nanoparticles in polybenzimidazole matrix

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Abstract. Impregnation of poly-2,2'-*p*-oxydiphenylene-5,5'-bis-benzimidazole by silver containing precursor - Ag(fod) (fod = 6,6,7,7,8,8,8-heptafluoro-2,2,3,5-dimethyl-octadionate) in formic acid and in supercritical carbon dioxide was carried out. Silver nanoparticles were formed in polymer films by continuous laser radiation at wavelengths of 405 and 532 nm and by heat treatment in the temperature range of 100-150°C. Formation of nanoparticles were confirmed by the appearance of band of plasmon resonance in the absorption spectra of the films, as well as by scanning electron microscopy.

Among wide range of known polymers polybenzimidazoles attract considerable attention of reseachers because of their excellent thermal and mechanical properties. Introduction of nanosized additives could result in formation of new functional materials, which in turn may contribute to a significant expansion of their practical application possibilities. From this position of great interest are polymer composites with nanoparticles of noble metals. Because of the unique optical, electronic, magnetic and catalytic properties of such nanoparticles, materials based on them could be used in optoelectronics, sensing, catalysis, and others. Thus, the aim of the present work was to create composite materials based on poly-2,2'-*p*-oxydiphenylene-5,5'-bis-benzimidazole (OPBI) and silver nanoparticles and the establishment of their optical properties.

Introduction Ag(fod) in OPBI was performed by two different approaches. First of them consist in solution mixing of the precursor and OPBI in formic acid and film forming by solution casting method, while the second one is based on supercritical carbon dioxide (scCO₂) assisted impregnation. Determination of silver content, conducted with an X-ray microanalyzer, showed that in the samples impregnated in scCO₂ medium a quantity of metal is 0.5-0.9 wt. %. In contrast, in the samples obtained by casting from the solution the silver content reached 3.5 wt. %.

Experiments on the selection of laser radiation parameters allowing to form nanoparticles in impregnated samples, avoiding degradation of the polymer were performed. The area of the irradiated portion of the film was 3 mm². The intensity of the laser radiation on the surface of the film was 15 W/cm². Photoreduction of molecular precursor to the silver nanoparticles, accompanied by partial shading film in the irradiated region, was occurred at irradiation by a laser with wavelengths of 405 and 532 nm. Plasmon band in the region of 450-460 nm was observed for all composite films. Obtained materials also were studied by SEM. It was found that in the case of irradiated samples formation of nanoparticles and their agglomerates is occurred only in place of irradiation. While in heat treated films generation of nanoparticles is occurred throughout all of the sample.

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Effect of the chemical structure of the photochromic component on the electrical performance of organic memory elements

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Memory elements based on organic field-effect transistors (OFETs) have been intensively developed during the last few years. These devices have a bistable nature, so the transistor can be reversibly switched between two distinct electrical states with different threshold voltages (V_{TH}). There are several approaches to realize two or more quasi-stable states in OFETs, which are based on using photosensitive or ferroelectric materials, as well as floating-gate device architecture [1]. However, poor reproducibility of the electrical characteristics of the existing types of devices and/or technological problems in their fabrication make their practical application rather challenging.

Photochromic compounds represent very promising group of materials for photoswitchable organic field-effect transistors and memory elements. Organic photochromes, e.g. bis(hetaryl)ethenes, undergo reversible isomerization under the illumination with light of certain wavelengths. Recently we have shown that using architecture of organic field-effect transistor with a layer of photosensitive receptor molecules sandwiched at the interface between the semiconductor and dielectric layers allows for a fast switching of the device between multiple quasi-stable states, which are characterized by considerably different voltages V_{th} . The optical memory elements based on organic photochromic materials demonstrated high ON/OFF current ratios between two different states ($I_{DS}(1)/I_{DS}(2) > 10^4-10^5$), short switching times (0.5-10 ms) and outstanding retention and write-read-erase cycling stability [2-3].

Here we investigated a series of photochromic bis(hetaryl)ethenes in order to establish some correlations between the molecular structures of the materials and their electrical performance in memory elements. In particular, we analyzed programming speeds, width of the memory windows, ON/OFF switching coefficients and write-read-erase cycling stability. A clear effect of the carbonyl group in the bridge part of the bis(hetaryl)ethane molecule on the performance of the devices has been revealed.

The obtained results strongly suggest that chemical engineering of the molecular structure of photochromic material provides additional wide opportunities for designing memory devices with different modes of switching between distinct states.

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This work was supported by the Russian Foundation for Basic Research (RFBR), grant no. 15-03-06175.

Ferrocene-containing polychalkones as precursors for magnetic nanomaterials

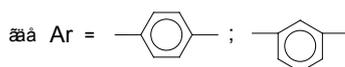
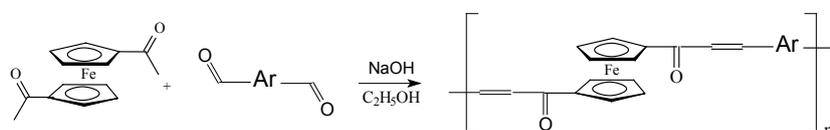
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New ferrocene-containing polychalkones were prepared either by conventional solution method or in supercritical carbon dioxide using technique described in [1] at 20 MPa and temperatures varied from 20 to 70°C in accordance with the scheme 1:



Scheme 1.

Structural transformations in the polymers occurring in the course of thermal treatment were used as the original approach to creation of composite materials [1,2] possessing magnetic properties.

Field-emission scanning electron microscope studies showed uniform distribution of magnetic nanoparticles in polymeric matrix (fig.1).

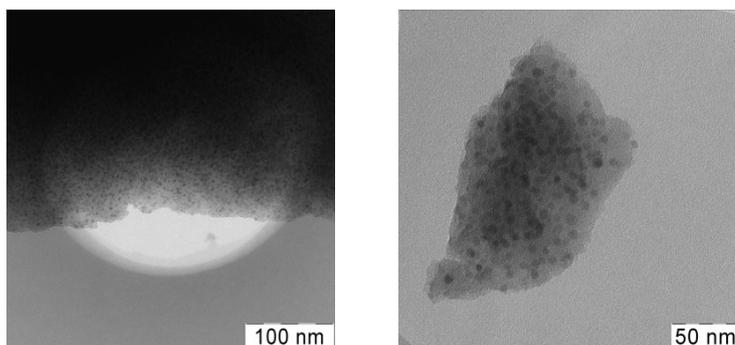


Fig. 1. Microfotographs of nanocomposites

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Influence of the thickness of nanometer film on the conducting polymer/polymer interface

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The present article is concerned with the experimental studies of the mechanism responsible for two-dimensional conductivity along the interface of two organic insulators based on «polar catastrophe». In particular, the influence of the thickness of upper polymer film on the conductivity along the interface of two organic insulators was investigated. The detected strong impacts of the thickness of upper polymer film on the conductivity along the polymer/polymer interface is explained by dipole oriented submicron polymer film.

The work [1] showed that the area density increase of dipole groups leads to a considerable conductivity increase along the interface. Apparently, other processes that lead to the dipole moment increase of the polymer film should lead to the similar effect too. One of these effects may be the orienting effect of surface fields on the dipole groups of the macromolecules when the surfaces approach close enough to interact. Thus, when the thickness of one of the forming polymer layers is decreasing, the conductivity increase as expected along the polymer/polymer interface.

We can conclude that the film thickness reduction in the polymer/polymer structure leads to a monotonic resistance decrease along the interface of the dielectric films. Upon reaching a certain thickness (in our case ~ 55 - 60 nm), an additional sharp by more than one order of magnitude greater decrease in the resistance is observed. It was established that this polymeric film thickness correlates with the crossover point on the viscosity versus the strength of the polymer solution and with the point of inflection on the polymer film thickness depending on the strength of the solution. Analyzing the facts, we may suggest the following explanation of the observed thickness dependence of the resistance along the interface between two dielectric polymer films. Since the conditions of the localization of two-dimensional electron gas along the interface are strongly dependent on the polarization of forming surfaces it must be assumed that at thicknesses of 55 - 60 nm the increase of this polarization takes place. This is due to a significant decrease in disorienting action of the bulk of the polymer film. In fact, in the case of a polymer film of this thickness we have to deal with the resultant field of two surface polarized planes. However, the question arises about the nature of this resulting interaction. Two variants are possible, in which the resultant field is the consequence of the compensating influence of two oppositely directed dipoles or field amplification due to the same orientation. In the latter case, the film should be close to the ferroelectric state. Obviously, to answer these questions we need additional experiments that go beyond the task.

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Synthesis of sequence – ordered copolyarylenphthalide having periodic structure with diphenyloxide and diphenylsulfide links in basic chain.

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One of the effective methods of the modification of polymer material features is a synthesis of copolymers using monomers with a complicated structure. This method was used to synthesize novel sequence – ordered copolyarylenphthalides with diphenyloxidephthalide (O) and diphenylsulfidephthalide (S) links in a basic chain. The methods of the synthesis of novel «macromonomers» with symmetric structure were developed: di(diphenyloxide)diphenylsulfidiphthalide, di(diphenylsulfide)diphenyl-oxidephthalide, di(diphenylsulfide) phthalide as well as diphenylsulfidiphenoxyphthalide with an asymmetric structure. For each monomer the methods of the synthesis and isolation have been worked out. The method of a column chromatography was used for the additional purification of compounds. With monomers obtained and pseudodichloranhydrides of bis – ortoketocarbonic acids using Fridel – Krafts electrophilic substitution sequence – ordered copolyarylenphthalides $(OOS)_n$, $(OSS)_n$, $(OOOS)_n$, and $(OSSS)_n$ having various molecular mass were produced, which do not contain defective and laced structure. The complete signals correlation in $C^{13}NMR$ spectra was carried out of low molecular model compounds and copolyarylenphthalides was carried out. The structure of these compounds was ascertained and confirmed by the data of an elemental analysis. The synthesized copolyarylenphthalides are well soluble in many organic solvents (chlorinated hydrocarbons, dimethyl formamide, dimethyl acetamide, cyclohexanone, nitrobenzene ect.), as well as in concentrated sulphuric acid. In organic solvents from solutions polymer films are formed. Periodic copolymers in molecular electronics can be applied for the production of organic semiconductor devices (diodes, transistors, as well chemo – and biosensors).

Poly-ether-ether-ketone (PEEK). Influence of residual solvent on the material properties

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Poly-ether-ether-ketone (PEEK) is a thermoplastic polymer, perspective for application in medicine and modern hi-tech branches of industry. PEEK may be uses in a wide temperature range from cryogenic (-250°C) to 250°C and even to 300°C in case of reinforced brand marks. This material has high chemical, creep and x-ray and γ -ray radiation resistance. By nature, PEEK possesses low inflammability and smoke emission.

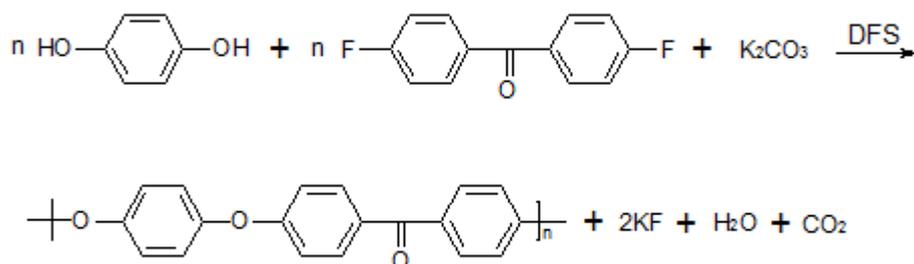


Fig. 1. Reaction scheme

In this scheme (fig. 1) instead of difluorobenzophenone (DFBP) may be used dichlorobenzophenone (DCBP). But, it was established that in this case the product of reaction has lower melt temperature and lower physic-mechanical properties. This explains by the difference in the synthesized polymers crystallinity.

In addition to molecular weight and crystallinity, the material properties notably depend on the removal of the solvent used for the polymer synthesis, namely diphenylsulfone (DFS). We established, that residual DFS content was a very important characteristic for the end product.

Purification efficiency depends on:

- solvent used for cleaning
- size of reaction particles
- temperature and cleaning time
- high-frequency mechanical fluctuations.

Effect of residual solvent on the PEEK hot-melt rheological characteristics was determined. High residual content of DFS decreases fluidity, in such a way complicates its processing. Thus, the stage of the polymer cleaning is very important in the technological scheme of the PEEK synthesis.

The effects of synthesis parameters on the microstructure of hyperbranched polyesters

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Synthesis parameters including the time of condensation reaction, the monomer-to-core ratio (2, 2-bis (hydroxymethyl) propionic acid) (pseudo-generation) and the type of catalyst were changed systematically to investigate their effects on the microstructure of resulting hyperbranched polyesters (HBPEs). Response surface methodology (RSM) was employed to uncover the relationship between changing variables and the number of terminal hydroxyl groups of HBPSs, by which the individual and interactive effects of the aforementioned synthesis parameters were explored. The degree of branching and molecular weight of the HBPEs were evaluated by titration of hydroxyl number and Gel Permeation Chromatography (GPC), respectively. Fourier Transform Infrared spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR) analyses confirmed the presence of functional groups in the prepared molecules. Interpretations based on RSM showed that increase of the number of the core molecules, which is equivalent of reduction of the pseudo-generation, narrows the molecular weight distribution of the prepared hyperbranched polyester; so that the lowest molecular weight distribution is obtained for the first pseudo-generation HBPEs with the monomer-to-core ratio of 3:1 and the average number of the terminal hydroxyl groups in between 6 and 8. The samples prepared by the sulfuric acid catalyst had the highest average number of terminal hydroxyl groups, at the same time narrowest molecular weight distribution.

Flame retardancy and mechanical properties of polyamide 6 with melamine polyphosphate and ionic liquid surfactant-treated montmorillonite

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The mechanical properties and inflammability of polyamide 6 (PA6) nanocomposites incorporated with Montmorillonite organoclay (MMT) modified with thermal stable ionic liquid surfactants were investigated. The compatibility between ionic liquid-treated MMT and PA6 matrix was improved and the intercalation morphology was achieved, which resulted in the increase of tensile modulus. However, the addition of organo-MMTs alone did not improve the inflammability of the PA6 nanocomposite, because of strong melt-dripping behavior of PA6 matrix. Addition of auxiliary melamine polyphosphate (MPP) intumescent flame retardant to the nanocomposite prevented the melt dripping and enhanced inflammability performance. The enhanced inflammability of PA6/organoclay/MPP nanocomposites was attributed to the synergistic effect between imidazolium or phosphonium organo-MMTs and intumescent flame retardant MPP.

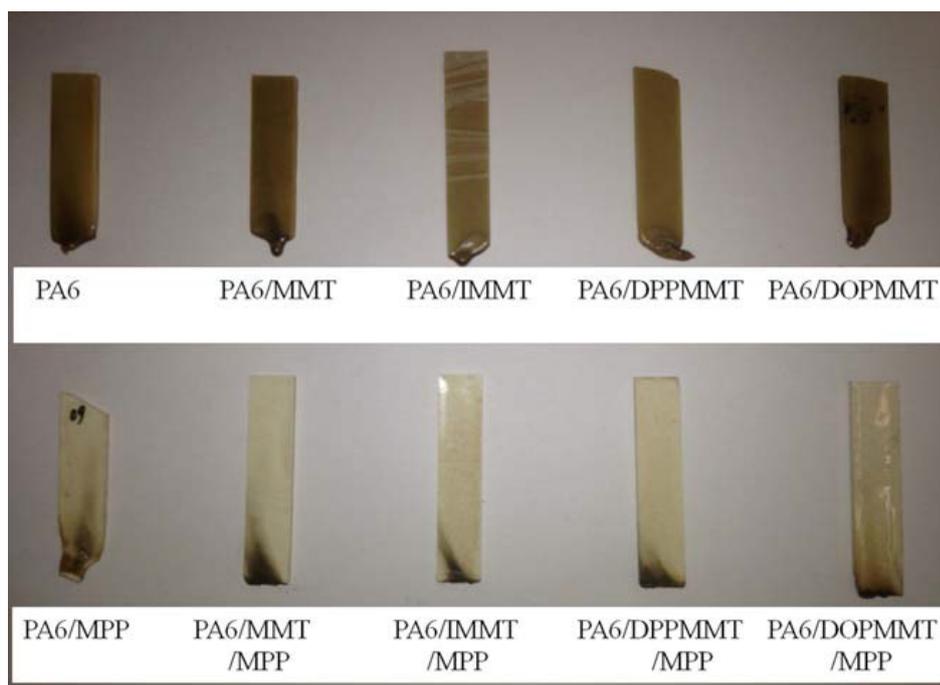


Fig. 1. Photographs of neat PA6, PA6/MMT, PA6/IMMT, PA6/DPP, PA6/DOPMMT nanocomposites combined with or without auxiliary flame retardant MPP after UL94 vertical burning tests.

A lignin-derived chemical platform for biobased polymers via ADMET

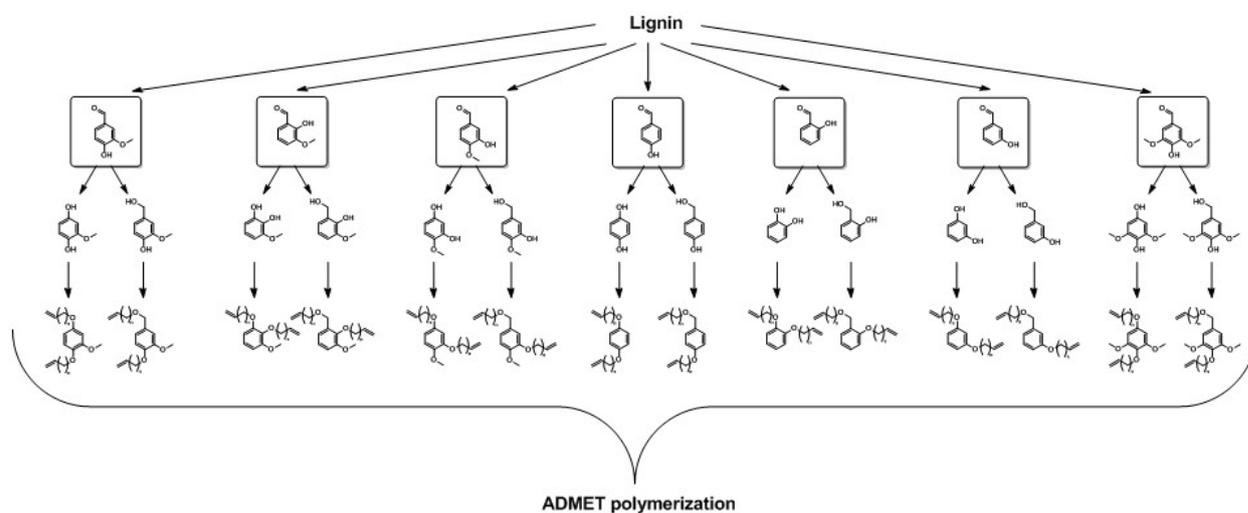
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In the past years, there has been a strong development in the field of polymer synthesis from renewable monomers, to provide alternatives to or replacements for crude oil based monomers. Some polymers based on renewables are already available on an industrial level. Yet, these polymers are largely derived from carbohydrates or triglycerides as renewable resources. However, a significant share of industrially relevant polymers contains aromatic entities to ensure certain thermal and mechanical properties, and thus the quest for renewable aromatic monomers has begun. Nowadays, renewable aromatic compounds can be derived from cashew nutshell liquid, polyphenols and lignin[1]. Lignocellulosic biomass is an especially promising resource since it is abundant and does not compete with food or feed.

Key intermediates in the synthesis of renewable aromatic building blocks from lignin are vanillin and vanillin-like derivatives, which can be converted into diols [1]. A versatile chemical platform (see scheme), consisting of dienes, was synthesized from potentially renewable lignin-derived diols containing an aromatic moiety. Subsequently, ADMET polymerization was performed on this series of dienes in order to investigate the influence of the substitution pattern in the monomers on the resulting thermal properties of the polymers. In addition, the remaining double bonds of the polymers, synthesized by ADMET polymerization, allow for further finetuning of the material properties by post-polymerization functionalization via, e.g. triazolinedione chemistry.



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ESR spectroscopy and cyclic voltammetry as a highly sensitive methods for determination of the intrinsic stability of conjugated polymers

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The best laboratory prototypes of organic solar cells demonstrate nowadays efficiencies exceeding 10%. However, practical application of organic photovoltaics (OPV) is limited severely by low stability of the active layer materials. Both p-type (e.g. conjugated polymers) and n-type (e.g. fullerene derivatives) semiconductor materials undergo photochemical and/or thermal degradation under the real solar cell operation conditions. Currently, there is very poor understanding of the nature and mechanisms of these degradation processes. Recently, we have shown that electron spin resonance (ESR) spectroscopy represents a very useful technique for controlling the quality of organic semiconductor materials [1] and for monitoring their photochemical and thermal degradation [2].

In the present work, we report a systematic analysis of intrinsic photostability of conjugated polymers composed of different building blocks such as thiophene, benzothiadiazole, benzoxadiazole, carbazole, silafluorene, fluorene, indolocarbazole, benzodithiophene and cyclopentadithiophene under anaerobic conditions. Comparing the photodegradation profiles of the polymers derived from the ESR spectroscopy data allowed us to reveal some correlations between the molecular structures of the materials and their stability.

In addition, we investigated photochemical stability of the aforementioned conjugated polymers in the presence of trace amounts (~800 ppm) of oxygen. This atmosphere models the environment inside the flexible solar modules produced using roll-to-roll coating technology with following encapsulation in air. A set of complimentary techniques involving ESR spectroscopy and cyclic voltammetry was applied to study the polymer photooxidation processes. We found that stability of all investigated conjugated polymers correlates well with their oxidation potentials: materials with the highest oxidation potentials were the most stable and *vice versa*.

The obtained results suggest that only the conjugated polymers with the highest oxidation potentials (preferably higher than +0.4 V vs Fc/Fc⁺) can be industrially applied for production of flexible plastic solar cells. The importance of this finding is reflected in the fact that virtually all highly efficient low band gap conjugated polymers known in the field have their oxidation potentials well below +0.4 V vs Fc/Fc⁺. These materials will undergo facile degradation in the presence of traces of oxygen, which are unavoidable within the industrially feasible roll-to-roll OPV production technologies. Therefore, a rational design of novel materials with deep-lying HOMO and LUMO energy levels is required to address successfully the challenge of OPV commercialization.

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Photovoltaic performance of some conventional and innovative fullerene- and polymer-based photoactive materials

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Institute for Problems of Chemical Physics of Russian Academy of Sciences (IPCP RAS) was involved in the development of organic bulk heterojunction solar cells since early 2000s. A number of novel fullerene derivatives and conjugated polymers were designed for highly efficient and stable organic photovoltaics (OPV). The accumulated scientific knowledge and expertise were reflected in a number of high-level publications and patents. In particular, it was shown that reliable performances of organic solar cells can be achieved only via a severe quality control of all employed organic semiconductor materials using the most sensitive analytical techniques (e.g. special ESR or impedance methods developed at IPCP RAS [1-3]).

IPCP RAS has launched recently a spin-off company FOMaterials LLC with the aim to provide high-quality fullerene- and polymer-based materials to the Russian and international research groups working in the field of organic electronics and, in particular, OPV. In this presentation we will discuss recent results of the collaborative research performed at FOMaterials LLC company and IPCP RAS and directed towards large-scale preparation of conventional (e.g. PCDTBT, F8TBT, PCBM, ICBA) and a number of innovative polymers and fullerene derivatives. In particular, we will present the data on photovoltaic performance of our materials in standard and inverted device geometries.

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Amphiphilic branched copoly lactides.

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Aliphatic polyesters based on hydroxy - lactic, glycolic, etc., are widely used in medicine due to their high biocompatibility and degradation to non-toxic and easily withdrawn from the body compounds. During the last decade the attention of numerous research teams have been devoted to the examination of amphiphilic aliphatic polyesters due to their biocompatibility and good surface-active properties. During the hydrolysis of such polymer, the natural for the body metabolites and highly biocompatible aliphatic ethers are formed; this makes the use of aliphatic polyester surfactants in biotechnology and medicine particularly attractive. In particular, polymers having a hydrophobic polymeric blocks based on hydroxy acids and hydrophilic blocks based on polyethylene oxide and polyglycerol may represent new biocompatible and biodegradable surfactants capable to rapid and complete excretion.

In presented study a series of new branched block copolactides and their amphiphilic derivatives (Fig. 1.) were synthesized and studied in respect to their physical-chemical and surface properties. It was established that all synthesized amphiphilic block copolymers possess pronounced surface properties depending on the ratio of the hydrophilic and lipophilic moieties in the macromolecule, as well as on the architecture of the copolymer. We present the successful use of biodegradable aliphatic copolyesters as surfactants for the preparation of microemulsions, and microparticles. It has been found that the size of emulsion droplets, stabilized by the branched copolymers, grew more slowly than emulsions stabilized linear copolymers. Microcapsules obtained using the branched copolymers as surfactants show a higher encapsulation efficiency as compared to those generated using linear copolymers.

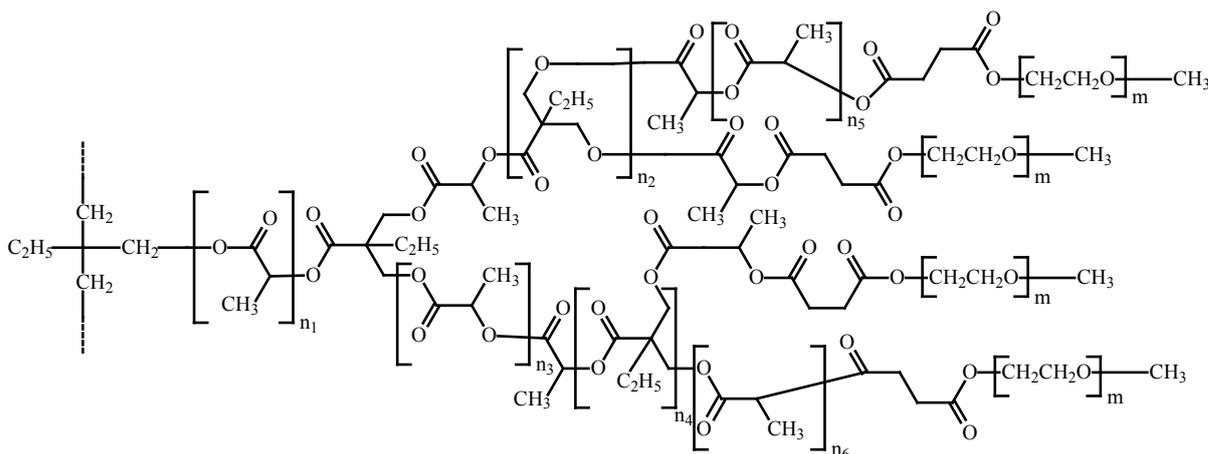


Fig. 1. Common structure of examined amphiphilic copoly lactides

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Acrylonitrile-butadiene rubber-modified polybenzoxazine for brake pads application

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Bisphenol A-aniline based polybenzoxazine (poly(BA-a)) was modified using acrylonitrile-butadiene rubber particles (NBR). The NBR contents were in a range from 0 to 15 % by weight. The results revealed the influence of NBR contents on tribological behaviors and microstructure, as well as thermal property of the polybenzoxazine. An increase of friction coefficient of the NBR-modified polybenzoxazine composites was a consequence of the presence of the NBR particles in the polybenzoxazine. This can be explained by an increase of actual contact area and surface roughness in the composites. The NBR content of 5 % by weight was recommended for improving the wear resistance of the polybenzoxazine. SEM micrographs reveal that the NBR particles in the polybenzoxazine show a good dispersion. While the deformed rubber particles on the NBR-modified polybenzoxazine surface was found to play a protective role against the wear damage to the composites. Glass transition temperature (T_g) of the NBR-modified polybenzoxazine composites evaluated by dynamic mechanical analysis (DMA) increased with increasing of NBR particle contents, i.e. from 170°C for the polybenzoxazine to 188°C for the polybenzoxazine filled with 15wt% NBR particles. This phenomenon is possible due to good interfacial adhesion between the NBR particle and the polybenzoxazine via ether linkages (C-O-C stretch) as confirmed by Fourier transform infrared spectroscopy (FTIR).

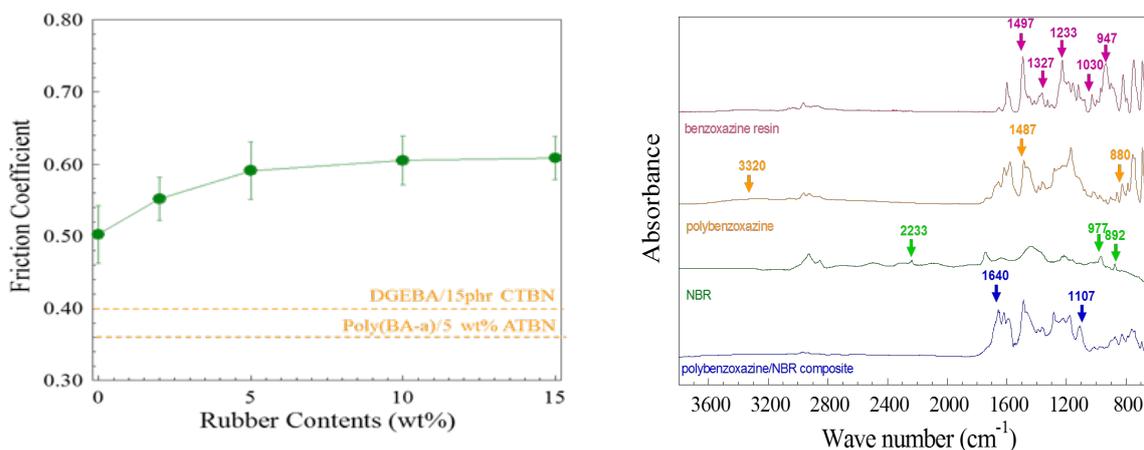


Fig. 1. Friction coefficient of NBR-modified poly(BA-a). **Fig. 2.** FTIR of NBR-modified poly(BA-a).

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Hydrolytic polycondensation of organoalkoxysilanes under pressure

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The basic industrial method of synthesis of organopolysiloxanes is a hydrolytic polycondensation of organochlorosilanes. Recently published investigations of the synthesis of polysiloxanes by reaction Piers–Rubinsztajn [1], by the condensation of alkoxysilanes in the active medium [2,3] allow us to consider alkoxysilanes as an alternative reagent for large scale production of polyorganosiloxanes. However, these methods have some limitations: in the first case - it is the side reactions and usage of an expensive catalyst, in the second – is the acetic acid excess and boiling of the reaction mixture for a long time to achieve full conversion of alkoxy groups.

Recently widely used synthetic methods occurring under the pressure in supercritical carbon dioxide [4,5].

The aim of this work is to investigate hydrolytic polycondensation of organoalkoxysilanes under pressure in carbonic acid and the influence of process conditions on the products composition.

Using a mixture of water and carbon dioxide is particularly interesting, because changing of pressure and temperature makes it to control of pH of the aqueous phase by the formation of carbonic acid, which allows the hydrolytic polycondensation of organoalkoxysilanes in a catalytic manner without of the use of catalysts and organic solvents.

In this report will be presented influence of process conditions (pressure, temperature, presence of carbon dioxide, time of the process) on the composition of products of polycondensation of the organoalkoxysilanes. All obtained products are identified and characterized by physicochemical analytical methods (GC, GPC, IR and ¹H-NMR spectroscopy).

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Fluorinated binder for microelectronics

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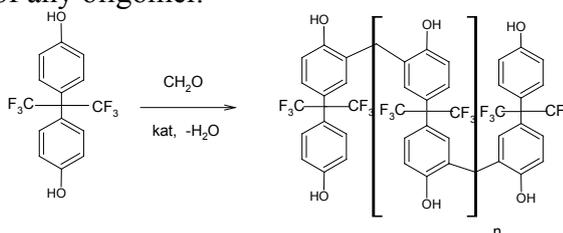
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Novolac and epoxy novolac resins are widely applied for protecting electronic components (including chips) from external impact. Fluorine containing oligomers due to its particular dielectric properties and low combustibility can be useful as protective composites.

The main component of a composite binder is a product of hexafluorodiphenylolpropane (bisphenol AF) and formaldehyde condensation. Condensation process was carried out in non-polar solvent in presence of acidic catalysts. Molar ratio bisphenol AF: formaldehyde – 1:0.85. Polycondensation temperature 100÷115⁰C, postcondensation 130÷135⁰C. The degree of conversion was controlled by amount of water released. Chemical reaction was catalyzed by phosphoric, trifluoroacetic and p-toluenesulfonic acids. Oligomeric products obtained were analyzed by NMR and GPC.

It was found, that adding of p-toluenesulfonic acids allows to obtain required oligomer (Scheme 1) in 2 hours. The resin has softening point 80 ⁰C and viscosity 400 Pa·s at 150 ⁰C. Using trifluoroacetic acid as catalyst forms the oligomer with low molecular weight and considerable methylol groups content, confirmed by NMR (Fig 1). Phosphoric acid as a catalyst doesn't lead to formation of any oligomer.



Scheme 1. Bisphenol AF - formaldehyde condensation

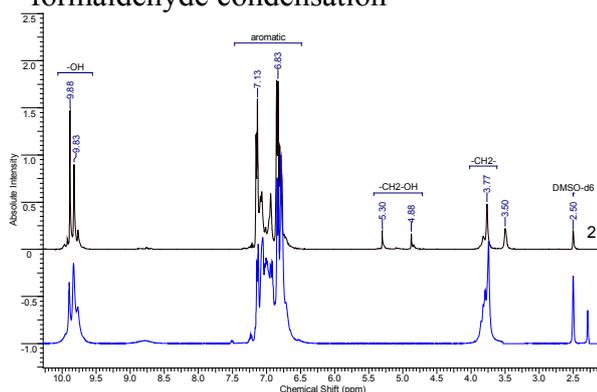


Fig 1. PMR spectrum of bisphenol AF novolac (1- catalyst toluenesulfonic acid; 2- catalyst trifluoroacetic acid)

Epoxydation of fluorine containing novolac resin allows to obtain solid epoxy oligomer with following properties: epoxy content 15-16 %, fluorine content 24%, softening point 45-50 ⁰C, melt viscosity 0.5-1 Pa·s (150 ⁰C).

Using fluorine containing novolac resin as hardener to state above epoxy novolac gives a product with Tg 205 ⁰C, compression strength 130 MPa and fluorine content 26 %. Curing epoxy bisphenol AF novolac with other types of hardeners presented in [1].

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A new anion exchange resin for selective sorption of heavy metal ions

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Modern technologies do not provide effective sewage treatment from ions of heavy metals. For the row of productions waste water treatment from metals and various salts is insufficient, since it is necessary to complete the industrial water treatment with removal of any, even the smallest impurities. One of the largest water users is the non-ferrous metallurgy. Thus, the greatest water consumption is characteristic for the nickel-cobalt production, which amounts to 1 270 million m³/year, while the number of discharged waste water reaches 165 million m³/year. Wastewaters appearing on the non-ferrous metallurgy enterprises, and contained in them heavy metals pose a serious threat to aquatic ecosystems. The use of chelating sorbents, that form stable complexes with them, promising to create a progressive scheme, leading to a reduction in needs of enterprises in the fresh water. In this regard, the development of new effective sorbent for the extraction of heavy metal ions is an urgent task.

On the base of glycidylbenzylamine (GBA), allyl glycidyl ether (AGE) and polyethyleneimine (PEI) by the method of polycondensation a new selective complexing crosslinked anion exchanger is synthesized. The purpose of the work – the investigation of its properties in selective extraction of divalent ions of copper, nickel and cobalt from the model of multi-component sulphate solutions. Sorption data cations conducted under static conditions obtained anion exchanger in the OH-form, depending on the concentration of solutions in a ratio of sorbent: solution of 1: 400, room temperature 20±2 °C, varying concentration of metals in the CuSO₄ solution – from 0.139 to 2.092 g/l, NiSO₄ – from 0.095 to 1.957 g/l, CoSO₄ – from 0.098 to 1.964 g/l. Sorption capacity was calculated from the difference between the initial and the equilibrium concentration of the solutions, which were determined by classical polarography method.

When removing the ions Cu²⁺, Ni²⁺ and Co²⁺ of three-component copper-sulfate, nickel and cobalt solutions was found that increasing the concentration of copper ions in the solution in the three 15-fold (0.14 to 2.09 g/l) leads to an increase in the anion exchanger sorption capacity by Cu²⁺ ions from 19.3 to 370.8 mg/g. The degree of removal is higher than bi-component copper-, cobalt-containing solutions. Ni²⁺ ions are absorbed by the anion exchanger is worse than copper cations. The maximum value for sorption capacity anion Ni²⁺ ions at a concentration in the initial solution of 1.96 g/l is 160.4 mg/g. The three-component copper-, nickel-, cobalt-containing solutions in the investigated concentration range (0.10-1.96 g/l) Co²⁺ ions are not adsorbed. The total exchange capacity of the anion exchanger for the ions of copper and nickel reaches 179.6-379.6 mg/g. Due to the selective properties of the anion exchanger based on the GBA, AGE and PEI can be used to extract a group of cations Cu²⁺ and Ni²⁺, separating them from the Co²⁺ ions.

By electron microscopy method it has been established that the anion exchanger based on GBA, AGE, and PEI has a folded surface with a developed system of macropores. Their size varies widely, from 0.246 to 1.953 microns. Probably, the presence of macropores and functional groups (secondary and tertiary amine groups, and OH-groups) promotes display selective properties.

Thus, it was found the presence of the ion selectivity of the sorption of Cu²⁺ and Ni²⁺, in the presence of Co²⁺ ions from model sulfate multicomponent solutions by new macroporous anion exchanger based GBA, AGE and PEI. In this regard, it is promising to use it for separation in hydrometallurgical processes and analytical chemistry.

Green Chemistry – a new approaches to the synthesis of redox polymers suitable as sorbents

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Synthesis of quinoid redox polymers is usually carried out through the stages of halogenmethylation, nitration and subsequent reduction of nitro groups, i.e. the process is many-staged and is carried out under stringent conditions, in harsh environments using a source of toxic reagents and accompanied by the release of harmful byproducts.

In recent years, a new direction in chemistry collects rates – green chemistry. It offers another way: reducing the number of stages, exclusion or minimization of the destruction and processing of waste products, pollution control, etc. Perspective from the point of view of green chemistry is a method, based on the use of industrial ready-made resins as a starting template for modification.

By condensation of quinones with weakly basic anion exchangers containing in its structure a primary and/or secondary amino groups (aminated polyvinyl chloride –APVCh, polyethylene polyamine – PEPA, polyethyleneimine – PEI, AN-31, EDE-10P and others) obtained aminoquinoid redox polymers (RP). The use of ready-aminated matrices reduces the number of steps in the preparation of the RP, the temperature and time of the process mode. Following positions of green chemistry the process was studied in green solvents – ethanol, water or their mixtures. The high polarity of these solvents provides a high yield of RP. Furthermore, another position of green chemistry is realized: the process proceeds without emission of toxic intermediate products requiring disposal. The distinguished hydrogen is expended flavoring of quinoid nucleus. Obtained RP were tested as sorbents of heavy and transition metals (see table). It can be seen that the synthesized RP by their sorption activity far superior industrial designs.

Table. Performance of the sorption of redox polymers based on polyamines and quinones per certain metal ions

RP \ Metal	Cu ²⁺	Ni ²⁺	Co ²⁺	Zn ²⁺	Cr ⁶⁺	Re ⁷⁺	V ⁵⁺
PEI-ChA	466.0	355.2	194.4	104.4	416.0	368.4	570
AN-31-Q	340.0	370.0	-	-	-	-	450
AV-17	-	-	-	60.1	231.6	-	-
AMP	111.2	103.0	121.3	-	240.4	-	-
AN-21	-	-	-	-	-	343.0	.-

Functional composites based on polybenzimidazoles and graphene

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Based on dispersions of different types of graphene nanoparticles a number of flexible and conductive composite films with polybenzimidazoles with a filler content up to 45% (wt.) were obtained. It was found that introduction of nanofiller in the heterocyclic polymer matrix increases the tensile strength of the materials and temperature of 10% weight loss. In addition, films have high conductivity reaching 480 S/cm. Moreover new three-dimensional grids based on graphene oxide and oligomeric benzimidazoles were obtained. Optimal temperature-time regimes of copolycondensation allowing fabrication of modified graphene materials with high N-content were found. Resulting materials with high specific surface area are promising as supercapacitor electrodes.

In recent years, along with the rapid development of the production of different types of polymers widespread of polymeric nanocomposites have received. One of the most attractive fillers from the viewpoint of impart various functional properties to composite materials are carbon nanoparticles (nanotubes, graphene (GP), graphene oxide (GO), graphite nanoplatelets (GNP), etc.). Along with this, polybenzimidazoles (PBI) are an important class of condensation type polymers because of their excellent thermal and mechanical properties. To support advances in different fields, it is highly desirable to further improve the properties and to impart new functionalities on these polymers. The introduction of nanoparticles to the polymer matrix is the most effective and simplest way. The aim of this work was preparation of mechanically strong and conductive graphene-type nanofiller/polybenzimidazole composite materials and three-dimensional grids based on graphene oxide and oligomeric benzimidazoles.

On the first stage approaches to the formation of stable dispersions of GNP and GP were developed. One of them consists in two-stage ultrasonic treatment of graphite in N-methyl-2-pyrrolidone. According to AFM-images GNP have thickness of 10-30 nm and lateral dimensions from 600-700 nm to 2-3 μm . As a precursor for obtaining of few-layered GP dispersions highly exfoliated graphite (HEG) was used. It was found that for creation of stable GP dispersions with concentration up to 2 mg/mL it is needed to use non-ionic surfactant – polyvinylpyrrolidone. Based on obtained dispersions a number of flexible and conductive composite films with polybenzimidazoles with filler content up to 45% (wt.) were obtained. It was found that introduction of nanofiller in the heterocyclic polymer matrix increases the tensile strength of the materials on 100% and temperature of 10% weight loss on 51-100°C. In addition, films have high conductivity ranging from 5×10^{-7} to 480 S/cm.

Second approach to formation of functional materials is condensation of GO and oligomeric benzimidazoles with terminal *o*-diamine groups resulted in three-dimensional grids. Optimal temperature-time regimes of copolycondensation allowing fabrication of modified graphene materials with high N-content and low O-content were found. Resulting grids with high specific surface area are promising materials for fabrication supercapacitor electrodes.

This work was supported by the Russian Foundation for Basic Research (RFBR), grants no.16-33-60155 mol_a_dk and 16-33-00218 mol_a.

Branched oligophenylenes with phenylene ethynylene fragments for optoelectronics

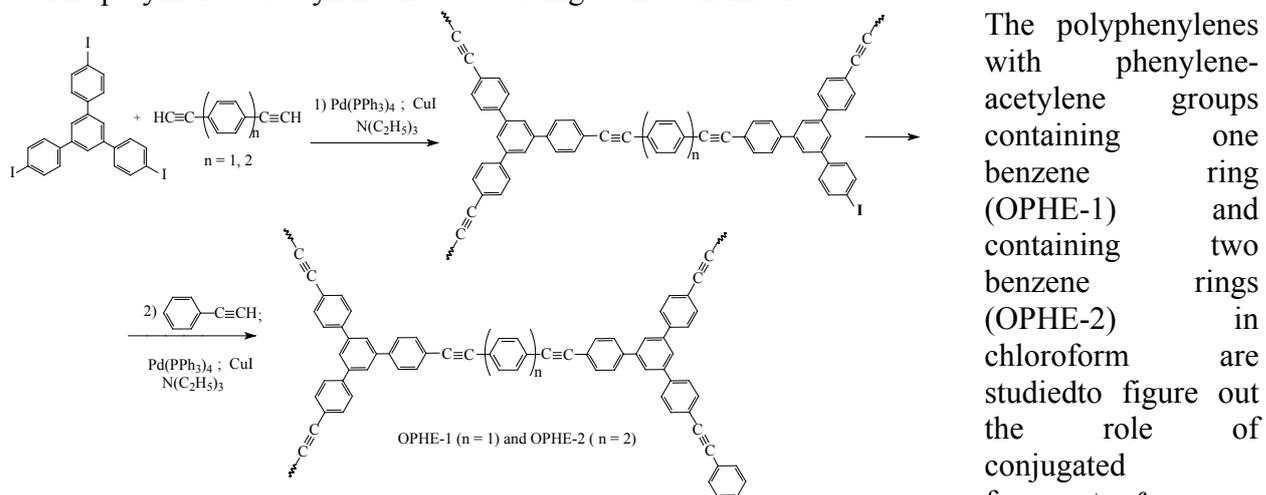
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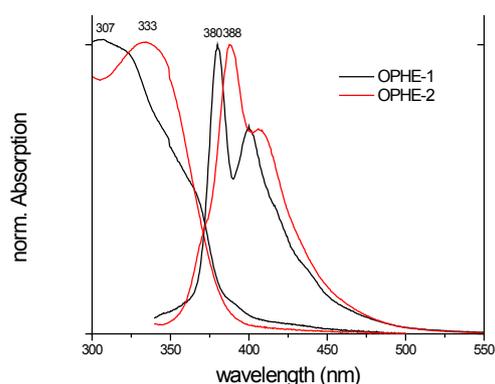
Using Sonogashira reaction a series of oligophenylenes containing electronacceptor phenylacetylene fragments emitting in the violet-blue region of the visible light was synthesized. These studies underscore the importance of learning how the structure of the building conjugated moieties affects the optical properties of the polymer.

The polymers were synthesized according to the scheme 1:



Scheme 1

different lengths, as linkers for the branching centres, on optical properties.



norm. PL intensity

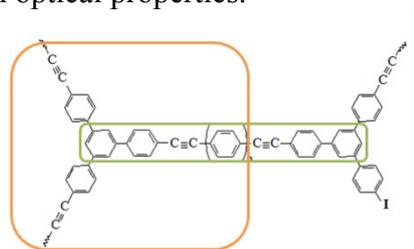


Fig 1. Absorption and fluorescence spectra of OPHE-1 (black line), OPHE-2 (red line), in solution. Excitation at 330 nm in the PL spectra.

OPHE-1 and OPHE-2 show absorption maxima at 305 nm (and shoulder at 365 nm) and 335 nm respectively. As expected, the maximum of absorption of the OPHE-2 is red-shifted with respect to OPHE-1, in agreement with extended conjugation.

The two oligophenylenes exhibit intriguing ultraviolet emission with appreciable ϕ_{PL} in the range 40-60%.

This work was supported by the Russian Foundation for Basic Research (RFBR), grants no. 14-03-00624; 15-53-78042; 16-03-00425.

Cascade hydrolytic polycondensation of organochlorosilanes at non-aqueous media – a new point of view on synthesis of polysiloxanes

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Hydrolytic polycondensation (HPC) of organosilicon monomers - one of the most important methods of modern technology of polyorganosiloxanes in the industry. At present time much attention is paid to improving the HPC methods and look for alternative ways of its realization. Among the research in this regard, a special place is occupied processes of HPC organosilicon monomers in homogeneous, non-aqueous media, in which water is generated during the process.

We have shown that organosilicon monomers (various organochlorosilane) spontaneously undergo fast oligomerization in contact with a non-aqueous urea and ketone in organic solvents not containing water [1, 2]. As the ketone carbonyl compounds of various structures may be used, for example, aliphatic, cycloaliphatic, aromatic and β -diketones.

The source of the water molecules for hydrolysis the chlorosilanes in this system is a dehydrocondensation process between ketone and carbamide, which proceeds only in the presence of HCl, incoming, in turn, to reaction zone through hydrolysis of chlorosilane.

Due to the presence of two interrelated coupled reactions (hydrolysis and dehydrocondensation), the HPC is developing as a typical cascade process.

In contrast to uncontrolled traditional HPC, which proceeds at heterogeneous aqueous dispersions, this approach allows to control appearance of water into the reaction zone - and hence the conditions for the formation of the macromolecules.

It is of particular interest for synthesis of silsesquioxane resins, containing $[\text{RSiO}_{1,5}]$ and $[\text{RSiO}(\text{OH})]$ structural units and also for block copolymers (BCP) of the general formula $\{[\text{Me}_2\text{SiO}]_n[\text{RSiO}_{1,5}]_{m-a}[\text{RSiO}(\text{OH})]_a\}_x$.

In particular, cycloliner BCPs, containing alternate linear and polycyclic blocks were synthesized by HPC of organotrichlorosilanes RSiCl_3 and oligoorganosiloxanes having Si-Cl bonds on the ends of linear chains. It appeared also, that this approach is applicable for the preparation of soluble BCP containing methylsilsesquioxane as rigid blocks.

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Microporous materials based on the polyphenylene matrix

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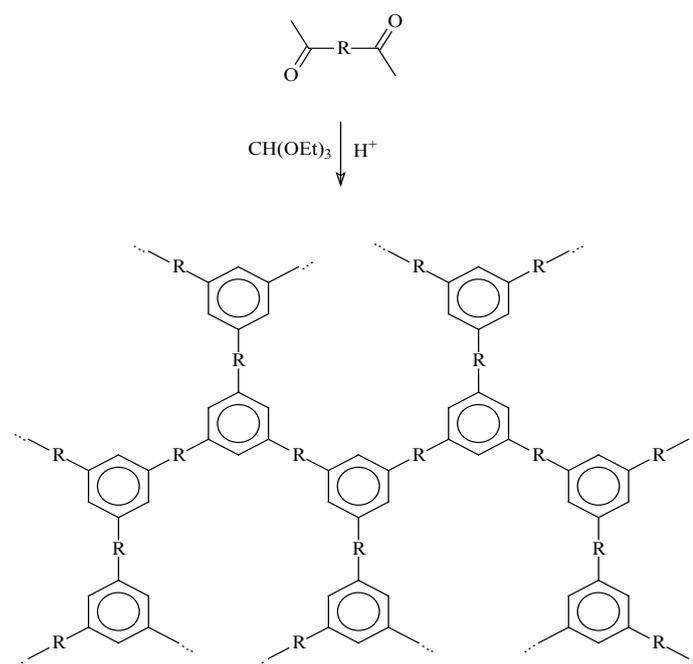
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The microporous structures in recent years become central in many areas of science and technology. They can be used in different fields such as heterogeneous catalysis, adsorption, separation and gas storage [1].

Most of the polymer molecules have sufficient conformational flexibility, allowing them to change their shape so that they are tightly packed, minimizing the amount of empty space, due to the increase of cohesive interaction of the molecule fragments. An approach to maximizing internal microporosity was to create polymers consisting of macromolecular fragments having high rigidity. It provides a structure of macromolecules, which does not allow them to be efficiently packed in the space.

In our work, microporous polymers are prepared by trimerisation/polycyclocondensation of different structure diacetyl aromatic compounds. In the result of the reaction, greatly hindering to rotation of the macromolecule fragments 1,3,5-trisubstituted benzene rings are formed as branching points.



These materials demonstrate relatively high apparent BET surface areas in the range up to 700 m² g⁻¹ (Ar adsorption).

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High molecular weight processable and thermally stable poly(cyclo)acetals

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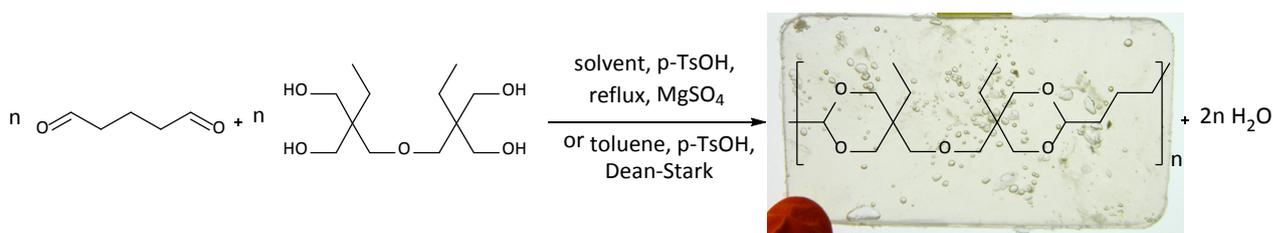
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Poly(cyclo)acetals are a class of polymers generally formed by the reaction of a tetravalent alcohol and a dialdehyde [1], which were first reported in 1912. Yet, only limited attention was given to this class of polymers despite their promising properties[2]. In the course of the polymerization, cyclic acetal moieties are formed resulting in a rigid polymer backbone. Poly(cyclo)acetals show an overall high thermal stability and extraordinary mechanical properties. However, it was reported earlier that these polymers could only reach low molecular weights, were not soluble in common organic solvents and/or not processable.

To improve the processability of the poly(cyclo)acetals, di(trimethylolpropane) instead of the commonly employed pentaerythritol was used successfully as tetravalent alcohol in the polyacetalization reaction with various commercially available dialdehydes.

In this way, processable poly(cyclo)acetals with high molar masses of up to 40 kDa were synthesized in a systematic manner. These polymers were thermally robust (degradation temperatures (T_d) of up to 370°C) and exhibited glass transition temperatures (T_g) in the range from 20 to 110 °C, depending on the employed dialdehyde. The trends in T_g modulation were confirmed by a theoretical simulation. Moreover, the poly(cyclo)acetals showed favourable mechanical and optical properties, such as ductile behaviour and transparency.



Scheme 1. Reaction of glutaraldehyde and Di-TMP in order to obtain a high MW and processable poly(cyclo)acetal.[3]

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Influence of inductive and steric effect under the polycondensation aryl(hydroxy)cyclotetrasiloxane isomers leading to the formation of the stereoregular cyclolinear polyorganosilsesquioxanes in the presence of layered-architecture

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We have recently reported that stereoregular cyclolinear polyphenylsilsesquioxanes macromolecules with isotactic, syndiotactic and columnar-shaped structure units were obtained via the polycondensation reaction of isomers 2,4,6,8-tetrahydroxy- 2,4,6,8-tetraphenylcyclotetrasiloxane: all-*cis*, *cis-trans-cis* and all-*trans* in the presence of layered-structure compounds (montmorillonite, coal) [1]. The method ^{29}Si -NMR spectroscopy was used to confirm the preservation of the conformation and relations of the initial cyclosiloxane isomers in the course of the polycondensation leading to the formation of the stereoregular polyphenylsil sesquioxanes[2].

To explore the inductive and steric influence of the substituents Si-atoms in organocyclotetrasiloxanes on the process of intercalation at the layered-architecture silicate Na⁺ MMT (montmorillonite) galleries in the reaction of polycondensation, we have synthesized all-*cis*-(tetrahydroxy)(tetra-*m*-tolyl)- (1) and *cis-trans-cis*-(tetrahydroxy)(tetra-*m*-chlorophenyl)-cyclosiloxane isomers (2) by hydrolytic polycondensation of *m*-tolyl- and *m*-chlorophenyltrichlorosilanes (Table 1).

Table 1

Compound	m.p. °C	Chemical shift (δ , ppm)	R _f	M ⁺ +H ₂ O
1	160	-70.16	0.05	626
2	>350	-71.81	0.50	

By polycondensation of isomers 1 and 2 in the presence of montmorillonite in the solution of toluene, anisole at the temperature of 110–140° C, cyclolinear polyorganosilsesquioxanes (3, 4) with the interchain distance of 13.2–13.5 Å were obtained. This suggests that besides phenyl other substituents with the increased Van-der-Waals volume can be used. The structure of 3 and 4 polymer units was confirmed by ^{29}Si NMR, IR spectroscopy, powder X-ray diffraction, viscosimetry, and GPC. In the ^{29}Si NMR spectra of the 3,4 polymers is present at -78.0 ÷ -80.0 ppm singlet with a narrow maximum in contrast to polyorganosilsesquioxanes obtained by anionic polymerization of oligomeric prepolymers *m*-tolyl - and *m*-chlorophenyl-(hydroxy)cyclosiloxanes.

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Through-space electronic interactions in the design of novel acceptor materials with reduced electron affinity for fullerene/polymer solar cells

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The power conversion efficiency of organic solar cells has been continuously increasing up to ca. 10-12% within last few years. This was possible due to the development of new materials such as low band gap polymers (p-type materials) and fullerene derivatives (n-type materials) with improved electronic properties. The present generation of fullerene derivatives with reduced electron affinity is represented mainly by compounds bearing two organic cyclic addends randomly distributed on the fullerene cage. This distribution of addends creates considerable disorder in thin films which inhibits charge-transport and affects badly photovoltaic performance of such materials.

We report the design and investigation of >50 fullerene derivatives whose electron affinity is lowered considerably due to the electron donating nature of a single organic addend attached to the fullerene cage. The electrochemical properties of the fullerene derivatives were investigated in solution and in thin composite films with conjugated polymers P3HT and PCDTBT. The best representatives of the designed families of compounds showed cathodic shifts of the first reduction potentials as large as 100-120 mV compared to [60]PCBM. It was revealed that increase in the LUMO energies of the designed fullerene derivatives is related to the through-space electronic interactions of the electron donating alkoxy groups with the fullerene cage.

The application of the designed fullerene derivatives as n-type components in organic bulk heterojunction solar cells led to increase in the open circuit voltage by 100-170 mV compared to the reference devices based on [60]PCBM. Few compounds provided even higher open circuit voltages (up to 770-780 mV with P3HT) than bis-PCBM bearing two organic addends on the fullerene cage. Moreover, using the best materials improved also the power conversion efficiency of organic solar cells where P3HT and PCDTBT were used as electron donor components. To our best knowledge this is one of the first examples of the fullerene derivatives with reduced electron affinity which outperform [60]PCBM in solar cells comprising non-crystalline conjugated copolymers such as PCDTBT.

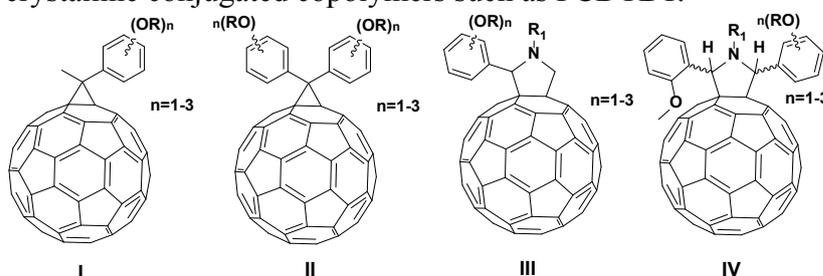


Fig. 1. General molecular formulas of the synthesized fullerene derivatives

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New approach to use thin polymer film as a detector of phase transition in metals

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The polymer thin film with non-linear electrophysical properties was used as detector for phase transition in metals. A voltage has been applied to the metal-polymer-metal structure and the current through structure has been measured as function of temperature. Two independent series of experiments were carried out when the polymer film is heated together with the metal and when the metal is heated only. They revealed sharp change in the current through experimental structure at the critical point of metals. This effect is related to a change in electrochemical potential when there is a phase transition in the metal and it results in a change of the temperature dependence of current. This method can be successfully used to detect the critical temperature without the need for direct contact of the polymer detector with the test material.

Experimental samples were sandwich-like structure of metal1-polymer-metal2 and metal1-polymer- metal1-metal2 where as metal1 was used copper and as metal2 – test metals. As the polymer layer was used poly(diphenylene phthalide) (PDP). PDP is heat-stable material. The softening temperature is 420°C in air and the breaking temperature is 440°C.

The technology of manufacturing of samples was as follows. On a glass substrate copper layer wide was deposited by thermo diffusion deposition. Next, it was completely covered with a polymer film. The film was applied by spin-coating from a solution of the polymer in a solvent (cyclohexanone). In experiments, test metals was located on the surface of the polymer films or on the surface of the second copper layer at different distances.

In the work a quite new and simple method has been tested for the phase transition detection in the metals. A thin film of the polymer was sensitive to the phase transitions in metals. This is due to the electrochemical potential changes during phase transitions. Thus, this approach can be applied to detect the first order, second order and structural phase transitions.

Experiments have shown that it is not necessary to locate the test material on the surface of the film. This allows to expand the temperature range of the materials using the polymer film as a remote sensor. From this point of view it could be a universal and very promising approach in the field of the phase transition physics. Experiments described in this report proved that the polymer film method could be successively applied to a broad class of materials.

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Improved photovoltaic performance of organic thin-film solar cells (OSCs) with Urchin-like gold nanoparticles (UL-AuNPs)

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Low bandgap polymers such as poly(3-hexylthiophene) (P3HT) blended with [6,6]-phenyl-C60-butyric acid methyl ester (PCBM) are widely used to semiconductor materials for bulk hetero-junction organic thin-film solar cells (OSCs). However, one issue with OSCs is a low efficiency of 10–15 %, which is not as high as silicon-based solar cells.[1]. An important challenge in the advancement of OSCs is enhancing the absorption in the organic layers while maintaining the thickness of the organic layers. Many researchers have tried to improve light absorption in OSCs, for example by tuning the bandgap of conjugated polymers for a large range of light absorption by chemical synthesis, adding an anti-reflection structure on OSCs to reduce the light reflection via an imprinting technique, and using the plasmonic properties of gold or silver nanoparticles as a light amplifier by blending them into OSCs. [2]. Urchin-like gold nanoparticles (UL-AuNPs) are a type of multi-pod gold nanostructures that have gold nanothorns on the surface with a wide range of light absorption and scattering compared with spherical gold nanoparticles of similar size. Moreover, UL-AuNPs can be synthesized via a one-pot synthesis technique that does not require stabilizers or capping agents. Hence, UL-AuNPs possess a bare gold surface and are soluble in water. In this study, we use UL-AuNPs for the application of OSCs. The results demonstrate that blending UL-AuNPs in the HTL plays an important role in improving the power conversion efficiency by enhancing the electric field and light scattering in OSCs. Furthermore, to understand the experimental results, finite-difference time-domain (FDTD) simulations were performed by estimating the UL-AuNP structures in the OSCs. FDTD simulations indicated an increased electric field distribution around the gold nanothorns, which corresponded well with the experimental results.

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Polymer gradient materials based on poly(epoxyisocyanurate) networks: chemical structure and its influence on the properties

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The properties were studied of polyepoxyisocyanurate networks, which are the basis for the type of gradient materials in which there is a smooth change in a given direction of the physical properties. A complex mixture of starting materials was used to produce polymer gradient materials: poly(tetramethyleneoxide), epoxy oligomer ED-20, and 2,4-TDI. Structures of networks were confirmed by following methods: NMR, IR spectroscopy, and elemental analysis. Dynamic mechanical analysis shows that these materials possess small values of $\text{tg}\delta$ like elastic materials (Figure 1), although the storage modulus values are as in conventional polymers transition zone and in this zone are maximum values $\text{tg}\delta$.

Fig.1. Dependence of $\text{tg}\delta$ on temperature.

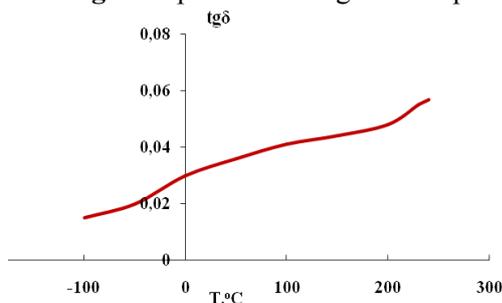
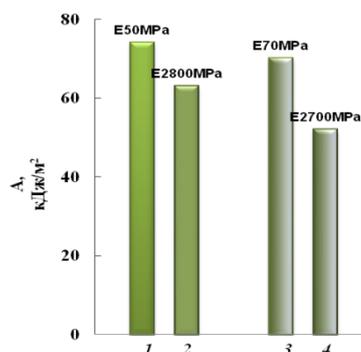
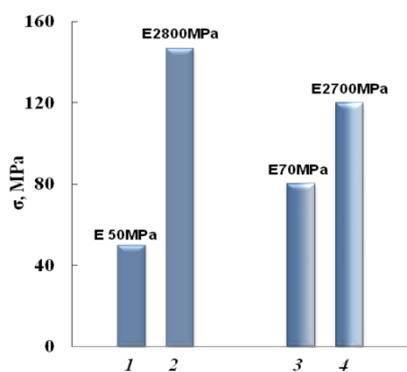
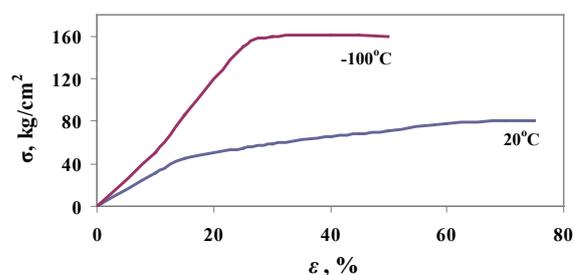


Fig.2. Stress-strain curves at various temperatures.



a

b

Fig.3 (1,2 – single modulus samples; 3,4 –gradient across the thickness).

The process of failure and deformation of gradient materials was studied because of their complex macromolecular structure. It is shown that the failure and deformation properties of the samples depend on the application of mechanical external conditions on each side of the field gradient material. Established high ultimate mechanical properties of composite materials; flexural strength is 160 MPa (Figure 3 a,b). In turn gradient film has no fragility in sub-zero temperatures; deformation at break is 30% at a temperature of -100°C (Figure 2).

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Tuning the optoelectronic and photovoltaic properties of conjugated polymers (-X-DADAD-)_n by using different acceptor (A) units

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Great improvement in the performance of organic bulk-heterojunction solar cells was achieved mostly due to successful design of novel photoactive materials. Recently, we have developed promising electron-donor copolymers (X-TTBTBT-)_n (X – fluorine, carbazole; B – benzothiadiazole; T – thiophene), which demonstrate good performances both in spin-coated (up to 7%) [1-3] and roll-to-roll processed (up to 6.2%) [4] devices.

In the present work we were aiming to improve further the optoelectronic characteristics of the designed copolymers (X-TTATATT-)_n via a systematic variation of the acceptor (A) units. We synthesized and investigated materials based on 2-alkylbenzotriazole, several different quinoxaline derivatives, benzoxadiazole and 5,6-bis(octyloxy)benzoxadiazole. We will discuss how the chemical structure of the acceptor building blocks affects the optoelectronic and physicochemical properties of the materials as well as their performance in organic solar cells. The revealed correlations provide useful guidelines for designing novel copolymers based on extended TTATATT units for efficient organic photovoltaics.

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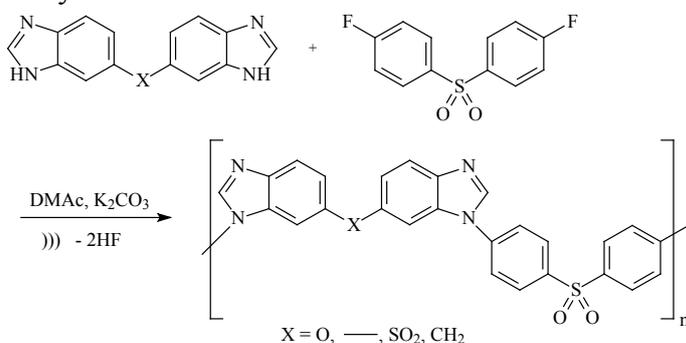
Synthesis and applications of poly(N-phenylenebenzimidazoles)

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Polybenzimidazoles (PBI) are heterocyclic high-performance polymers, traditionally obtained via condensation of aromatic tetraamines and dicarboxylic acids in Eaton's reagent or polyphosphoric acid. In our work we developed a different pathway for the synthesis of new polymers from this family. In this method poly(N-phenylenebenzimidazoles) (NuPBI) were synthesized by means of nucleophilic aromatic substitution reaction between dihalogen monomers and the preliminary synthesized bis(benzimidazoles) BisBI. Different methods for synthesis of BisBI monomers (with different X) were developed, including reductive heterocyclization of bis(*o*-nitoanilines) in formic acid-water media with hydrogen on Pt/C catalyst.



NuPBI may replace traditional PBI in some applications. The obtained NuPBI-O-SO₂ was tested in proton-conductive membranes of fuel cell in a complex with phosphoric acid [1]. The I-V characteristics of the NuPBI test cells were close to that of the commercially available Celtec P1000 developed by BASF [2]. As a part of our work on carbonized nanofiber electrodes for fuel cell, some NuPBI were tested in electrospinning process and nonwoven nanofiber materials were obtained.

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This work was supported by Russian Foundation for Basic Research (RFBR), grants no. 14-03-31964 mol_a and 14-29-04011 ofi_m.

Synthesis and properties of new poly(arylene thiophenes)

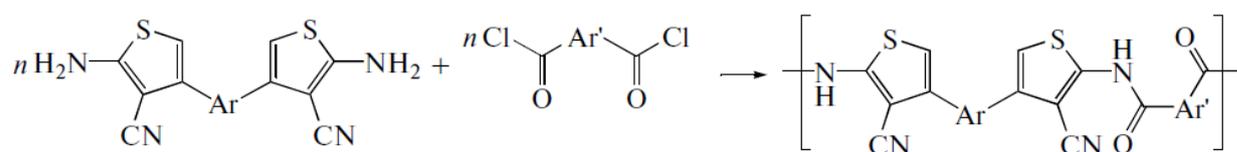
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Thiophene-containing polymers, primarily poly-thiophene and its derivatives, have attracted the attention of researchers owing to their wide spectrum of properties, such as conductance, luminescence, and electroluminescence. These properties predetermine their possible application as organic conductors and semiconductors, light-emitting diodes, sensors, etc. However, the infusibility and insolubility of polythiophenes make them difficult to process and restrict their practical applications. The processability of thiophene-containing polymers may be improved via incorporation of hinge bridge fragments into their chains. However, simultaneously with improved processability of rigid-chain polymers, the incorporation of hinge bridge fragments into the structure of rigid-chain polymers may lead to the breakage of their conjugation chains and deterioration of their electrophysical properties. Therefore, from our point of view, the most promising method includes the incorporation of bridge fragments that will not break the conjugation chain or that will restore it through polymer-analogous transformations in the course of processing.

Earlier, we synthesized new arylene-bis(2-aminothiophene-3-carbonitrile)s via the Gewald reaction. In our opinion, these compounds are promising as monomers for the synthesis of thiophene-containing polymers characterized by improved processability and the ability to form poly-conjugated structures. At the same time, the presence of nitrile groups in thiophene fragments is interesting from the standpoint of both the synthesis of polymers with new photoelectric properties and the feasibility of their subsequent chemical transformations. In this study, we investigated the synthesis of polythiophenes with main-chain acrylamide groups.



Scheme 1.

According to the TGA data, polymers are stable in air up to ~300°C and completely decompose with no carbon residue by a temperature of 550°C. Their optical and luminescent properties are currently being studied.

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Effect of polymers chemical structure on the membrane characteristics

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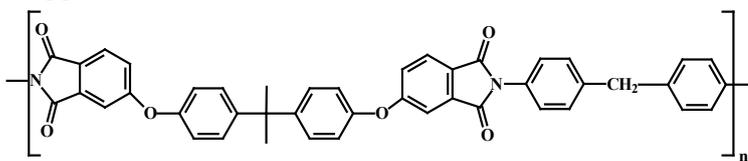
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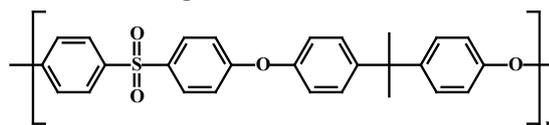
One of the most perspective and fast growing development trends of membrane separation technology is a gas separation by non-porous polymeric membranes. Search and modification of the membrane forming polymer is of great practical interest due to the constantly increasing demand for thermal and chemical stability of the membrane materials. Such membrane-forming polymers are polysulfones and polyimides. Due to high mechanical characteristics, thermal and chemical stability these materials membranes may be used at elevated temperatures and pressures and in the aggressive environment.

As the objects of study were chosen the following polymers: polysulfone adhesive powder grade CPM-1, produced by the polycondensation reaction between the bisphenol-A and 4,4'-dichlorodiphenylsulfon (polymer **2**) [17] and polyetherimide based on 4,4'-diaminodiphenylsulfone and 4,4'-(4,4'-izopropilidendifenoksi) bis(phthalic anhydride) Extem® brand [18] (polymer **3**).

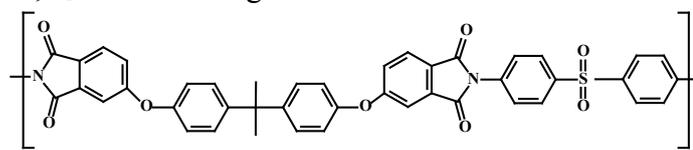
essures and in the aggressive environment.



$A_{fr}=24.95 \text{ \AA}$, $T_g=217^\circ\text{C}$, $V_f=0,2189 \text{ cm}^3/\text{g}$



$A_{fr}=16.31 \text{ \AA}$, $T_g=180^\circ\text{C}$, $V_f=0.2716 \text{ cm}^3/\text{g}$



$A_{fr}=22.90 \text{ \AA}$, $T_g=239^\circ\text{C}$, $V_f=0.2713 \text{ cm}^3/\text{g}$

It is shown that the choice of solvent has a significant influence on gas transport characteristics of polyimides. It is shown that the values of the density of the polymer depends on the Van der Waals volume of solvent molecules which is desorbed at a different speed and effects the formation of the morphological structure. Introduction to the polyimide sulfone bridge instead of methylene leads to an increase in the glass transition temperature, the permeability coefficients and slightly reduces the selectivity of this polymer membrane.

Effect of ionic liquids with thiocyanate anion on epoxy-rubber composition curing rheokinetics

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The effect of ionic liquids (IL) with thiocyanate anion on rheokinetic patterns of epoxy-rubber composition curing with anhydride curing system was studied. Dependences of viscosity (η) on time (τ) and the gelling time (τ^*) of the epoxy-temperature rubber composition were described by the following expressions:

$$\eta = \eta_0 \exp(K\tau) \quad (1),$$

$$\tau^* = \tau_\infty \exp(E_r/RT), \quad (2),$$

η_0 – constant, K – rheokinetic constant, τ_∞ – constant, E_r – effective gelling activation energy, R – universal gas constant.

The table shows the constants of curing and gelling of the rubber-epoxy composition without IL and of one containing 0.0026 mol of IL per 100g composition, calculated on the basis of experimental data.

#	IL		η_0 , cPs (70°C)	K , min ⁻¹ (70°C)	τ_∞ , min	E_r , kJ/mol
	Cation	Anion				
1		SCN ⁻	0.132	$8.488 \cdot 10^{-3}$	$6.216 \cdot 10^{-9}$	71.9
2		SCN ⁻	0.132	0.012	$4.945 \cdot 10^{-9}$	72.6
3	IL free		0.116	$6.579 \cdot 10^{-4}$	$6.521 \cdot 10^{-6}$	56.2

The research results evidence of the effectiveness of IL bearing thiocyanate anion in advancing epoxy-rubber composition curing, they also show that there is no significant effect of the chemical structure of the IL cation on their catalytic activity.

Carbon nanofiber paper based on heterocyclic polymers for high temperature polymer electrolyte membrane fuel cells

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Different types of carbon nanofiber paper (CNFP) were obtained from a scope of various heterocyclic polymers. Polybenzimidazoles (PBI), polyacrylonitrile (PAN), «polymer of intrinsic microporosity» (PIM-1), polyphenyleneoxide (PPO) and nucleophilic polybenzimidazole (NuPBI) were used as precursors for CNFP in order to tailor its physical properties. For this aim, the synthesized initial polymers were electrospun on a flat surface providing polymer nanofiber mats. On the next step, during oxidation (stabilization) in air at 250 - 350 °C, partially oxidized nanofiber polymer mats with condensed heterocycles in their structure were obtained. Final CNFPs were formed when stabilized polymer mats were pyrolyzed (carbonized) at 900 – 1200 °C under vacuum.

Physical properties of the resulting material may vary in a wide scale depending on such factors as initial structure of the precursor polymer, temperatures of stabilization and carbonization, and introducing of many different additives (such as polyvinylpyrrolidone, Ni, Fe, Co, Zr salts, etc.) which were added to polymer solutions and electrospun. As it is shown by the method of standard contact porosimetry and electron microscopy, a highly macro- and microporous conductive composite nanofiber material where each nanofiber possesses its own inner inherent porosity was obtained.

The composite CNFPs are suitable for nanocrystalline platinum (1.5 – 5 nm) deposition by dipping directly into H₂[PtCl₆] aqueous solution as confirmed by electron microscopy (TEM). As a result, a new type of fuel cell electrodes is formed which allows avoiding some drawbacks of traditional «ink-type» electrode preparation. It is shown that given gas diffusion electrodes can be used as anodes [1] and cathodes [2] for polymer electrolyte membrane fuel cell with PBI/H₃PO₄ membrane [3].

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High performance polymer/fullerene solar cells processed from environment-friendly non-halogenated solvent

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In connection with the depletion of fossil fuels, a lot of attention is paid to the development of alternative energy sources such as photovoltaics. Thin film organic solar cells represent a promising technology, which has been already commercialized with respect to some niche applications and holds a promise to enter on-grid market within the next decade, particularly owing to the high throughput and low cost production based on roll-to-roll coating and printing technologies. Inherent advantages of organic solar cells such as light weight and mechanical flexibility make them very promising for powering various portable and even implantable electronics. Plastic solar cells based on organic semiconductor materials such as conjugated polymers and fullerene derivatives are commonly considered as environment friendly devices, which can be easily utilized at the end of the life cycle as a general house waste. However, production of organic photovoltaics raises serious environmental concerns due to massive use of halogenated solvents and additives (chlorobenzene, 1,2-dichlorobenzene, 1-chloronaphthalene).

Here we present a novel group of electron donor statistical copolymers comprising carbazole, fluorene, thiophene and benzothiadiazole units, which can be processed in highly efficient bulk heterojunction organic solar cells using non-halogenated solvents and [70]PCBM as an electron acceptor counterpart. Optimization of the component ratios, active layer thicknesses and thermal annealing regimes delivered power conversion efficiencies of 6.0-6.7%. Very comparable performances were also reached for the best devices fabricated using 1,2-dichlorobenzene as a solvent.

It should be emphasized that the designed materials showed superior photochemical stability in thin films, which enabled long operation lifetimes of the laboratory prototypes of organic solar cells. This result correlates with our previous reports on the advanced stability of a series of TTBTBTT-carbazole copolymers [1-2]. Additionally, these and similar conjugated polymers were successfully processed using slot-die-coating film deposition technique on a pilot roll coating machine, providing efficiencies exceeding 6% [3].

We strongly believe that results obtained in this work will facilitate industrial application of the designed materials in a large-scale environment-friendly manufacturing of plastic solar cells delivering both high efficiency and long-term operation stability.

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Novel TTBTBTT-based copolymers for organic solar cells designed using Suzuki and Stille polycondensation reactions

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Development of novel organic semiconductors for solar cell applications is performed nowadays in many research laboratories worldwide. Electron donor p-type materials are typically represented by conjugated polymers with alternating electron rich and electron deficient blocks. We have shown previously that conjugated polymer P1a (Fig. 1) represents a promising photoactive material delivering high power conversion efficiencies in organic solar cells in combination with advanced operation stability [1].

Here we report a family of novel conjugated polymers P2-P7 bearing a modified TTBTBTT unit (2-ethylhexyl or n-decyl side chains) combined with different electron donor blocks such as fluorene (P2), silafluorene (P3), benzo[1,2-b:4,5-b']dithiophene (P4-P5), cyclopentadithiophene (P6) and indolocarbazole (P7) (Fig. 1).

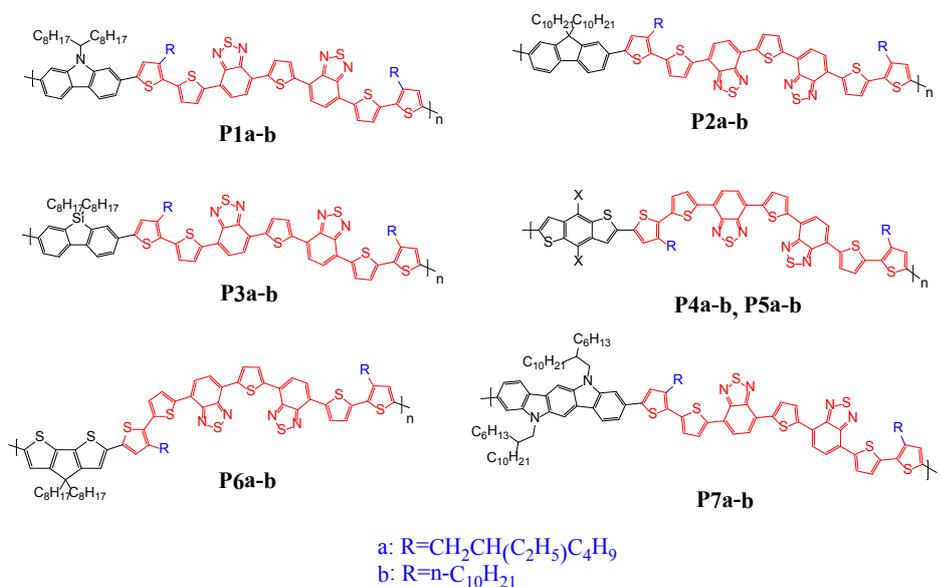


Fig. 1. Molecular structures of P1-P7

Preliminary evaluation of P2-P7 as electron donor materials in organic solar cells allowed us to achieve power conversion efficiencies >5.0%. We expect that further optimization of the materials (e.g. molecular weights or side chains) and devices (active layer morphology, buffer layers and etc.) will deliver higher performances.

The results on the operational stability of the solar cells based on polymers **P2-P7** will be also discussed and molecular structure-efficiency-stability relationship will be presented.

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Electrolyte membrane based on silica-containing copolymer for lithium batteries

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A method for the synthesis of silicon-containing copolymers based on tetraethoxysilane, 3-mercaptopropyl trimethoxysilane and polyethylene glycolsilane of molecular weight 1000 and with silicon content of 20 to 50% was developed. Interaction of the monomers to form a silicon-containing copolymer goes through hydrolytic polycondensation reaction. Synthesis of a series of copolymers with different contents of starting monomers, a method of purifying them, a procedure of formation of thin solid films, as well as mechanical and conductive properties of copolymeric materials were carried out. For the copolymers obtained by the polymer electrolyte with conductivity by lithium cations optimal conditions for the preparation of films, including lithium salts content were selected.

The composition of the films in low vacuum scanning JSM-6610LV electron microscope with a thermionic cathode (LaB6) company "JOEL" was studied. It was found that by increasing the salt load of 0.4 to 1.0 g / 1 g of polymer amount in the sample the elemental lithium content is increased from 2.8 to 4.1 wt. %. Meanwhile this lithium salt is uniformly distributed in volume and area of the sample. The lithium content in the film is reduced from a value of 4.1 to 3.0 wt. % after their operation for 100 hours in the electrolysis cell.

The ionic conductivity of the films was measured at room temperature by impedance spectroscopy between two electrodes in the frequency range 4,0-100,0 kHz. It is found that the ion conductivity of the prepared film was $3-5 \cdot 10^{-6}$ S / cm, depending on their composition. We studied their current-voltage characteristics for more information on the chemical composition of the films. It was revealed that the acidic electrolyte media samples show high values of current, and with increasing concentrations of lithium salts, they increase. Thus, when the initial salt content $0,4 \times 10^{-4}$ g / 1 g of polymer current value in the range from 0.05 to 0.10 falls in more than three times as compared with the initial sample load $1,0 \times 10^{-4}$ g salt / 1 g of polymer. At higher pH, this difference becomes more apparent but simultaneously decreases the absolute value of current in the system, due to a decrease in the degree of dissociation of the salt by lowering the pH in the system. We have previously determined that a voltage in the range of 0.05 to 0.10 the beta-peak of dielectric permittivity of membrane is observed. Consequently identified effect is due to the very nature of silico-organic membrane. Based on these experimental data the electrolytic cell with an electrolyte membrane containing 0.6 g of lithium perchlorate salt per 1 g of dry polymer base or about 3.0 wt. % of lithium ions was developed. The most effective operation of the membrane takes place in an acidic electrolyte saturated with lithium perchlorate at a pH of about 2.0.

Synthesis of reactive oligoimides by thermichemical cyclization in the presence of alkyltriethoxysilane- trialkylamine

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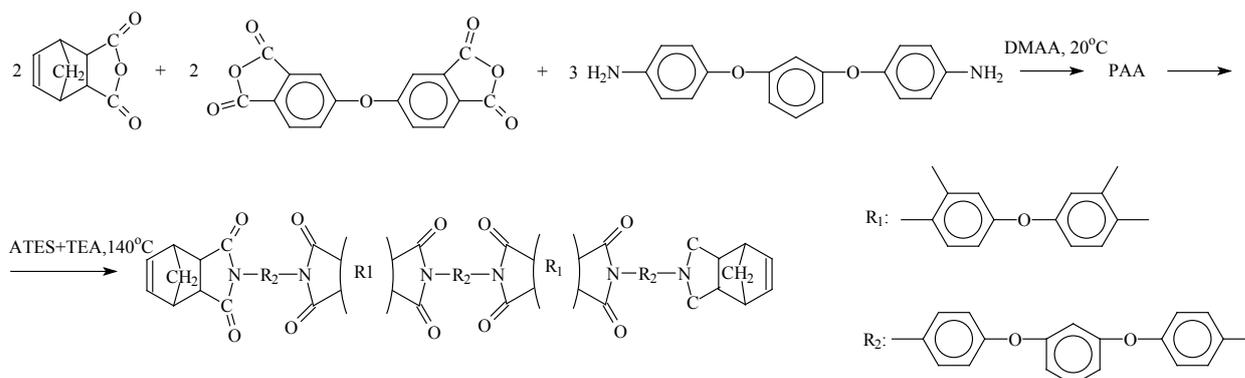
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One of most promising and ecologically pure methods for obtaining polymer composition materials on the basis of carbon fibers or fabric and polyimide matrix is deposition on fiber of a semi-product – completely imidized oligoimides containing unsaturated terminal moieties as a meltable powder, followed by thermal treatment of all the material under pressure. The advantage of this method in comparison with impregnating of fiber with solution of imide forming reactants is avoiding the necessity of solvent regeneration and a avoiding problem of toxic diamines leakage in a form of vapor. To obtain thermoplastic reactive oligoimides (OIs), they usually use the two-stage method including the low-temperature polycondensation of the mixture of aromatic tetracarboxylic acid dianhydride, nadic anhydride and aromatic diamine followed by

“chemical cyclization” of oligoamido acid (OAA). Cyclization occurs in the presence of the “acetic anhydride-pyridine” cyclization system which is toxic. Substitution of the latter on new more appropriate one is a task of importance.

In present work we offer new synthesis method of reactive OIs preparation comprising in that the cyclization stage of OAA is carried out in the presence of the cyclization system alkyltriethoxysilane- trialkylamine at 130-140°C for 20 min. Completely imidized product as a solid powder precipitate can be easily separated by filtration. One of variants of method is presented in a Scheme 1.



Scheme1

The yield is about 80%. The OI structure was confirmed by means of IR and NMR ¹H. IR spectra: (CsI) ν/cm^{-1} : 1780 ; 1720 (C=O in imide cycle), 1340 (C-N in imide cycle), 720 (C-O in imide cycle). NMR ¹H (chloroform-d₆, δ , ppm, *J*/Hz): 7.19-7.32 (m, 8H, CH(5, 6, 7, 10)); 7.37-7.44 (m, 2H, CH(12)); 7.65 (t, 2H, CH(13), *J*=8.1); 7.76-7.84 (m, 2H, CH(14)); 8,36 (c, 2H, CH(19, 20)).

Cryopolycondensation of poly(dimethylsiloxane) with tetraethoxysilane in the medium of moderately-frozen benzene

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Polycondensation processes occurring in the media of moderately-frozen solutions of the respective precursors are, in comparison with cryopolymerization, studied rather poorly [1]. In both types of such processes the formation of polymeric chains proceeds within the volume of so-called ‘unfrozen liquid microphase’ [2], in which the reagents are concentrated. Quite owing to this effect chemical reactions are able to occur, and reduced temperature preserves thermosensitive substances, e.g. temperature-unstable derivatives of biological molecules. In addition, both the cryopolymerization and cryopolycondensation allow preparing cross-linked macroporous polymeric gel materials – cryogels [1] that possess a set of valuable properties desirable for materials of biomedical and biotechnological interests.

In this work we prepared organosilicon-based cryogels, studied peculiarities of their formation, their properties and microstructure. Such matrices were prepared via the tin-diethylcaprylate catalyzed polycondensation of poly(dimethylsiloxane) (PDMS), which contain end silanol groups, with tetraethoxysilane (TEOS), when the process was carried out in the medium of moderately-frozen benzene within the temperature range of 10...35° below the freezing point of a neat benzene (+5.5°C). Initial molar ratio of the reagents was as follows: PDMS : TEOS : catalyst = 1:8:4; total their concentration was 20 wt.%.

It was found that over the indicated reaction temperature range, the values of gel-fraction yield are high and depend insignificantly on the freezing temperature, whereas the temperature dependences of swelling extent and elastic modulus for the resultant cryogels are of bell-like character (fig.1), similar to that inherent in known cryogels formed via cryopolymerization technique.

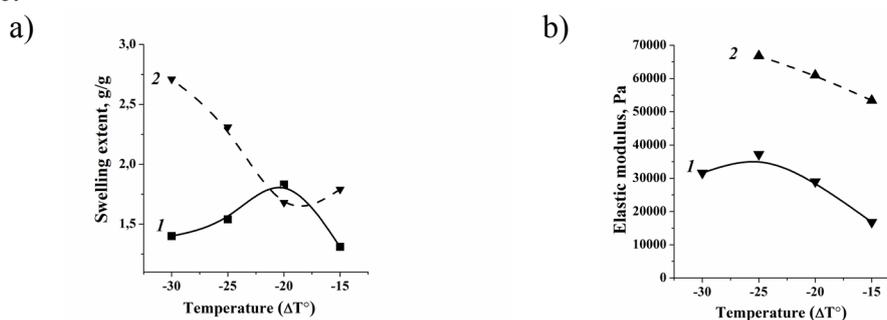


Fig. 1. Dependences of the swelling extent (a) and elastic modulus (b) of poly(dimethylsiloxane) cryogels on the synthesis temperature (1 – conventional freezing; 2 – ‘fast’ freezing).

Polysiloxane cryogels that have been prepared in this study had spongy morphology, their pore size was mainly ensured by the temperature regimes of both the cryotropic gel-formation and thermal history of the reacting system (the route of bringing the system to the reaction temperature).

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Synthesis of polyurethanes in macroporous polymer matrix

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The synthesis of new polymer composite materials (CM) with a given set of characteristics that are widely used in medicine, in industry of equipment production, in construction, etc. is a dynamically developing area of polymer chemistry and technology. One way to CM obtaining is the two-step process including the synthesis of porous matrix from the first polymer and subsequent filling of its pores by the second polymer. Polymer with the related open pore system, based on dimethacrylate oligomers compositions obtained by photopolymerization, can be used as the porous matrix [1]. The polyurethane, which forms respectively in the pore volume, can be used as the second polymer. In this work the processes of porous polymer formation are investigated, filling mode of the polymer matrix pore volume by polyol – polyisocyanate mixture and mode of its subsequent curing are elaborated. Porous polymer matrices were synthesized from photopolymerizable compositions (PPC), consisting of the mixture of dimethacrylate oligomers and porogens. We use two dimethacrylate, belonging to different oligomer classes - MDP-2 and OCM-2. n-Butanol, n-hexanol and n-octanol were used as porogens. The morphology of the polymers was investigated by atomic force microscopy, the gravimetric method was used to study of polymers sorption (with respect to water and benzene). It was found that the average pore size of polymers based on MDP-2 at the transition from n-butanol to n-hexanol and n-octanol at its concentrations in the PPC equal to 30 wt. % increases from 0.5 to 3 microns, and for polymers based on OCM-2 - from 0.3 to 1.5 microns, respectively. Polymers on the basis of MDP-2 and all investigated alcohols sorb water and benzene. For polymers, based on OCM-2, only polymers from n-butanol composition have sorption capacity. The processes of pore volume filling in polymer matrices with pore size equal to 0.3 and 3 microns by polyurethane-forming mixtures and the processes of its polymerization were investigated. Industrial components of mixtures - polyisocyanate RM-200 and a series of polyols, the viscosity of which varies from 120 to 650 cps, were used. It has been established that polymers with the pore size at about 3 micron effectively fill by mixtures PM-200 with polyols independently of polyols viscosity. The polymer matrix with the pore size of 0.3 microns doesn't fill by mixtures with polyols having a viscosity greater than 600 cps. The influence of curing time of PM-200 – Laprol 502 system in the pore volume on the gap stress for polymers was studied using polymeric matrices with average pore size about 0.3 and 3 microns. These results suggest the possibility of the CM synthesis by photolytic formation of porous polymeric matrix, the subsequent filling of the pore volume by the polyurethane-forming mixture and its polymerization.

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The influence of oxygen on the charge carriers transport in thin films of poly(difenylenephthalide)

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The thin film polymers poly(difenylenephthalide) capable under certain conditions to show high electrical conductivity. The most experimental results on these material was obtained in the air without control and accounting of atmospheric composition. However, as shown by the results of this work, the influence of the atmosphere makes a negative contribution to the results. In particular experiment found that the amount of current flowing through the sample-This depends on measurement conditions (vacuum, inert environment or air). The largest current value observed when measured in vacuum and in an inert atmosphere.

It is known that, by oxygen oxidation products are formed, which act as traps and lower the carrier mobility [1]. In this work, quantum-chemical calculations by the density functional theory, the energy of the electron affinity and the spin density for complex PDP/gas (O₂, Ar, He, N₂, CO₂) monomer were carried out. According to the results shown in the table, the main contribution to the conductivity of thin polymer films PDP brings oxygen. At the same time the inert gases do not have a significant impact. In [1] it is noted that in all organic compounds have a group of deep traps appropriate oxygen traps.

	Monomer (PDP)	Complex PDP/O ₂	Complex PDP/N ₂	Complex PDP/Ar
HOMO, eV	-6,93	-6,34	-6,94	-6,93
LUMO, eV	-1,75	-4,35	-1,76	-1,75

Based on the results presented in Table, on the structure (Al-PDF-Sb) were measurements current-voltage characteristics. IV measurements showed that inert gases (Ar, N₂) has no effect on the conductivity of PDP. At the same time, increasing the oxygen concentration has a profound effect on the properties of films PDP. It is established that about 60 minutes of exposure of the sample in a vacuum, it is possible to lower the oxygen concentration in the polymer film. This is reflected in an increase in current flowing through the sample.

In the report discusses the results and their interpretation.

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Poly(3-hydroxybutyrate) and its blends with polyethylene glycol – high potential materials for tissue engineering

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Nowadays, polyhydroxyalkanoates are the one of extensively investigated and high-potential biodegradable polymers for tissue engineering. Poly(ethylene glycol) (PEG) is a nontoxic hydrophilic polymer approved by the U.S. Food and Drug Administration (FDA) for internal consumption. It is frequently used as a plasticizer agent to modify different polymer properties.

In current work we examine the thermal, dynamic and biological properties of materials based on natural polymer of microbiological origin poly(3-hydroxybutyrate) (PHB).

Copolymer PHB and PEG (PHB-PEG, ($M_w = 2,17 \times 10^5$ kDa) was obtained biotechnologically from strain *Azotobacter chroococcum* 7B, by adding PEG to the culture medium of microorganisms and by changing the parameters of cultivation compared to the homopolymer PHB yield. The composite material PHB + PEG has been obtained by adding PEG ($M_w = 1500$) in an amount of 30% by weight to the PHB ($M_w = 4,85 \times 10^5$). Sample films were about 200-300 microns in thickness, produced by standard casting.

The composite material has the highest hydrophilicity from these three samples and the highest crystallinity. It might be explained by the high percentage of PEG (30%) which is very hydrophilic and has a high crystallinity (85,7%) [1], while the proportion of PEG in the copolymer is about 0,3%. The thermal degradation temperature for PHB, PHB-PEG and PHB+PEG are 218 °C, 226 °C and 240 °C respectively, which indicates that PHB+PEG exhibits a better thermal stability than homo- and copolymer.

Materials exhibit typical reduction in dynamic elastic modulus with increasing temperature. At body temperature the copolymer has the highest absolute value of the storage modulus and the minimum tensile strain, namely more rigid, while the composite PHB+PEG shows low level of storage modulus level, but greater elongation.

Biocompatibility was estimated by cytotoxicity test in vitro, using the fibroblast cell line 3T3. Cell proliferation and viability were measured by the cell proliferation reagent XTT (XTT Cell Proliferation Kit, Biological Industries, Israel). All films do not demonstrate cytotoxicity in the culture for 5 days.

Thus, PEG adding to PHB as a composite increases the hydrophilicity, crystallinity and thermal stability, while the copolymerization does not lead to significant changes of hydrophilicity or crystallinity, but increases the storage modulus. All types of materials are not cytotoxic.

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Synthesis of bisphenols containing pendant furyl group based on chemicals derived from lignocellulose and their utilization for preparation of clickable aromatic polyesters

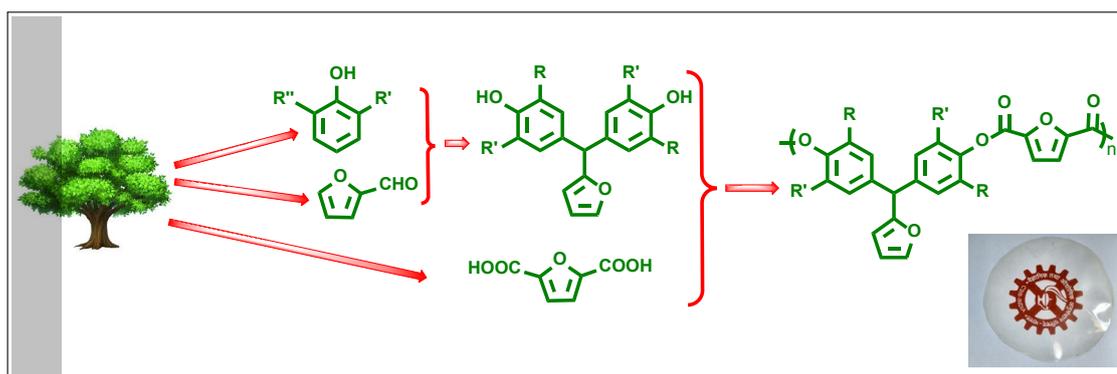
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Lignocellulose-derived chemicals such as furfural, furandicarboxylic acid, syringol, guaiacol, etc are highly attractive as sustainable alternatives to petrochemicals for the synthesis of monomers and polymers^{1,2}. We wish to report herein the facile synthesis of fully bio-based bisphenols containing pendant furyl group by base-catalyzed condensation of furfural with guaiacol/syringol³ (Scheme 1). Bisphenols possessing pendant furyl group represent valuable monomers for the synthesis of a range of polymers which include epoxy resins, polyesters, polycarbonates, poly(aryl ether)s, etc⁴. A series of aromatic polyesters containing pendant furyl groups was synthesized by phase transfer catalysed interfacial polycondensation of furyl containing bisphenols with aromatic diacid chlorides namely, terephthaloyl chloride, isophthaloyl chloride, and 2,5-furandicarboxylic acid chloride. Polyesters showed inherent viscosities in the range 0.44-0.78 dLg⁻¹ and number average molecular weights (M_n), obtained from gel permeation chromatography (GPC), were in the range 28000 - 45000. Furyl containing bisphenol based aromatic polyesters exhibited improved solubility characteristics compared to conventional bisphenols-A based aromatic polyesters and were soluble in common organic solvents such as dichloromethane, chloroform, etc. Polyesters could be cast into tough, transparent and flexible films from chloroform solutions. X-Ray diffraction studies indicated amorphous nature of polyesters. Polyesters showed T_g values in the range 152-214 °C while T₁₀ values were in the range 377-400 °C indicating their excellent thermal stability. Additionally, the pendant furyl groups in aromatic polyesters provide reactive sites for chemical modifications and crosslinking *via* Diels-Alder reaction with maleimides and bismaleimides, respectively.



Scheme 1. Synthesis of bisphenols and polyesters starting from lignocellulose-derived chemicals

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Synthesis and investigation of aromatic (co)polyamides and their application in the optical fibre technology

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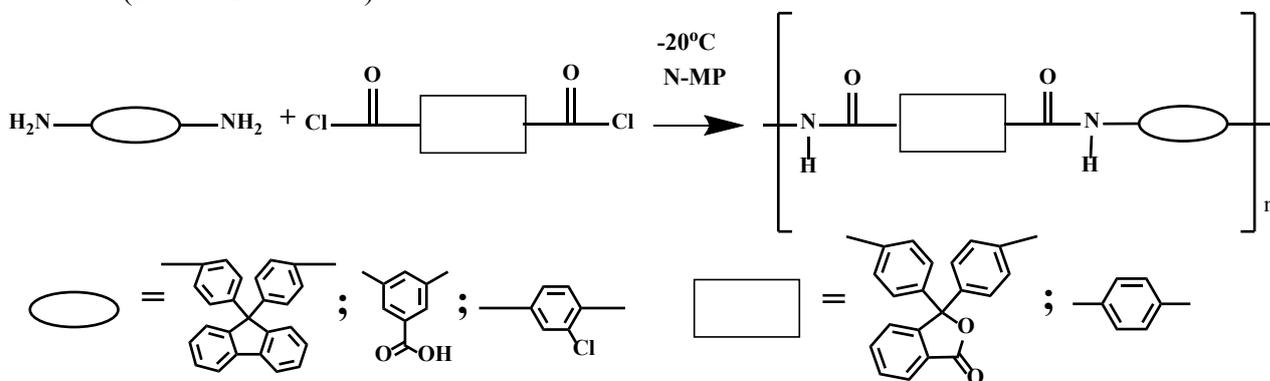
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It is known that for using in medicine, Oil & Gas industry, etc. protective optical fibre coatings should withstand the impact of high temperatures and corrosive environments. Aromatic polyamides possess high thermal and mechanical properties, but previously only polyimides and polyamidoimides have been described as high-temperature optical fiber coatings.

The presence of cardo groups in different hetero- and carbon chain polymers endows very specific properties: excellent solubility together with high thermal properties, which is of particular importance in aromatic heterocyclic rigid chain polymers. It makes possible to use such polymers as films, adhesives, binders and coatings.

In this work we have synthesized cardo homo- and (co)polyamides according to the **Scheme 1**. Obtained polymers have high molecular weights ($\eta_{inh} = 0.7 \div 1.8$ dL/g) and the following thermal characteristics: $360^{\circ}\text{C} < T_g < 390^{\circ}\text{C}$; $470^{\circ}\text{C} < T_{10\%} < 510^{\circ}\text{C}$ (in air). Casted from N-methyl-2-pyrrolidone (N-MP) solutions films have high tensile strength ($100 \div 140$ MPa) and tensile modulus ($1600 \div 2300$ MPa).



Scheme 1.

The compatibility of the resultant material with the optical fibre drawing process and the properties of optical fibres coated by new polymers were studied. The smooth uniform coatings formed from N-MP solutions are characterized by high thermal stability and good adhesion to the fibre surface without any coupling agent. Study of the optical fibres properties before and after thermal tests showed that the bending strength of the samples decreases up to 10% only after exposure for 24 and 72 h at 300 and 250°C, respectively.

Thus it was demonstrated that aromatic cardo (co)polyamides as appropriate polyimides and polyamidoimides are promising coatings for high-temperature optical fibres applications.

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Development of a new masterbatch system containing chain extenders for poly(ethylene terephthalate)

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Poly(ethylene terephthalate) (PET) is one of the most widely used technical polymers. The usage of PET was about $37.85 \cdot 10^6$ tons in the world in 2012 [1]. It is the most important polyester and its main applications are fibers and food packages like e. g. bottles for soft drink beverages or fruit boxes. The importance of PET for many applications can be attributed to its good properties such as high tensile strength and impact strength, clarity, good processability, high chemical resistance and high thermal stability. Another important property of PET is the ability to reuse PET after recycling. The consumption of PET is very high; thus, interest in the recycling of PET is also very high.

However, some problems can arise during and after repeated recycling of PET. Due to repeated thermal treatments, PET becomes more and more grey, which could be critical for fiber applications [2]. A further problem is caused by the thermal decomposition of this polyester which can occur during recycling. This results in reduced viscosities after multiple recycling steps. To solve this problem, different methods can be used to increase the molar mass of recycled PET. The commonly used method to increase the molar mass of PET is the solid state polycondensation (SSP) process. This process is mainly used in bottle-to-bottle (closed-loop) recycling industries where high molar masses are necessary. For the open-loop-recycling (for instance recycling of bottle to fiber), lower molar masses are needed. In that case, the molar mass can be handled by addition of small amounts of virgin PET or chain extenders. The known chain extender 1,3-phenylene-bis-oxazoline (1,3-PBO) reacts with the carboxyl end groups of PET. Another chain extender which reacts with the hydroxyl end groups of PET is *N,N*-carbonylbis-caprolactam (CBC). The use of these additives in masterbatch systems is still challenging. The usage of common polyesters as masterbatch carriers is impossible, as the additives would react with the carrier during masterbatch manufacturing.

In this work, the development of a polyester based masterbatch containing chain extenders is presented. Spinning tests were carried out in pilot plant tests at high velocities with the aid of masterbatches containing 1,3-PBO and/or CBC as chain extenders. The results show that the quality of post-consumer PET can be improved by applying masterbatches containing chain extenders in the spinning process.

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Controllable Surface Imprinting on Silica-gel via Atom Transfer Radical Polymerization for *S*-1-(1-naphthyl) Ethylamine Recognition

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Molecular imprinting represents an attractive technique for design highly cross-linked porous polymers with specific adsorption or recognition sites to a given target or group of target molecules since 1970s. Nowadays, surface modification of support materials with a controllable imprinting polymer layer has become one of the most important techniques in molecular imprinting field. In this work, controlled grafting of *S*-1-(1-naphthyl)Ethylamine-imprinting polymer layer on the silica-gel was carried out by the surface-initiated atom transfer radical polymerization (ATRP) in ionic liquid. Polymerization time was used as the independent variable to manipulate the amount of grafted imprinting polymer on the silica-gel. For comparison, molecularly imprinted polymers (MIPs) without silica-gel also prepared at the same condition. SEM, FT-IR and UV spectrum were used to study the structural morphology and selectivity of polymers and probe the incorporation of imprinted polymer layer on the surface of substrates. Results indicate that the integration of ATRP and molecularly imprinted polymerization realize preparation of molecular selective polymers and it is possible to tune selectivity and morphology in rational way by changing polymerization times. Surface imprinted polymer (SIPs) shows a higher binding capacity than the MIPs does and with the increase of polymerization time, binding capacity also increased. The maximum saturated binding capacity of surface imprinted polymer to *S*-1-(1-Naphthyl) ethylamine and *R*-1-(1-Naphthyl) ethylamine was about 7.9332 and 4.6063 $\mu\text{mol}\cdot\text{g}^{-1}$. Meanwhile, we achieve a reference strategy for the development of SIPs for drugs and to handle forms in certain applications such as chromatographic stationary phases for chiral separations.

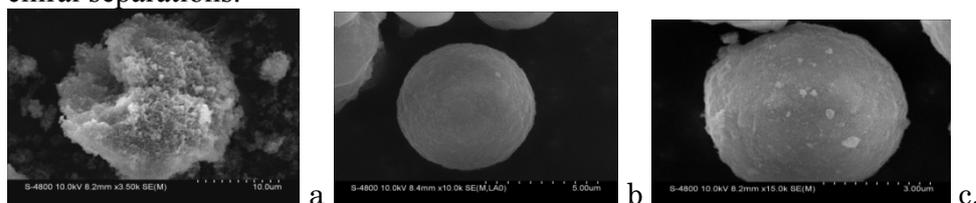


Fig.1. SEM images of of MIPs (image a), silica-gel(image b) and SIPs (16h, image c)

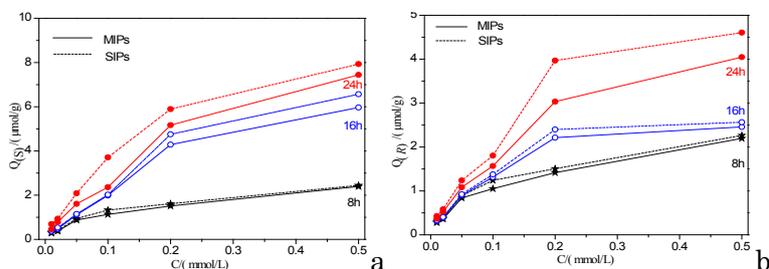


Fig.2. Selective binding to *S*-1-(1-Naphthyl) ethylamine and *R*-1-(1-Naphthyl) ethylamine of MIPs and (SIPs) a. *S*-1-(1-Naphthyl) ethylamine b. to *R*-1-(1-Naphthyl) ethylamine

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Renewable citrimides as building block for polyesters

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In coating resins there is a drive for using bio-based building blocks to obtain more sustainable coatings. For alkyds an imide from citric acid with either glycine or phenylalanine was made with the structure below [1].

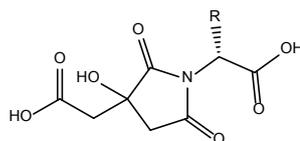


Fig. 1. Bio-based imide building (R = H for glycine; R = benzyl for phenylalanine).

These structures were built into alkyds and it was shown that these resins give promising results in highly bio-based content coatings.

In this poster the results obtained with model polyesters based on the citrimids will be shown and the polymerization and the properties discussed.

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Acknowledgements

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Synthesis and properties of transparent polyimides derived from dianhydrides containing cyclohexane unit

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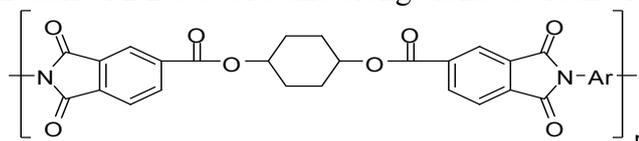
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Aromatic polyimides are well-known as high performance polymer materials due to their excellent thermal stabilities and balanced mechanical and electric properties. The optical transparency of polyimide films is of special importance in some applications, such as flexible solar radiation protectors, orientation films in liquid crystal display devices, optical waveguides for communication interconnects, and optical half-waveplates for planar lightwave circuits. However, the wholly aromatic polyimides are pale yellow or deep reddish yellow because of their highly conjugated aromatic structures and/or the intermolecular charge-transfer complex (CTC) formation, limited their widespread application in optical fields.^[1] Therefore, considerable efforts have gotten progress on the development of transparent aromatic polyimide films based on structural design by modification of monomers, including introduction of trifluoromethyl group, asymmetric backbone, bulky substituents and alicyclic units as monomers.

Compared with aromatic polyimides, the semi-aromatic polyimides derived from dianhydrides containing alicyclic units exhibited excellent optical transmittance and solubility. Recently, our group has reported transparent semi-aromatic polyimides by the incorporation of aliphatic cyclohexane into two phthalic anhydrides, which introduced an alicyclic structure without sacrificing the reactivity of the monomers.^[2] Furthermore, poly(ether imide)s (PEIs) based on bis(ether anhydride)s decrease the T_g due to the introduction of flexible ether linkage, while poly(ester imide)s (PEIs) achieved higher T_g and lower water absorption (W_A) *etc.*, owing to some intermolecular interactions between the ester C=O groups in addition to the imide C=O/imide C=O interactions, which was widely used in electronic devices such as integrated circuits.

Therefore, the PEIs derived from *trans/cis*-1,4-cyclohexylene bis(trimellitate anhydride) (TACH) would be a best strategy to obtain combined excellent properties. The existence of ester group would remain the excellent properties of poly(ester imide)s, such as high T_g and low W_A , while introduced aliphatic cyclohexane could also enhance the optical transmittance in the visible light region. The resulting polyimide films showed higher T_g , lower coloration with cut-off wavelength of 318-369 nm, and exhibited good mechanical properties with tensile strengths of 50-90 MPa, tensile moduli of 2.2-3.9 GPa and elongations to break of 2.9-5.8%.



Scheme 1. Polyimides derived from dianhydride TACH

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Dilute solution properties of polyetherimide via hydrodynamics study

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Polyheteroarylenes possess good mechanical properties, may be used at high temperatures, and have high interchain-interaction energies. Moreover, the optimum equilibrium chain rigidity may be reached if the chemical structure of the chain of a cycle-containing polymer is consciously chosen and various bridge elements are inserted into repeat unit of the chain. An optimally tuned chain rigidity combined with strong intermolecular interactions makes it possible to use polyheteroarylenes as a basis for preparing polymeric materials with required properties. It is well known, that a substantial drawback of commercial polyheteroarylenes is their poor processability, which is due to both a narrow interval between the softening temperature and the onset temperature of thermo-oxidative degradation and their insolubility in organic solvents. The development of thermally and chemically stable polyheteroarylenes soluble in organic solvents is a topical task of polymer science. One of the approaches to the synthesis of such soluble polyheteroarylenes as polyetherimides (PEIs) is the polycondensation of multinuclear dianhydrides of tetracarboxylic acids and diamines in solutions of an amide solvent such as N-methyl-2-pyrrolidone (MP) followed by thermal imidization (in a solution or the solid state) of the resulting poly(amic acid). Systematic data on the molecular characteristics of both polymer precursors (polyamic acids) and polyimides formed from them are scarce.

Of great interest are investigations of hydrodynamic, molecular, and conformational characteristics of PEIs synthesized through this method, because they provide valuable information about the formation and transformation of macromolecules during the synthesis. The goals of the present study are to perform a complex investigation of the properties of soluble polyetherimides via the methods of molecular hydrodynamics, to estimate molecular masses of the samples, to establish scaling ratios relating hydrodynamic characteristics to molecular mass, and to determine conformational characteristics of their molecular chains. The investigation was carried out on a sufficiently big number of PEI samples for precise determination of hydrodynamic characteristics. According to the sedimentation–diffusion analysis, the molecular masses of the samples are in the range $(5 - 65) \times 10^3$ g/mol. Scaling ratios relating hydrodynamic characteristics to molecular masses are ascertained, and the conformational characteristics of polyetherimide molecular chains are determined. The statistical segment calculated from the translational- and rotational-friction data is 2.7 ± 0.7 nm. A comparison of this value with the statistical segment calculated for freely jointed chains yields to a rotation-hindrance parameter of 1.16. Note that this study was devoted to a rare type of macromolecules, for which the statistical segment is shorter than the chain repeating unit, a circumstance that is explained by the presence of a large number of hinged elements in the chain repeating unit. Special attention was paid to investigation of differences/peculiarities in hydrodynamic characteristics of samples with different heat treatment.

Preparation and characterization of transparent polyimide hybrid films with low thermal expansion coefficient

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In recent years, the flexible electronics, such as rollable and bendable liquid crystal display (LCD), organic light-emitting diodes (OLED) as well as the thin solar film panels, have received much attention due to their potential for the fabrication of the light weight and ultra-thin devices. The flexible polymeric films, such as PET, PEN, PC, PES and PI, are very promising materials to be the substrates in the flexible devices with advantageous of transparency, light weight, flexibility, robustness, low cost and suitable for mass production *via* roll-to-roll processes [1]. In our previous work, a series of semi-aromatic polyimide films were successfully prepared based on fluorinated aromatic diamines and alicyclic dianhydrides [2]. These polyimide films not only exhibited the high thermal stabilities with the glass transition temperature over 300°C, but also showed good optical properties with the transmittances higher than 90% in the visible range. However, one of the great disadvantages of the semi-aromatic polyimide films is their high coefficient of thermal expansion (CTE), which are not sufficient to satisfy the demands of flexible devices [3].

In this work, a series of transparent polyimide hybrid films were prepared by incorporation of silica with different silica content in the semi-aromatic polyimide matrix. The effects of silica species, hybrid methods as well as silica contents on the optical, thermal and mechanical properties of the polyimide hybrid films were investigated. The results indicated that these hybrid films exhibited good thermal and mechanical properties. The thermal expansion coefficient (CTE) of polyimide hybrid films decreases dramatically with the increase of silica content. The polyimide hybrid film with the silica content of 40% gave the in-plane CTE in the range of 50-200°C as low as 28 ppm/°C, which was only half of the value for pure polyimide film. The optical properties of these polyimide hybrid films could be maintained after addition of silica. The transmittance of polyimide hybrid films was over 80% at 500 nm as the silica content as high as 40%, which is attributed to the homogenous dispersion of silica nano particles in the polyimide matrix.

Table 1. Physical properties of PI/SiO₂ films

	T _g (°C)	T _s (MPa)	Y _M (GPa)	CTE (ppm/°C)
PI	384	102	3.1	56
PI/SiO ₂ -5%	385	112	2.8	48
PI/SiO ₂ -10%	385	111	3.0	46
PI/SiO ₂ -20%	387	99	3.3	41
PI/SiO ₂ -30%	380	93	3.8	32
PI/SiO ₂ -40%	384	64	3.5	28

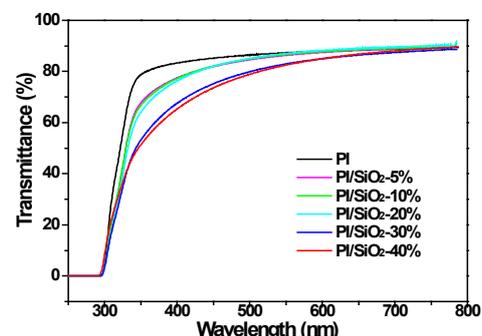


Fig. 1. UV-visible spectra of PI/SiO₂ films

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Microwave synthesis of the polyfluorenes. OLEDs with stable blue electroluminescence

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Polyfluorenes (PF) are one of the best polymers for OLEDs due to high fluorescent quantum yields, easy syntheses and structure modification, good solubility in common organic solvents and acceptable charge mobility [1]. The most common method for PF preparation is the Suzuki polycondensation. This method have significant disadvantage. It's very long-continued. One spend 72 h for PF synthesis. In present work microwave synthesis of the PF was developed. Reaction was carried out in THF/2M K₂CO₃ mixture in closed ampoules at 120-130 °C. The CEM Discover SP microwave reactor was used. It was found that for the synthesis of PF with high MW it is necessary about 40-50 min using insoluble Pd polymer bound catalyst and 15-20 min using soluble Pd(0)[PPh₃]₄. The application of the insoluble Pd polymer bound catalyst allows us to minimize catalyst poisoning of the polymer.

The microwave synthesis was used for the preparation of a number of PFs (Fig. 1). To improve color stability 1,4-dibromo-2,5-difluorobenzene(33 mol %) was added to the main chain of the PF, according to the literature [2]. All samples demonstrate good spectral stability under heating to 180 °C. The naphthalimide component attached to carbazole (NI, Fig. 1) at the quantity of 0.25 mol % highly increase the luminescence intensity of PFs. The effect from hole transport agents T-1 and T-2 (Fig. 1) was analyzed. The best result was demonstrated at the sample with T-1 agent at the quantity of 16.75 mol %: electroluminescence intensity was 2830 cd/m², CIE x=0.168, y=0.228.

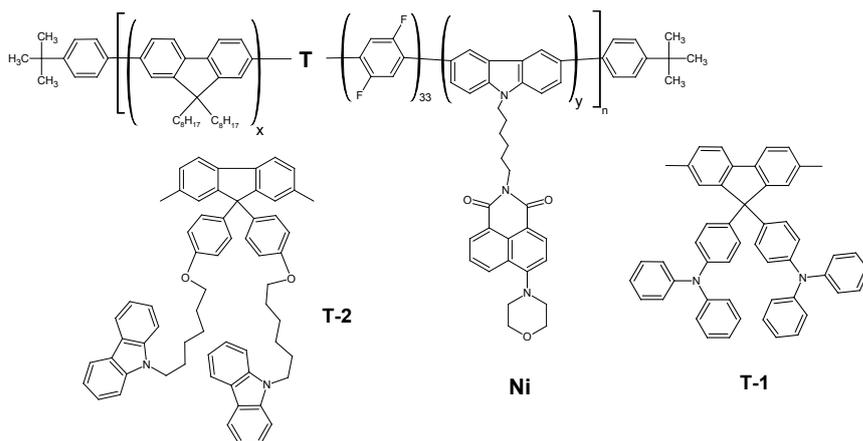


Fig. 1. Chemical structure of the PF under study

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Biobased monomers from the furanic platform in polyesters

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The last ten years, with the development of bio-based polymers, furanics derivatives received an increasing interest. Among all monomers from the furanic platform, 2,5-furandicarboxylic acid (FDCA) is widely studied and is becoming an industrial reality to substitute petrochemical terephthalic acid. Moreover, in addition of being biobased, the furanic counterpart of terephthalic polyester show some improved properties. As an example poly(ethylene furanoate) (PEF) displays higher heat resistance (T_g) and barrier properties than conventional PET [1].

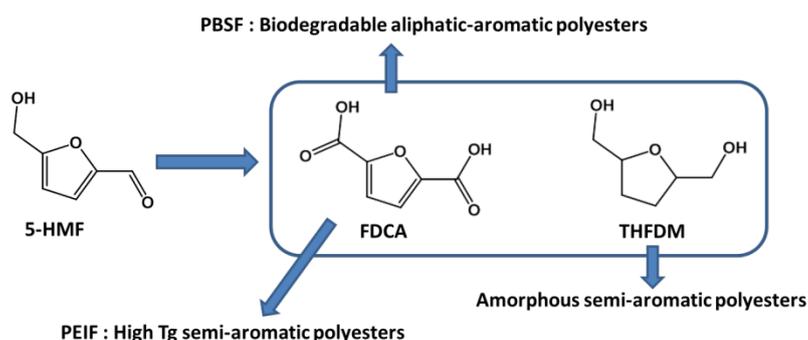


Fig. 1. Polyesters from the furanic platform;

The use of FDCA derivatives was studied in different kind of polyesters. As an example, amorphous semi-aromatic polyesters with improved heat resistance were obtained when FDCA was polymerized with ethylene glycol and isosorbide (PEIF) [2]. Also some biodegradable PBAT-like aliphatic-aromatic polyesters have been obtained by copolymerization of FDCA in poly(butylene succinate) in order to obtain a fully bio-based polymer (PBSF) [3; 4].

Other furanic derivatives, such as the tetrahydrofuran dimethanol (THFDM), have also been investigated as a potential bio-based substitute of cyclohexane dimethanol. Thus, some bio-based PET_g-like amorphous polymers have been synthesised. [5; 6]

Reference

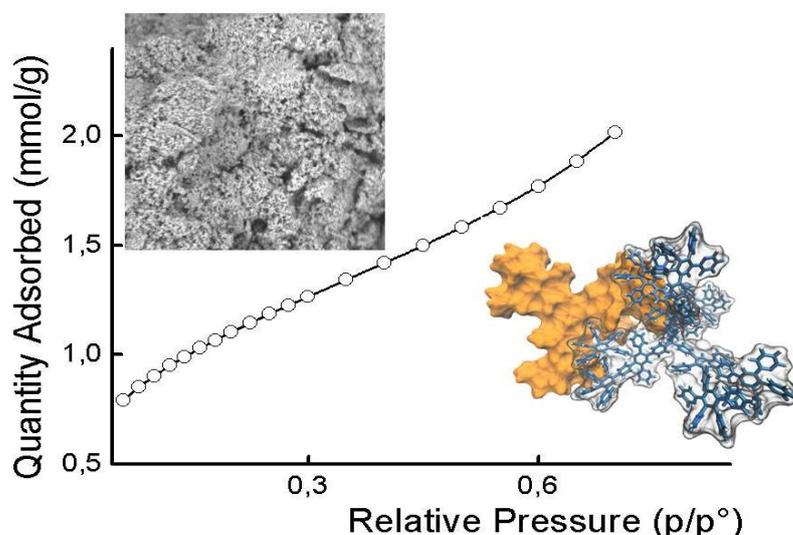
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Surface properties of pyridylphenylene dendrimers

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Research on the dendrimers is still one the hottest field in the macromolecular chemistry. Solvent accessibility of the dendrimer voids, the directed molecular design of the dendrimers allowing the chemical modifications their interior and periphery, provide the approach to the chemical sensor development. In spite of progress in development of dendrimer modified sorbents, the information on specific surface area of dendrimers in solid state is very limited. Here, we present our contribution in this field focusing on the study of sorption processes, the surface properties of pyridylphenylene dendrimers. According to theoretical assessments, the specific surface area of these dendrimers can reach several thousands square meters per 1 g of the substance. The specific surface areas of dendrimers defined with traditional methods for adsorption analysis are not exceeded 100 m²/g. *A priori* developed surface of dendrimers is inactive for physical adsorption. It was supposed the approach which is based on considering the surface properties of dendrimers as the sum of the molecular surfaces of individual particles is incorrect and does not describe their actual surface area.



The dendrimer macromolecule is not able to hold the adsorbate because of weak disperse interactions both with inner and outer surfaces. In case of chemisorption, the presence nitrogen atoms in dendrimers as active sorption centers allows an effective adsorption. One more issue which can influence the sorption characteristics of dendrimers is their packing density. This might be primary cause to promote the non-micropore surface formation for dendrimers of small generations.

This work was supported by Russian Science Foundation (RSF), grant no.15-13-30026.

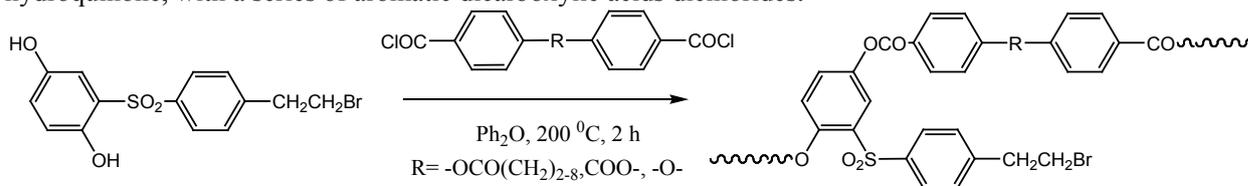
Multicenter polyester initiators for preparation of graft copolymers with oligo(2-ethyl-2-oxazoline) side chains

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Molecular brushes are linear macromolecules with pendant polymer side chains at high grafting densities. The side chain crowding leads to a strong stretching of both backbone and the polymer side chains that makes the entire molecular brush adopt an entropically unfavourable elongated cylindrical or worm-like shape. Due to their unique structure, molecular brushes exhibit some novel properties and are being discussed for potential implementation as sensors, elastomers as well as unimolecular templates for nanowires. The application of a wide range of available functional initiators for the cationic ring opening polymerization (CROP) of 2-oxazolines enables the straightforward synthesis of comb and graft copolymers containing thermoresponsive polyoxazolines as side chains of several polymeric backbones, such as PS or poly(methacrylates) [1]. Far less data are available regarding the synthesis of polymer brushes with other backbones, e.g., polyester ones. Polyester type macroinitiators for ring-opening cationic polymerization of oxazolines were prepared by high temperature polycondensation of specially designed monomer - 2-(4-(2-bromoethyl) phenylsulfonyl hydroquinone, with a series of aromatic dicarboxylic acids dichlorides.



Their liquid crystalline and molecular weight characteristics as well as Khun segments were defined. It was found out that these polyesters could be used as the initiators for CROP of 2-ethyl-2-oxazoline. It was shown [2] that such graft-copolymers are able to form aqueous colloid solutions with narrow particle size distribution and have the lower critical solution temperature.

Table. Properties of poly-2-(4-(2-bromoethyl)phenylsulfonyl)arylates

R	$[\eta]$ dl/g, CHCl ₃ , 25°C	M_w 10 ^{-3*}	PDI	Transition temperatures, °C	A_2 , ml/mol, CHCl ₃ , 25°C
(CH ₂) ₂	0.20	18	2.2	S-155-LC-200-I	0,06
(CH ₂) ₃	0.18	17	2.3	S-110-LC-115-I	0,04
(CH ₂) ₄	0.24	23	2.2	S-125-LC-205-I	0,06
(CH ₂) ₅	0.21	20	2.1	S-105-LC-125-I	0,05
(CH ₂) ₆	0.20	19	2.3	S-75-LC-145-I	0,06
(CH ₂) ₇	0.22	20	2.4	S-95-LC-110-I	0,05
(CH ₂) ₈	0.19	18	2.2	S-104-LC-150-I	0,04
O	0.38	27	1.9	220	0.09

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The hydrodynamic properties of hyperbranched pyridylphenylene polymer solutions

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Steady interest in the synthesis and investigation of branched polymers (BPs) is related to the unique architecture, as well as the potentialities inherent in their surface modification using various functional groups. This is why (BPs) find numerous applications in technological processes. Also there are obvious advantages of such macromolecules over dendrimers (another branched molecule, which is monodisperse in regard to both size and structure), viz the facile synthesis and relatively low cost of final product. Furthermore BPs possess higher solubility and lower viscosity, than linear polymers of analogous structure.

Recently the $A_6 + B_2$ approach has been proposed to the synthesizing of hyperbranched pyridylphenylene polymers using Diels-Alder polycycloaddition of the first-generation, six-functional pyridine-phenylene dendrimer (A_6) and the aromatic bis(cyclopenta-dienone)s (B_2) [1]. The newly synthesized samples were studied in present work and their conformational and optical characteristics were obtained. The study has been accomplished using the unique combination of molecular hydrodynamics and optical methods viz viscometry, densitometry, velocity sedimentation, dynamic light scattering and flow birefringence. The gathered data have been thoroughly analyzed and its self-consistency was demonstrated. On the basis of hydrodynamic data the conclusions on conformational parameters were formulated. Furthermore, the conformational comparison of synthesized sample series was carried out considering the initial synthesis conditions.

Moreover computer simulation of studied samples was conducted with HYDRO software and conformational parameters were calculated for two limiting cases (first, sphere and, second, rod model) [2]. The simulation results were compared with experimental data.

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Amphiphilic diblock copolymers based on poly(3-hexylthiophene)

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Conductive polymers have attained much research interests as an alternative to inorganic semiconductors for a range of applications due to their excellent optoelectronic properties. Their electric and optical properties are highly dependent on their self-assembled structures. Therefore, understanding their nanometer scale morphology is essential for creating new materials. Among the solution processable conjugated polymers, poly(3-hexylthiophene) (P3HT) has been one of the most studied semiconducting polymers because of their high hole mobility.

For the past decades, there are considerable researches for polymer thin film techniques. However, typical thin films of P3HT has many grain boundaries and defects, that hamper efficient charge transport. In place of thin film study, solution-phase self-assembly of conjugated amphiphilic polymers is emerging as an alternative method. P3HTs are usually formed into nanofiber due to their strong π - π interaction, whereas the nature of amphiphilic polymers lets them self-assemble into various nanostructures. This interesting phenomenon has been studied recently, but it is not yet well understood.

For this reason, we are interested in amphiphilic diblock copolymers containing P3HT. In the previous work, we have found that functionalized P3HT could be synthesized by thiol-ene click reaction. The end group of P3HT was easily transformed into atomic transfer radical polymerization (ATRP) initiating sites by using this method. Then we used oligo(ethylene glycol) methacrylate (OEGMA) and 2-(2-methoxyethoxy)ethyl methacrylate (MEO₂MA) as a hydrophilic monomer to make conjugated amphiphilic polymers. Their LCST temperature in water could be changed by monomer ratio of OEGMA and MEO₂MA and they formed a spherical micelle as a self-assembled structure in water. During the analysis of the heated aqueous solution, micelles were aggregated each other to stabilize the whole structure. The polymer solution which had low molecular weight of P3HT also exhibited color change during heating in water. The blue shift of the maximum wavelength of P3HT and decrease of shoulder at 610 nm proved disruption of packing of P3HT by aggregation.



Optimization of the macromolecular design for enhancing of bulk conductivity and electrochemical stability of poly(ionic liquid)s

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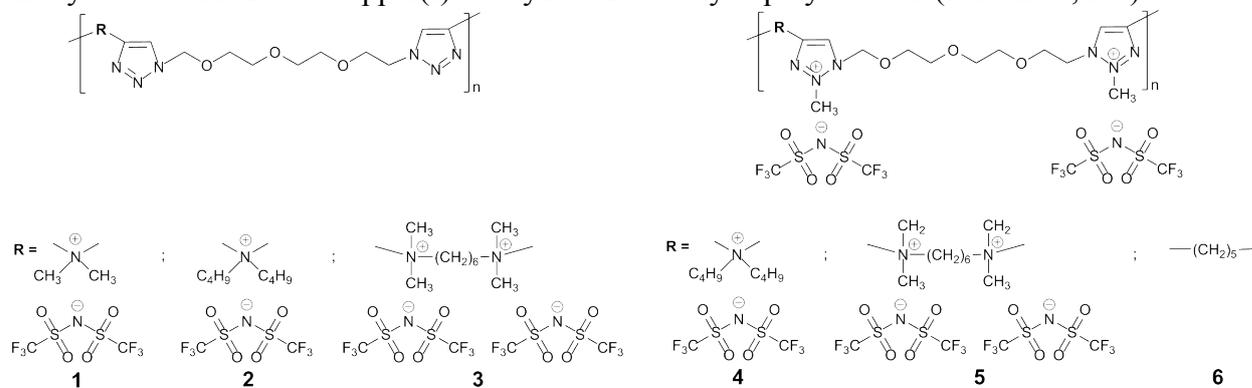
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The scientific interest in the materials based on poly(ionic liquid)s (PILs) has gradually increased over the last decades [1]. PILs represent a special class of polyelectrolytes that ideally combine the beneficial properties of ionic liquids (ILs) with those of polymers and thus exhibit desired properties such as tunable solubility, high ionic conductivity (σ_{DC}), high (electro)chemical and thermal stabilities, as well as film forming and processing capacities. While PILs are usually accessed by chain growth polymerization of IL monomers or by post-polymerization chemical modification of neutral precursors [2], the polycondensation is rarely used for their preparation. Thus, the purpose of this study was to design the new monomers for the synthesis of PILs via copper(I)-catalyzed azide-alkyne polyaddition (Scheme 1, **1-6**).



Scheme 1.

PILs polyelectrolytes bearing from one (1,2) up to four cations (5) in a repeating unit have been developed (Scheme 1). Moreover, as a rare example, some of PILs (4,5) possessed both ammonium and 1,2,3-triazolium cations. Their physical, ion conducting and electrochemical properties were studied in detail. While the presence of ammonium cations tend to decrease polyelectrolyte's bulk conductivity, the quaternization of 1,2,3-triazoles led to its enhancement. Among synthesized series, PIL 6 showed the highest σ_{DC} equal to $1.6 \times 10^{-5} \text{ S/cm}$ at 25°C along with lowest T_g (-32.3°C). Finally, the newly prepared PILs demonstrated wide electrochemical stability with the maximum reaching 4.1 V vs. Li^+/Li .

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Thermoreversible conversion between macrocycle and linear oligomers

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Hexakis(m-phenyleneimine) macrocycle (**Cm6**) (**Figure 1**) was formed quantitatively from AB-type monomer based on π -stacked precipitation-driven cyclization of linear oligomers and dynamic covalent chemistry (DCC, imine metathesis). Mutual conversion between the macrocycle and the soluble linear oligomers by a heat stimulus was observed in water-containing organic solvent such as THF, and collapse-regeneration of the macrocycle was a thermoreversible process. A proposed mechanism is illustrated in **Figure 2**. The regeneration rate was dramatically accelerated by the addition of a small amount of the macrocycle, which implies a self-replication and a self-healing on the template. In this presentation, the synthetic method and the characterization will be reported.

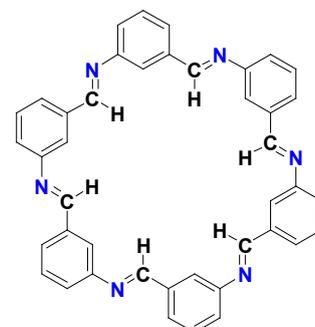


Figure 1. *Hexakis(m-phenyleneimine)* macrocycle (**Cm6**)

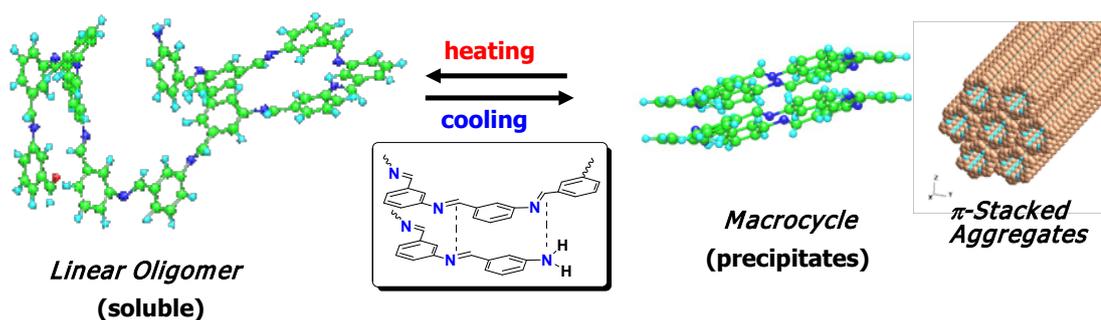


Figure 2. Possible mechanism for thermoreversible conversion of macrocycle (**Cm6**) and the linear oligomers.

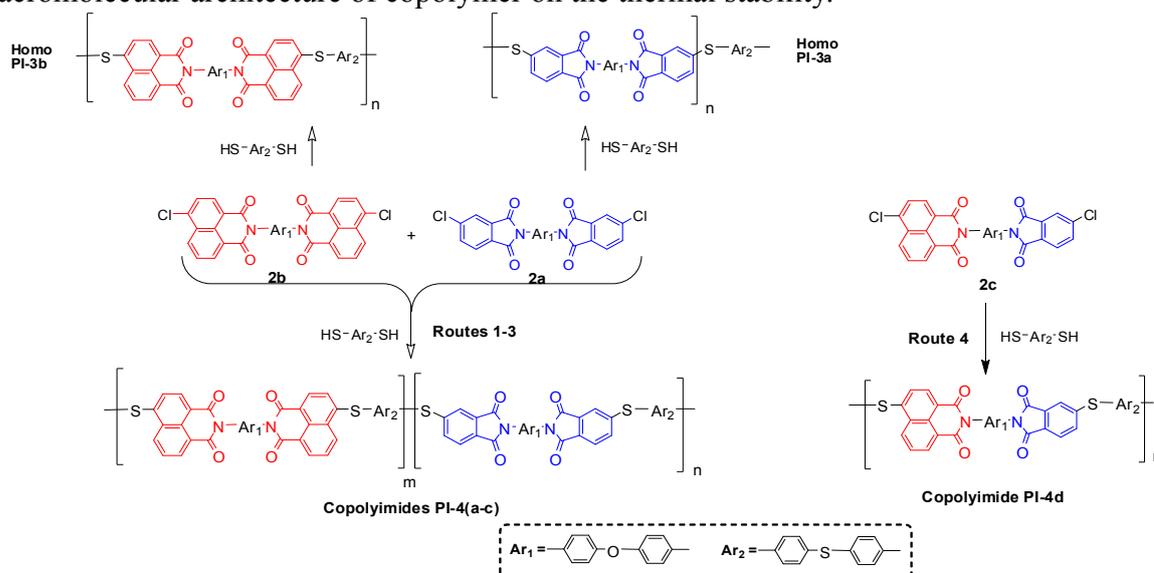
Different macromolecular architectures of poly(phthalimide-co-naphthalimide)s by controlling relative reactivity of monomers

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Aromatic polyimides represent an important class of high performance polymer materials in various applications such as gas separation membranes, adhesives, coatings, composite matrices, optoelectronic and aerospace. Polyphthalimides possess excellent processability and solubility in organic solvents, while polynaphthalimides display superior thermal properties, hydrolytic stability and fire resistance [1,2]. To investigate and integrate the excellent properties of naphthalimide and phthalimide, different molecular architectures (homo, random and block) polymers were synthesized by aromatic nucleophilic substitution polymerization. Three different bischloro-imide monomers [bischlorophthalimide **2a**, bischloronaphthalimide **2b**, bischloro (naphthalimide-phthalimide) **2c**] were prepared and reacted with 4,4'-thiobisbenzenethiol by different synthetic routes, to synthesize homo **3a-b**, block **4a** and random (**4c-d**) copolyimides (Scheme 1). For studying molecular architecture of polymers, the relative reactivity of bischloro-imide monomers (**2a-b**) was examined by gas chromatography mass spectrometry (GC-MS) using model compounds *N*-phenyl-4-chloro-1,8-naphthalimide and *N*-phenyl-4-chlorophthalimide. In comparison with homopolyimides **3a-b**, naphthalimide-phthalimide based copolyimides **4b-d** demonstrated good solubility in aprotic solvents and better mechanical properties. These polymers exhibited high glass transition temperature (T_g) of 198-319°C and good thermal stability based on 5% weight loss temperature ($T_{5\%}$) of 492-524 and 480-531 °C in nitrogen and air, respectively. In addition, thermal degradation kinetics of random **4b** and block **4a** copolymers in inert (flowing nitrogen) atmosphere is studied, to investigate the effects of macromolecular architecture of copolymer on the thermal stability.



Scheme 1. Synthesis of homo **3a-b** and copolyimides **4a-d** by different synthetic routes

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Molecular dynamics simulations of uniaxial deformation of thermoplastic polyimides

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The results of atomistic molecular-dynamics simulations of mechanical properties of heterocyclic polymer subjected to uniaxial deformation are reported. A new amorphous thermoplastic polyimide R-BAPO with a repeat unit consisting of dianhydride 1,3-bis-(3',4'-dicarboxyphenoxy)benzene (dianhydride R) and diamine 4,4'-bis-(4'-aminophenoxy)diphenyloxide (diamine BAPO) was chosen for the simulations. Our primary goal was to establish the impact of various factors (method of sample preparation, molecular mass, and cooling and deformation rates) on the elasticity modulus. In particular, we found that the elasticity modulus was only slightly affected by the degree of equilibration, the molecular mass and the size of the simulation box. This is most likely due to the fact that the main contribution to the elasticity modulus is from processes on scales smaller than the entanglement length. Essentially, our simulations reproduce the logarithmic dependence of the elasticity modulus on cooling and deformation rates, which is normally observing in experiments. On the base of the temperature dependence analysis of the elasticity modulus we determined the flow temperature of R-BAPO to be 580 K in line with the experimental data available. Furthermore, we found that the application of high external pressure to the polymer sample during uniaxial deformation can improve the mechanical properties of the polyimide. Overall, the results of our simulations clearly demonstrate that atomistic molecular-dynamics simulations represent a powerful and accurate tool for studying the mechanical properties of heterocyclic polymers and can therefore be useful for the virtual design of new materials, thereby supporting cost-effective synthesis and experimental research.

The study was carried out with the financial support of the Ministry of Education and Science of the Russian Federation under the Contract no. 14.Z50.31.0002 (Megagrant of the Government of the Russian Federation according to the Resolution no. 220 of April 9, 2010). All simulations have been performed using the computational resources of the Institute of Macromolecular Compounds, Russian Academy of Sciences, Chebyshev and Lomonosov supercomputers at Moscow State University, and computational resources of MCC NRC "Kurchatov Institute".

Conductive Properties of a Polystyrene Composite Films with Covalently Linked Graphene Oxide

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We report on polymer composite with embedded graphene and multilayer graphene flakes, which exhibit a current-voltage characteristic of Josephson type up to $T = 300$ K. In the present study, we have investigated the conductivity of polystyrene synthesized simultaneously with modified oxide graphene flakes (GF) [1]. Single and multilayer GF have been obtained from an aqueous suspension of graphene oxide [2]. The length of the individual GF attained several microns, and their transverse dimensions were several hundred nm. Surface modification of the GF was carried out for subsequent reaction with styrene. Details of synthesis of composite can be found in [1]. As a result of this polymerization, a composite was obtained in which all components appear to be linked by covalent bonds. In the polymer composite (PC), the distance between the individual GF was several tenths of a millimetre. PC films were deposited on polished metal electrodes from toluene solution. After a short time drying at 70°C , the second electrode, was placed in contact with the free polymer surface under slight mechanical pressure (less than 1 kg/cm^2). The thicknesses of the PC films varied from a hundred nm to a few microns. Current-voltage characteristic (CVC) measurements were performed by using the two-probe method. The experiment showed that when the thickness of a PC is more than 500 nm in superconductor-PC-superconductor (S-PC-S) structures, metallic conductivity is observed, with a finite resistance at low temperatures. With decreasing film thickness of the PC, down to 200-300 nm, a Josephson type of CVC was observed for S-PC-S structures (Figure 1).

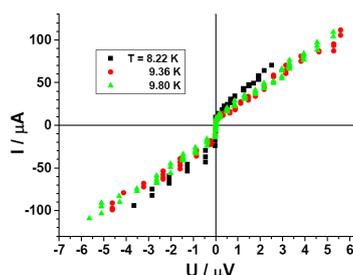


Fig. 1. Josephson CVC of Nb-PC-Nb construction with PC film-thickness about 150 nm

The most interesting observation was the fact that the Josephson type CVC did not disappear at $T \geq T_C$, i.e. when the electrodes transitioned to the normal state ($T_{C, \text{Nb}} = 9.3\text{ K}$) [3]. The occurrence of superconductivity in the PC may be due to the fact that GF are exposed to various deformation stresses due to the different thermal expansion coefficients of polystyrene and graphene. In this case, there is a probability of occurrence of superconductivity under the scenario suggested by the above theoretical works [4, 5].

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Surface and morphological investigation of synthesized nanostructured ridges from electrospun polyvinyl alcohol – egg albumin blend using atomic force microscopy

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Synthesized electrospun Polyvinyl Alcohol – Egg Albumin (PVA-EA) composite has been characterized as what we call “nanoridges”, long narrow elevation from the flat substrate (Fig. 1) –different from our previously reported study on PVA Gelatin blend in which nanofibers are observed [1,2]. Prior studies on electrospun PVA-EA blends claim to produce nanofiber morphology [3, 4]; we hypothesize that it is the solvent changes on the solution that developed such morphology on this study. On the characterization of general surface topology, formations of valleys are predominant as all skewness values are positive and most of the profiles are largely sharp with excess kurtosis values $k > 0$. The surface has non-Gaussian distribution and is similar with the typical kurtosis and skewness envelope values of materials that had undergone turning, shaping, or electrodischarge machining processes. We also analyzed the effect of solution and processing parameters on the surface characteristics and the ridge curvature using Taguchi method. Processing parameter flow rate predominantly affected ridge height and root mean square (RMS) roughness, and tip-to-collector distance greatly influenced the curvature and RMS roughness of the material; solution parameter PVA-EA ratio affected the ridge height of the material.

Evaluation of surface and morphological response to its solution and processing parameters can provide insight on the control of production, in which the novel morphology of electrospun PVA-EA composite could be used in vast areas of applications from organic electronics to scaffolds for tissue engineering.

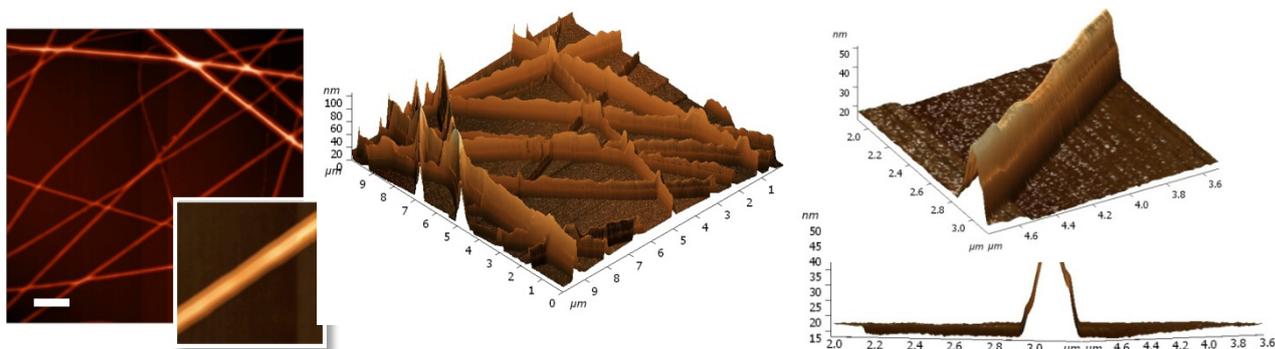


Fig. 1. Sample synthesized from run #8. Left pane: 2D AFM rendered image (inset figure: single ridge micrograph). Center pane: 3D AFM micrographs. Right pane: (upper) 3D isometric view and (lower) front view of a single ridge. Scale bar = 1 μm .

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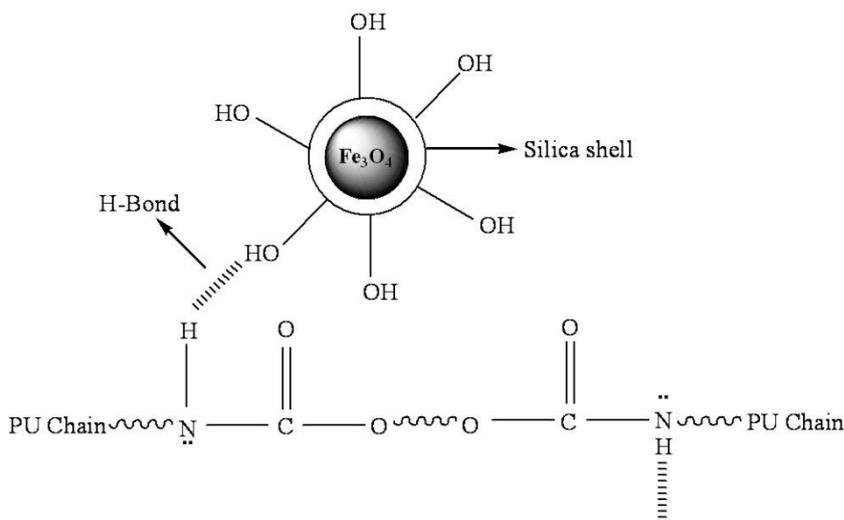
Novel polyurethane flexible foam/modified iron oxide nanocomposites

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Novel magnetic polyurethane flexible foam nanocomposites were synthesized by incorporation of modified magnetic iron oxide nanoparticles into polyurethane flexible foam (Scheme 1). Magnetic nanoparticles (MNPs) of $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ were synthesized *via* coprecipitation and sol-gel methods, respectively. The prepared nanocomposites were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), vibrating sample magnetometry (VSM), thermo-mechanical analysis (TMA), and thermogravimetric analysis (TGA). The magnetic core-shell NPs were used with different percentages in the foam formulation and the optimum amount of the nano structures in the foam formulation was defined.



Scheme 1. Formation of PU flexible foam nanocomposites

Synthesis of conjugated polymers by Stille coupling of semifluorinated thiophenes

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The importance of organic electronics increased remarkably in the last years due to the fact that processing is much more easier than in conventional silica-based electronics and the resulting parts are flexible. Techniques like roll-to-roll or printing can be applied because the organic materials are solution processable. Also here, the semiconductor is the base material of the device. Organic electronics requires organic (polymeric) semiconductors with good processability, high stability and high charge carrier mobility. Substituted poly(thiophene)s play an important role because the electronic properties are tunable by the substituent. Self-organization in the semiconductor layer has been shown to improve the charge carrier mobility [1], while fluorine atoms lower both HOMO and LUMO energy levels and improve the stability against oxygen [2]. Therefore, the influence of self-organizing semifluorinated side chains on the properties of poly(thiophene) semiconductors are studied.

In the present work, poly(thiophene) copolymers with semifluorinated side chains were synthesized because of the well-known property of semifluorinated chains to self-assemble into highly ordered layered structures [3]. The polycondensations were carried out by Stille coupling with two equivalents of 2,5-bis(trimethylstannyl)thiophene as a linking agent, one eq. of 3-hexylthiophene, and one eq. of 11,11,12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,20,20-henicosafluoreicosane-1-ole (semifluorinated thiophene) (Fig. 1). The polymers show strong X-ray reflections indicating the formation of self-organized layered structures both in bulk as in thin films. These structures may raise the charge carrier mobility (which will be addressed in future works).

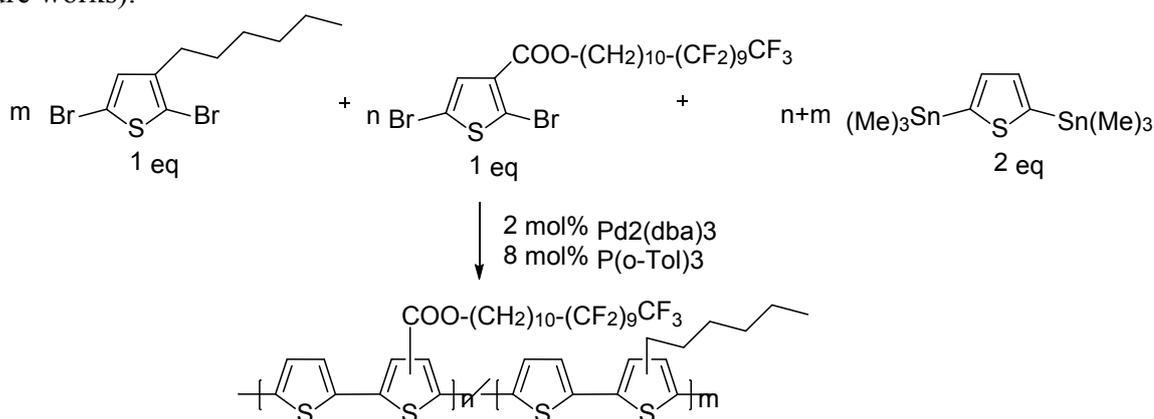


Figure 1. Polycondensation of semifluorinated thiophenes

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Synthesis and using oforgano soluble(co)polyimides in optical fibrescoatings production

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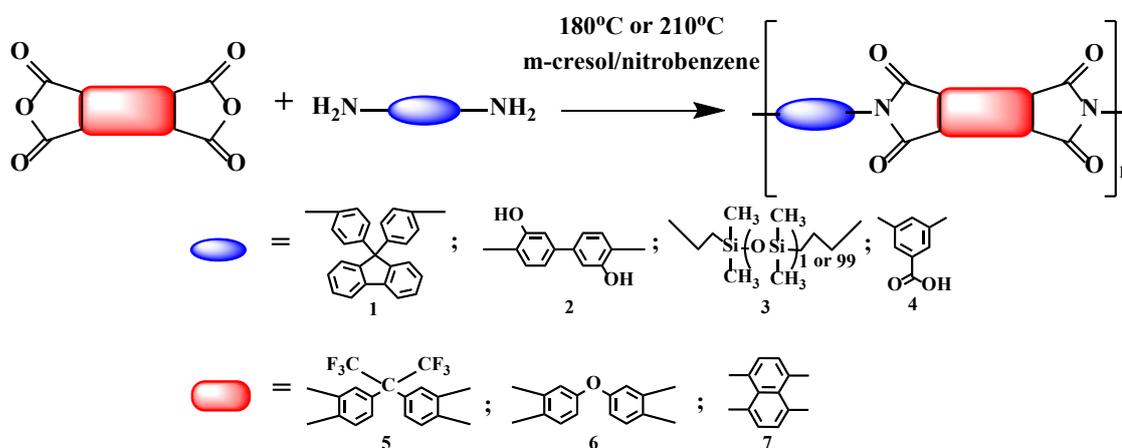
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Polyimide (PI) coatings of optical fibers have several advantages over the conventional polyacrylates and other polymers, namely, high strength and thermal properties, resistance to aggressive environment. Traditionally the formation of polyimide coating is based on the use of hydrolytically and thermally unstable precursor – poly(amic acid) (PAA), which undergo imidisation after the coating process. This is accompanied by a number of drawbacks including difficulty of PAA complete cyclization, several solution deposition cycles, storage of PAA solution at reduced temperatures, etc. The aim of this work is the synthesis of organosoluble cardo (co)polyimides and their use in the coatings formulation, which allows to eliminate utilization of unstable PAA and its further cyclization.

Cardo (co)polyimides with presented structures (**Scheme 1**) have been synthesized and their varnishes in different organic solvents have been applied to produce optical fiber coatings.



Scheme 1.

Obtained polymers have high molecular weights ($\eta_{inh} = 0.4 \div 1.8$ dL/g) and improved thermal characteristics: $315^\circ\text{C} < T_g < 390^\circ\text{C}$; $420^\circ\text{C} < T_{10\%} < 580^\circ\text{C}$ (in air). Casted films have high tensile strength ($60 \div 140$ MPa) and modulus ($1100 \div 2300$ MPa).

The following parameters influencing on the coatings quality have been estimated: polyimide structure, molecular weight and properties, nature of the solvent, drawing technological parameters, the viscosity of the polymer solution, etc. It was found that copolyimides bearing side hydroxyl and carboxyl groups formulate the coatings with good adhesion in the absence of coupling agent. The fibers with elaborated PI coatings have high thermal stability. For some of them 10% reduction of the fiber's bending strength takes place only after heating for 72 h at $250 - 300^\circ\text{C}$. Moreover strength of the fibres didn't change after 14 days water treatment.

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Hyperbranched polypyridylphenylenes: synthesis and templating of metal nanoparticles

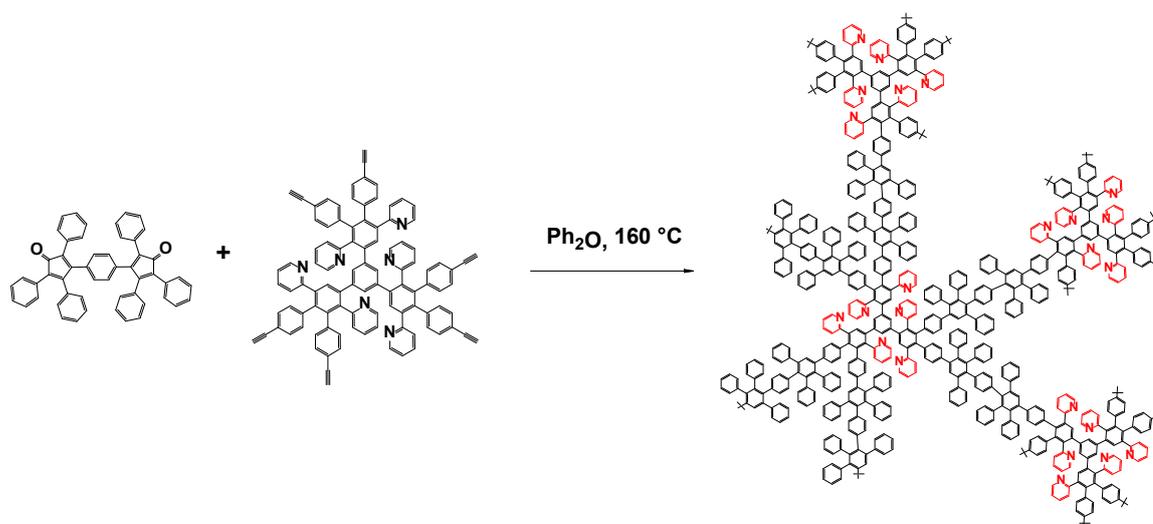
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Hyperbranched polymers are highly branched macromolecules, which are characterized by low viscosity, high solubility compared to that of linear polymers, a generous amount of terminal functional groups. Here the synthesis of novel hyperbranched polypyridylphenylenes through the Diels-Alder cycloaddition is presented. The first generation pyridylphenylene dendrimer with six ethynyl functionalities was used as a monomer A6 while the different phenylsubstituted bicyclopentadienones acted as B2 monomers in polymer synthesis [1]. The detailed analysis of reaction condition allowed us control the structure and molecular weight of the polymers. To prove the polymer structure the ¹H and inverse-gated decoupling ¹³C nuclear magnetic resonance spectroscopy was successfully applied.



The example of hyperbranched pyridylphenylene polymer

The polymers synthesized were used as templates for encapsulation of metal nanoparticles. As a result new magnetically separable catalysts based on iron oxide and ZnO nanoparticles were developed. The STEM EDS mapping and TEM have been carried out to assess the composition and morphology of nanoparticles formed. The nanocomposites were tested in methanol synthesis from syngas.

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Grafting of 1,2,3-triazolium-based poly(ionic liquid)s on ionic polyimide as an approach for conductive and flexible films

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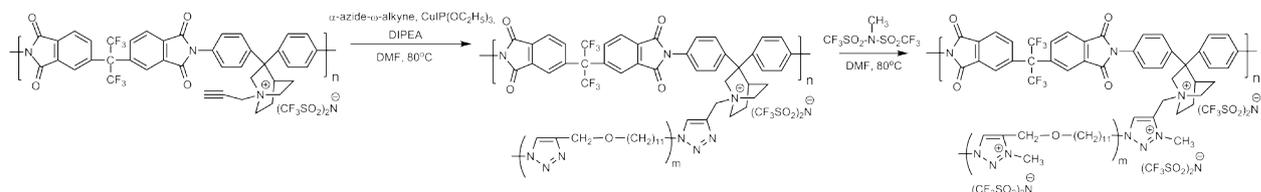
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The application of ionic liquids chemistry to the macromolecular synthesis resulted in the appearance of a new intriguing subclass of polyelectrolytes, namely poly(ionic liquid)s (PILs). Nowadays the maximum conductivity measured in dry conditions for thoroughly purified high molecular weight PILs is around 3×10^{-5} S/cm at 25°C [1]. At this, as a general trend, linear relationship between the polymer T_g and its bulk ionic conductivity was established, clearly stating that PILs with higher ionic conductivity showed the lowest T_g , i.e. represented gummy like materials at r.t. Thus, this trend prevents the implementation of linear PILs in such intriguing area as creation of all-solid-state artificial muscles, where the polyelectrolyte is awaiting to demonstrate both high conductivity and excellent mechanical properties. To overcome this problem the synthesis of ionically conductive polymer films with high stretchability and good elasticity is suggested by grafting of poly(1,2,3-triazole) by straightforward polyaddition of α -azide- ω -alkyne monomer onto polyimide's side propargyl chain, followed by direct quaternization with N-methyl bis(trifluoromethylsulfonyl)imide (Scheme 1).



Scheme 1.

The suggested approach allows for simultaneous imparting of high ionic conductivity (3.0×10^{-6} S/cm at 25°C) and excellent mechanical properties (tensile strength up to 2260 kPa, elongation up to 120%) to a single high MM ($M_n = 96500$, $M_w/M_n = 1.74$) polymer material.

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Bisphenol-A-formaldehyde sols: preparation, structure, and properties

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Organic aerogels represent a new class of polymeric foams that are widely used in various branches of science and technology as laser targets, sorbents, model porous media, super condensers, elements of acoustic devices, etc.

It is recognized that formation of chemically cross-linked gels goes through a stage of phase decomposition, which can develop according to colloidal type (particle birth, growth and aggregation into the three-dimensional networks) or polymer type (spinodal decomposition). We have experimentally demonstrated that in super-weak solution (2 mg/ml or less) of resin (BF), obtained during the process of condensation of bisphenol-A and formaldehyde, phase decomposition develops according to the colloidal type. According to the GPC data, BF resin represents an aqueous-alkaline solution of mixture of tetramethylol derivative of bisphenol-A (39.7 % wt), its dimer (19.9%), trimer (14.7%), and tetramer (25.7%) [1]. During the process of curing there have been obtained stable stationary sols having particle size of about 30–40 nm (according to the FE-SEM data). (**Fig.1**)

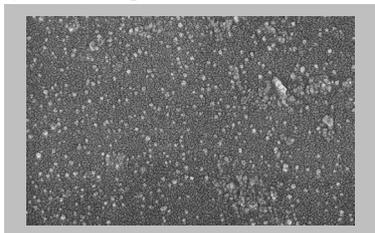


Fig. 1.

Particle sizes were measured by dynamic light scattering methods and by using electron microscopy. The particle sizes, obtained by these independent methods for solutions of equal concentrations and curing time, correlate with each other. Temperature-time intervals of sols forming were determined. The sols are being formed at a temperature from 150°C to 205°C and holding periods from 30 minutes to 9 hours. The peculiarity of the sol formation is a narrow time interval of existence, beyond which the sol almost instantly turns into a gel.

Preparation of organic bisphenol-A -formaldehyde sols opens up broad prospects in the sol-gel technology of organic aerogels for the purposeful formation of their structure and properties using techniques of purification, concentration, fractionation, and completion of growing of the particles up to the desired sizes.

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Structure of lactide-based block copolymers in solution revealed by small-angle x-ray scattering

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It has been shown that biodegradable and biocompatible polylactide (PLA) is one of the most perspective polymers for production of eco-friendly packaging, disposables and a great variety of biomedical products [1]. Stereochemical structure of PLA can be easily modified via control of L- and D-lactide content leading to either amorphous or semi-crystalline material [2]. Block copolymers based on PLA are of special interest. Amphiphilic block copolymers attracted increased attention for decades due to their ability to self-assemble, segregate, and form highly organized structures in solution, on surface, and in bulk [3]. These structures can serve as templates for control of inorganic nanoparticle formation or lead to well-defined hybrid superstructures. Formation of self-assembled nanostructures (micelles) in selective solvents, and in particular in aqueous media, is of special interest due to their possible biomedical applications [4]. Structural variability of the block copolymers in solution is a convenient platform to create materials with well-defined properties. Thus, the understanding of the solution behavior of block copolymers is crucial for control over the structure and properties of the resultant materials.

In the present work small-angle X-ray scattering was used for detailed structural characterization of nanoparticles formed in solution by PLA-based di- and tri-block copolymers. Obtained scattering data have been analyzed by advanced methods of SAXS data interpretation and modeling to design 3D structural models of the di- and tri-block copolymers. Additionally, analysis of the block copolymers capacity to absorb and release bioactive substances allowed us to evaluate the prospects of usage of the block copolymers as drug delivery systems.

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The structure and properties of the hybrid film materials on the basis of the heterocyclic polymers and MQ-resins

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Polyimide silicone polymer hybrid composites consist of aromatic polyimides (PI) of different chemical structure, namely the PM (the condensation product of pyromellitic dianhydride and 4,4'-oxydianiline), PI containing fragments of phenylbenzimidazole (PM-FBZ), PI containing terminated alkyltriethoxysilane groups (PM-APEC), polyamidoimide containing imide, amide groups and free carboxyl groups (PAI) and MQ-resins were synthesized. For the formation of a polyimide-silicone hybrid composites have been used MQ-resins (designed and synthesized in the laboratory of A.M. Muzafarov): MQ-classical Resins $[\text{SiO}_2]_n[\text{R}_3\text{SiO}_{0.5}]_k$, containing alkyl and/or phenyl substituents in the M-link [1], and MQ-copolymers modified by introducing different groups, such as phenyl, silanol or methoxy, vinyl and amine groups, to improve compatibility of imide and silicone components. The results of the investigation of glass transition temperature of the compositions, obtained by DMA method showed the presence of two glass transition temperatures in synthesized hybrid silicone-polyimide composites, it indicated the presence of two phases. Electron microscopy analysis of low temperature fracture surfaces of synthesized films also showed the presence in hybrid composites of two-phases, in which the dispersion phase of PI is filled with dispersed Si-organic reinforcing particles. The size of particles ranges from 1 to 20 microns, depending on the contents of MQ copolymer in composite. It is shown that the formation of the dispersed phase occurs at the stage of preparing film samples during the process of removing the solvent prior to curing. The uniform distribution of silicone component, the best adhesive interaction of the two phases was observed in the dispersion medium of polyimide PM or PAI. The investigation showed that the optimum dispersed phases for improving the compatibility of components in composite were polyphenylsilsesquioxanes with both the silanol groups and bisimide fragments.

It was shown that on the basis of polyimides of different chemical structure and not film-forming MQ-resins were prepared polyimide-silicone film-forming composites containing up to 60 wt.% of organosilicon component. These composites had high thermal stability (τ_5) 480-580°C and 440-510°C in an inert atmosphere and in air. The films had high physical and thermo-mechanical characteristics: (E) 1.5-2.5 GPa, (σ_{br}) 55-140 MPa, (ϵ_{br}) 12- 71%, (T_g) 368-398°C. All film hybrid compositions are suitable for practical use as coatings with high thermo- and thermo-oxidative stability.

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Silica Precursor Hyperbranched Polyethoxysiloxane (PEOS) as PP Additive

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The application of hyperbranched polyethoxysiloxane (PEOS) as a polymer additive gives rise to various novel properties of common polymers. We show how melt modification of isotactic polypropylene (iPP) by PEOS results after the in-situ condensation reaction depending on the reaction conditions, whether in nanocomposites[1] containing homogeneous distributed silica nanoparticle, or, after migration, thin film silica surface layers at the iPP formed component.

PEOS is a liquid silica precursor polymer synthesized by a water and solvent free one-step polycondensation process[2]. Because of temperature stability, up to about 250°C, and high amounts of end groups, molecules can be tailored with regard to compatibility and miscibility with the polymer melt, as well as to the hydrophilic – lipophilic balance. Addition of a water releasing compound into the iPP/PEOS melt mixture, or passing water vapor during processing yields in nanocomposites which contain 20 nm silica particles.

Here, we present a new concept using the high migration potential of the hydrophobic PEOS to the iPP surface during processing in absence of water, which can be subsequently converted into a hydrophilic silica surface layer by environmental humidity. This concept overcomes the main hindrance of hydrophilic additive migration to a non-polar surface.

Synthesis of end group modified PEOS can be carried out in two different ways. First, the so called co-monomer route leads to hydrolytically stable Si-C end groups. Otherwise, Si-O-C bonded end groups can be realized by a transesterification reaction with alcohols. Both kind of modified PEOS molecules migrate to the polymer surface. But, only the Si-O-C bonded PEOS version can be converted to silica by hydrolysis in contact with environmental humidity or by conditioning under formation of hydrophilic silica surface coating by splitting off the hydrophobic end groups. To reach a high migration potential the surface energy of our PEOS additive has to be lower than the surface energy of the matrix material. Surface energy measurements at different temperatures were used to investigate the influence of the temperature during melt processing on migration efficiency. Besides, the miscibility of PEOS in PP melt and the decrease of miscibility during the cooling down “bleeding” shows strong influence too. To analyse the change in miscibility during the change of temperature miscibility tests are carried out either in melt at 210°C or in a model system at room temperature. These results are correlated with the thermal and hydrolytic stability of our precursor modifications.

The prediction of diffusion properties of variously modified PEOS additives is a very useful tool for future research in the field of PEOS.

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Synthesis of hyperbranched and star-shape polyimides in catalytic medium

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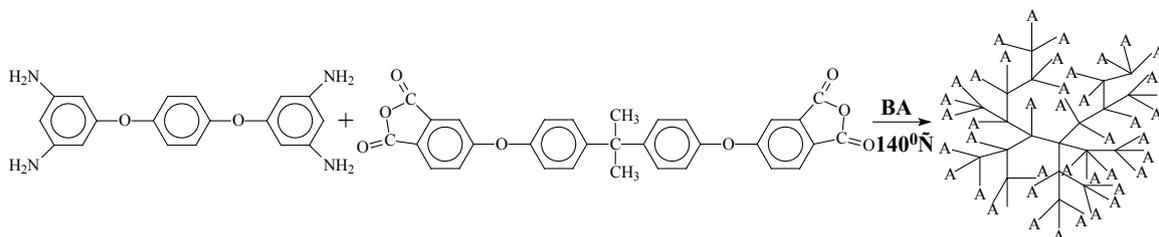
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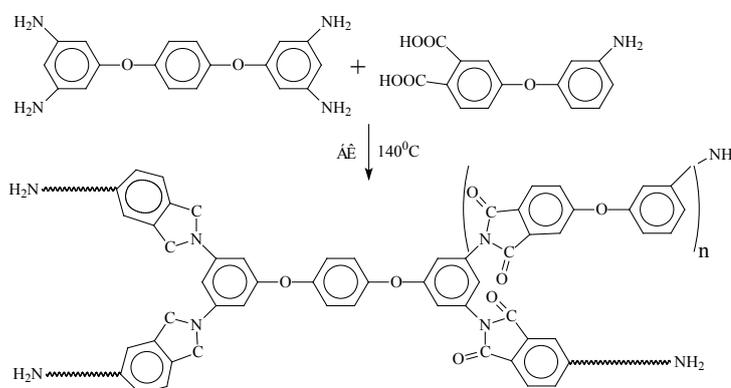
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Molten benzoic acid (BA) is convenient solvent for the one-pot synthesis of linear and hyperbranched polyimides (PI) [1,2,]. In present work, this approach was applied for obtaining hyperbranched PIs via (A4+B2) (Scheme 1) from a pair of comonomers tetraamine-tetracarboxylic acid dianhydride (1:1-mol.), and a star-shape PIs via (A4+A'B') (Scheme 2) - (1:10-vol.). 1,4-phenylene-bis(4-oxy-1,3-phenylene diamine) (A4), 2,2-propilidene-bis(4-oxyphthalic acid) dianhydride (B2) and 3-aminophenoxyphthalic acid (A'B') were used starting monomers. A4 was synthesized by nucleophilic substitution of trinitrobenzene with kalium salt of hydroquinone followed by reduction of nitrogroups with hydrazine using FeCl₃/active carbon system. Synthesis (schemes 1, 2) was carried out in molten BA under inert gas at 140^oC for 2 hours. The products are completely imidized PIs with terminal amino groups. They were characterized by NMR, IR spectra and DSC. The ability of terminal amino groups for consequent chemical transformations was confirmed by their acylation with acetic and phthalic anhydrides.



Scheme 1.



Scheme 2.

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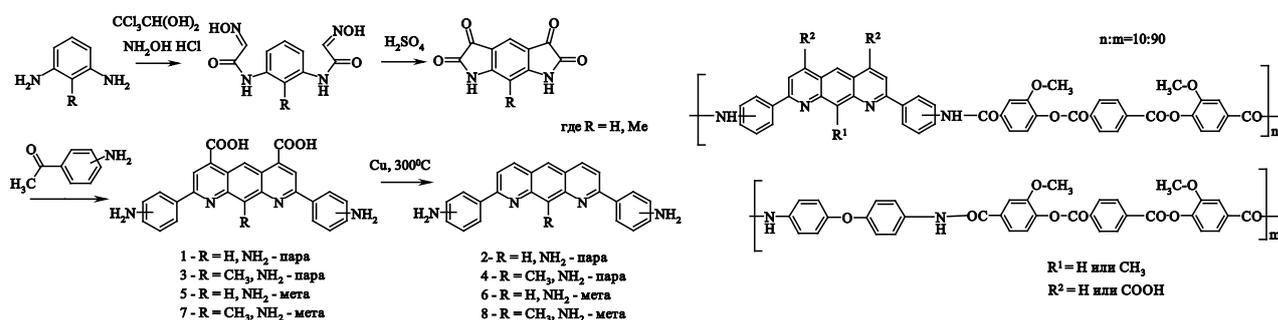
Copolyamides with luminofore anthrazoline groups in the backbone

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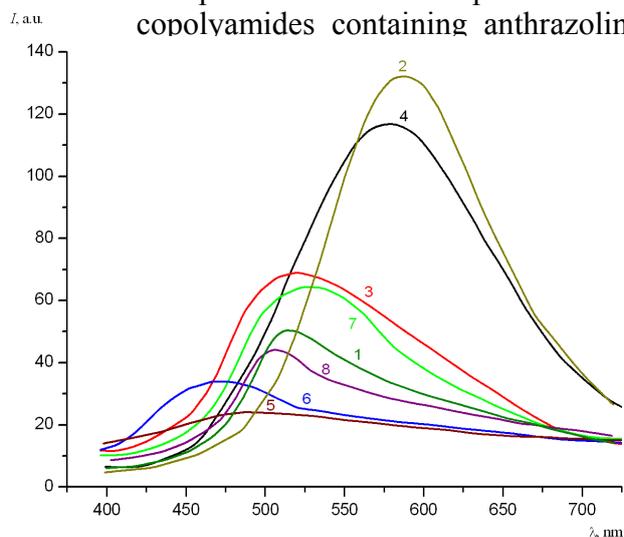
A series of anthrazoline-containing diamines (1-8) based on bis-isatins and aminoacetophenones of various structure were synthesized. New copolyamides with anthrazoline groups in the main chain were obtained by the method of low-temperature polycondensation.



It is shown that all the polymers demonstrate high mechanical and thermal properties ($E=2,6-3,7$ GPa, $\sigma_s=130-190$ MPa, $\varepsilon_s=25-60$ %, $\tau_5=250-390$ °C) and possess the intensive photoluminescence in the 450-675 nm.

The investigation gave the opportunity to determine the effect of substituents in anthrazoline cycle on the mechanical, thermal and optical properties of copolyamides with anthrazoline units in the main chain, which allow for us to develop the modeling principles of polymers with optimum characteristics.

The photoluminescence spectra of the copolyamides containing anthrazoline



Thermal transportation properties for composite containing mixed alumina and graphene

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Modern electronics need more efficient heat dissipation systems due to their increasing power densities and decreasing size and weight.^[1] Thermal interface materials (TIMs), applied between heat sources and heat sinks, are essential ingredients of efficient heat removal.^[2] Graphene is a new carbonaceous material of two-dimensional honeycomb lattice structure. Because of a very high thermal conductivity, graphene is a good filler to prepare TIMs of excellent heat transfer performance. In this work, a novel approach was developed for obtaining a strong three-dimensional network of heat conducting path by filling Alumina (Al₂O₃) and graphene the poly(ethylene-co-vinyl acetate) (EVA). This unique structure effectively prevents the inter-sheet restacking of graphene and minimizes the thermal contact resistance between fillers and interface.

In order to maximize the utilization of heat conduction offered by fillers, the graphene and Al₂O₃ hybrid fillers are mixed with EVA to enhance their thermal conductivity. The thermal conductivity of composite presented in Fig.1 indicated a strong synergistic effect when graphene is filled. The resultant exhibits a high thermal conductivity of 2.40 ± 0.07 W/m·K, which is much higher than single filler at the same loading. Additionally, a strong synergistic effect can also be observed, and 3-dimensional schematic models were simulated for this enhancement.

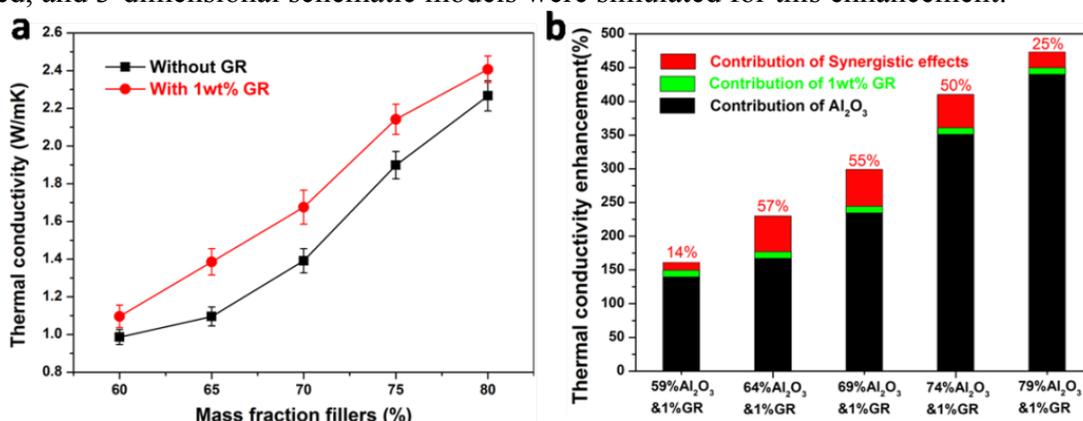


Fig. 1. Comparison of thermal conductivity (a) and thermal conductivity enhancement (b) of EVA with and without graphene (GR) at different filler loading.

The experimental data indicates that graphene can form the thermal conductivity bridge in the alumina filler, and it can further enhance the packing density filler and provide more thermal pathway, thus reducing the interfacial thermal resistance between the filler and the polymer matrix^[3] and enhance the thermal conductivity of the novel EVA.

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Effect of graphene nanoplatelet on the dielectric property of PVDF/PMMA blends

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Poly(vinylidene fluoride) (PVDF) based nanocomposites with excellent dielectric constant play important roles in electromechanical fields such as high performance sensors, actuators, artificial muscles, as well as bypass capacitors in microelectronics and energy-storage devices. In this work, PVDF/poly(methyl methacrylate) (PMMA)/Graphene nanoplatelet (GNP) ternary nanocomposites were prepared via solution blending and hot-press processing. The PVDF/PMMA matrix with the mass ratio of 70/30 exhibits the best balance of hydrophilicity, hardness and mechanical strength. XRD and DSC results demonstrate that PMMA and GNP promote the formation of β and γ phases crystals in PVDF. PVDF is known for its polymorphism crystalline structure and complicated microstructure with five distinct crystal polymorphs depending on the crystallization conditions. Among them, the polar β phase with all trans-TTT planar zigzag structure has the largest spontaneous polarization per unit cell and the γ phase ranks second, thus providing the piezoelectric properties. It is demonstrated that GNP can be used to increase the dielectric constant of PVDF/PMMA blend at very low weight fractions and the electrical percolation threshold is formed at a certain GNP content between 4.5 and 5 wt%. The dielectric constant of nanocomposite is as high as 450 and the electrical conductivity of that is around $10^{-5} \sim 10^{-4}$ S/cm at 10^2 Hz when the weight fraction of GNP is 5%. It can be interpreted that the high dielectric constant and the low electrical conductivity of the nanocomposite with 5 wt% GNP stems from the charge accumulation at interfacial layers between polymer chains and GNP and the formation of microcapacitors. This study may provide a possible approach for designing promising capacitor dielectrics from PVDF based ferroelectric polymers.

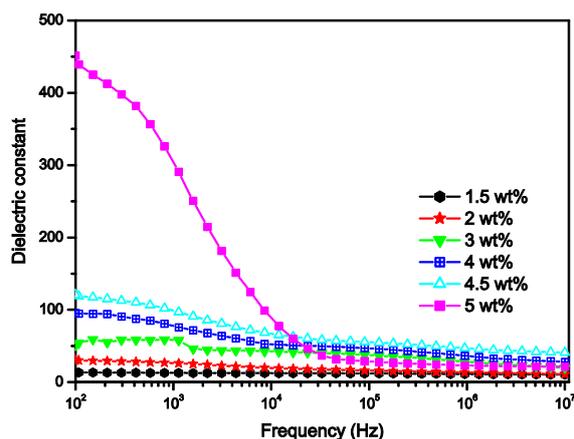


Fig. 1. Frequency-dependent dielectric constant of PVDF/PMMA/GNP nanocomposites at different contents of GNP

This work was supported by the Natural Science Foundation of Shanghai (No. 15ZR1417100), and the key subject of Shanghai Polytechnic University (Material Science and Engineering, XXKYS1601).

“Head-to Head” polyarylenediphthalides of polyphenylene series as structural isomers of polyarylenephthalides

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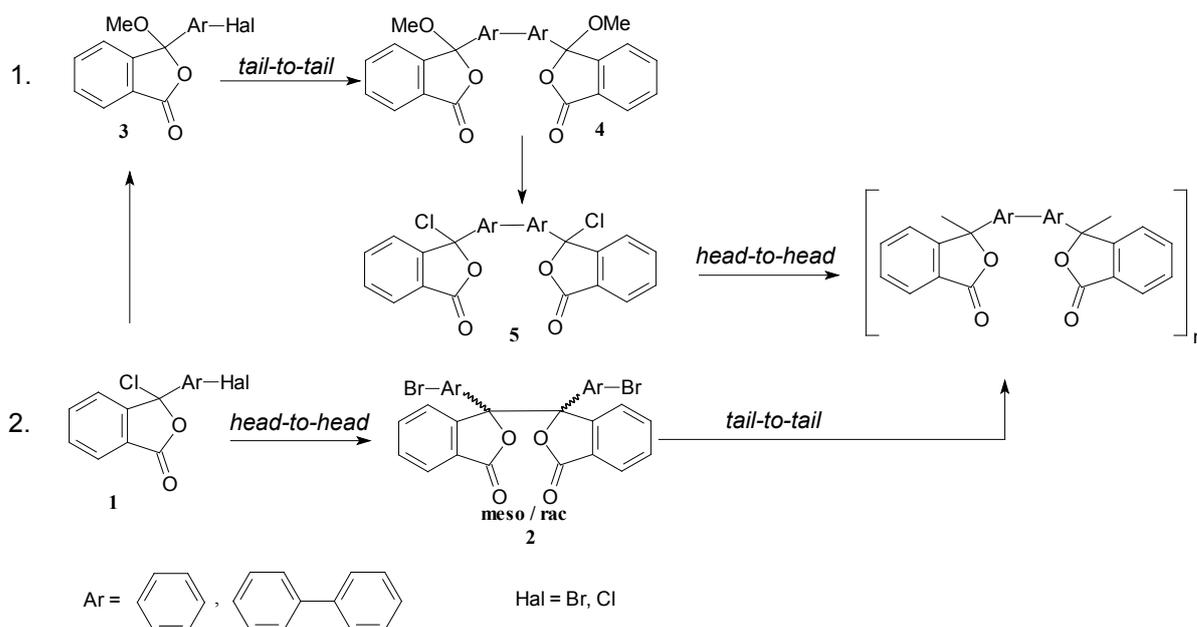
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All polyarylenephthalides synthesized to date on the base of ortho-keto-mono- and dicarboxylic pseudoacids chlorides [1] are constructed by “Head-to-Tail” type.

The present report deals with results concerning the synthesis of polyarylenediphthalides being first polyarylenephthalides constructed by “Head-to-Head” type, which are essentially a new class of phthalide-type polyheteroarylenes. Polyarylenediphthalides represent the structural isomers of “classical” polyarylenephthalides and contain in comparison with them a doubled amount of aromatic fragments and phthalide groups.

“Head-to-Head” polyarylenediphthalides were obtained using dehalogenation reaction in two ways. In the first, at the beginning the cyclic esters **3** were “tail-to tail” coupled by Ni(0) [2], then produced diacid dichlorides **5** had been “head-to-head” polymerized using Bhatt’s method [3]. In another, at dimerization stage the monoacid chlorides **1** were “head-to-head” coupled and at subsequent stage “tail-to tail” polymerization of halogen substituted biaryl-3,3'-diphthalides **2** was performed.



In the first case the polymers with a statistical microstructure are produced, in the second the stereoregular polymers with meso- and racemic configuration of diphthalide groups in polymeric chain are formed. Stereoregular polyarylenediphthalides of racemic-diphthalide type have a good solubility in the main classes of organic solvents but those of meso-type are soluble only in concentrated sulfuric acid. All obtained polymers are distinguished by bright photoluminescence.

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Polyamide reinforcing by modified single-walled carbon nanotubes as the protective coatings for optical fibre

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The primary factor restricting the application of optical fibres in a various areas, such as the oil and gas industry, chemical industry and medicine, is their insufficient resistance to the aggressive attack of the ambient medium and temperature, which is determined primarily by the properties of their protective coating. Coating should protect the surface of optical glass fibres against mechanical damage and direct contact with the ambient medium. Widely used (acrylate-based) protective polymer coatings allow optical fibres to be employed at temperatures no higher than 85 °C. They are sensitive to the presence of many chemicals in the ambient medium. Currently protective coatings based on polyimides are the most progressive. Polyimides provide improved thermal stability, oil, acid resistance and etc. However, the main imperfections of polyimides are the multistage coating method and significant variation in mechanical strength.

In this research, we present our first results on the fabrication of new, high performance coatings for optical fibres based on polycapromamide/carbon nanotubes nanocomposites. The polycapromamide (PCA) composites were obtained by anionic in situ ϵ -caprolactam polymerization in the presence of 0.001-0.1 wt. % of previously functionalized by polyimides single-walled carbon nanotubes (SWCNTs). Such nanotubes modification provides their homogeneous distribution within the polymer as well as improves some performance properties of PCA.

Two methods for the modification of SWCNTs were proposed: covalent and non-covalent functionalization by polyimides. The modified nanotubes as well as PCA/SWCNTs composites were thoroughly examined by the series of instrumental techniques including thermogravimetric and elemental analysis, XPS, SEM, TMA, mechanical tests, etc. It was shown both methods of nanotubes modification allow increase thermal stability; enhance the compression modulus and impact strength of polymer blocks and advance the tensile strength and elongation of polymer films.

Elaborated composites were used as coatings for optical fibers. These composites as the coatings have high adhesion to the optical fibers, feature sufficient resistance to the aggressive medium and possess a combination of valuable mechanical properties.

This work was supported by the Russian Science Foundation (RSF), grant no. 14-13-01273.

Novel polycondensation method of improving high-temperature properties of rolivsan microheterogeneous copolymers modified by inserting epoxy and imide bridges between spherical microdomains

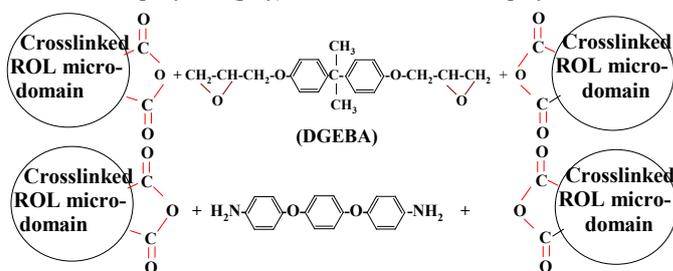
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A new approach to chemical modification of rolivsan thermosetting resins (ROLs) has been recently proposed [1,2]. Microheterogeneous highly crosslinked copolymers functionalized with anhydride units comprising microdomains and polymer interlayers are formed at full ROLs cure [3,4]. According to the approach, high temperature post cure reactions of ROLs/epoxies and ROLs/diamine(ADA) blends lead to additional crosslinking of these supramolecular

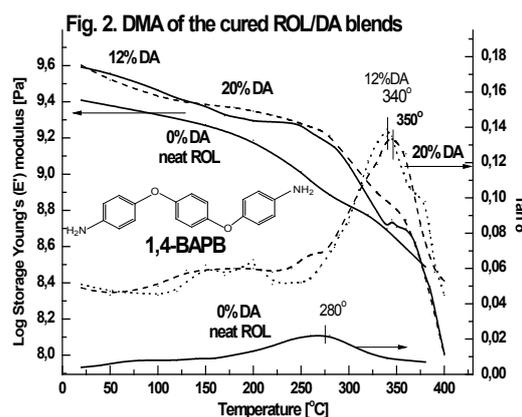
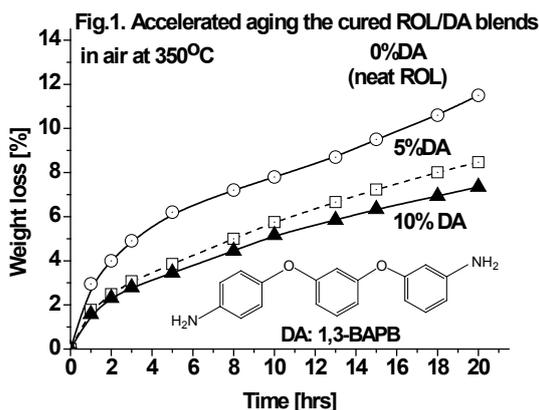
Scheme.1. High temperature reactions in the microheterogeneous crosslinked epoxy and (poly)imide modified ROLs copolymers



(8±2 wt.%) of ADA (via bulk (poly)-

formations (Scheme 1). Judging from weight loss of samples at thermal aging in air at 350°C, DMA, TGA and DTA studies of the cured ROLs-ADA blends (Fig.1 and 2) demonstrate a lot more resistance to thermooxidative destruction as compared with the cured neat ROLs, for example. Thus, High-temperature properties of ROLs co-cured with a small amounts

reactions of radical crosslinking, acylation, and oxidative polymerization) can be substantially improved compared to the cured neat ROLs.



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Polyimides and sulfonated polyimides based on 1,1-diphenylethylene derivatives: polymer substrates for new proton exchange membranes

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Polyimides and sulfonated polyimides are widely used as engineering thermoplastic materials for applications as membranes in gas separation processes [1] and as proton exchange membranes in fuel cells [2]. The chemical and physical characteristics such as good chemical and thermal stability, high mechanical strength, excellent oxidative resistance and good film-forming ability make polyimide derivatives the materials of choice for use as membrane substrates [1]. The current research involves the utilization of a symmetrically difunctionalized 1,1-diphenylethylene derivative, 1,1-bis(4-aminophenyl)ethylene (**3**) in polycondensation reactions. A series of new aromatic polyimide derivatives were prepared by step growth polymerization methods by the polycondensation reactions of 4,4'-oxydiphthalic anhydride (**1**) with different mole percentage ratios of 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**2**) and 1,1-bis(4-aminophenyl)ethylene (**3**) as monomer precursors [3]. The intermediate polyamic acids were subjected to a thermal imidization process to provide the corresponding polyimide derivatives. The resulting polyimide derivatives were subjected to post polymerization sulfonation reactions via the thiol-ene click reaction with sulfonating agents to form polyimides with the sulfonate group pendant to the polymer backbone. Polyimides with excellent chemical and thermal properties are obtained. The sulfonated polyimide derivatives are good candidates as polymeric substrates for proton exchange membranes for fuel cells.

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Nanoparticle-bound doxorubicin for chemotherapy of glioblastoma

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Insufficient efficacy of the chemotherapy of brain diseases is often due to the limited ability of many drugs to circumvent the blood–brain barrier (BBB). Thus poor brain uptake of doxorubicin is perhaps the main reason why this potentially active anti-tumour antibiotic is not used for the chemotherapy of glioblastoma.

Our previous studies demonstrated that the promising approach to the non-invasive brain delivery is the drug binding to nanoparticles. In particular, intravenous administration of doxorubicin bound to the surfactant-coated poly(lactide-co-glycolide) nanoparticles (Dox-PLGA) enabled considerable growth inhibition of the intracranially implanted 101.8 glioblastoma in rats and long-term remission in >20% animals, whereas the conventional formulation was only marginally effective. This antitumour action was also confirmed by histology. The microscopical studies revealed the effective intratumoral penetration and accumulation of the nanoparticles.

Preclinical studies demonstrated that Dox-PLGA has a favourable toxicological profile. The most important finding is the reduction of cardiotoxicity, evidenced by both functional and histological assessment. The lower toxicity of the nanoparticle formulation is most probably explained by the altered biodistribution of the drug mediated by the nanoparticles.

A Phase 1 trial of the doxorubicin formulation based on PLGA nanoparticles coated with poloxamer 188 is currently on-going in Russia.

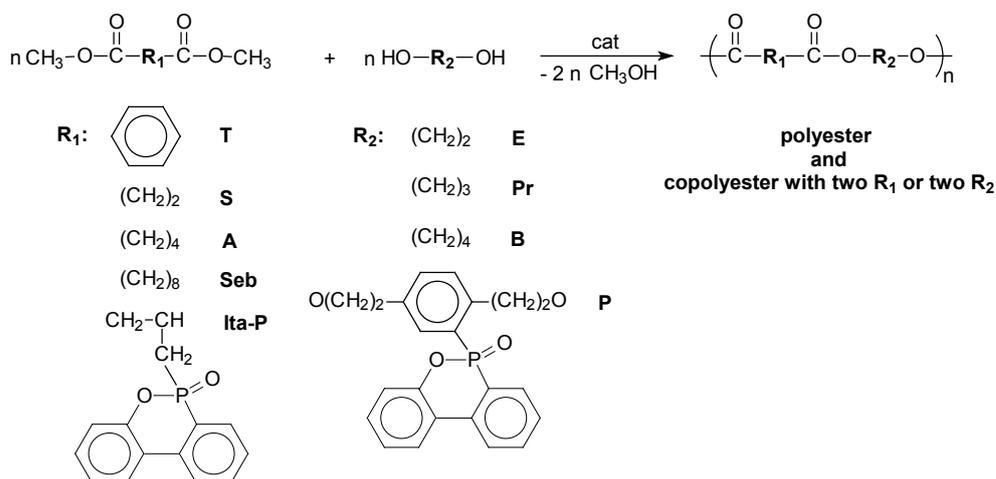
Synthesis and characterization of DOPO-containing biobased polyesters and copolyesters

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Some monomers for aliphatic polyesters, like, e.g., poly(butylene succinate) (PBS), are available from biobased sources and offer the possibility to increase sustainability in the field of polymers. However, aliphatic polyesters are easily combustible with high heat release capacities [1] and require flame retardant additives. Polyesters with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) substituents have already been shown to improve flame retardancy of poly(butylene terephthalate) (PBT) [2]. Therefore, this concept was applied as well for preparation of DOPO-substituted aliphatic polyesters based on itaconic acid with stepwise varied chemical structure as outlined in Scheme 1.



Scheme 1. Synthesis of aliphatic DOPO (co)polyesters by polycondensation.

The polyesters were prepared by transesterification polycondensation in the melt. The poster will show synthesis results from lab-scale and autoclave experiments. In all experiments, high molar mass products with high dispersity \bar{D} were obtained. DOPO-substituted (co)polyesters are amorphous without crystallinity due to the bulky substituents. The amorphous structure results in reduced elongation at break ϵ_B values (except for the sebacate copolyesters). To avoid this drawback the phosphorus content was enhanced by combination of two DOPO-containing monomers. High limiting oxygen indices (LOI) up to 54 were observed, indicating the high flame retardancy potential of the materials. The (co)polyesters were used in blends with PBS as flame retardancy additives.

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Tailored design of polyurethane coatings from PET recycling for applying in corrosion protection

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In this study, polyethylene terephthalate (PET) waste bottle was recycled via glycolysis process using Pentaerethrol, to be used as starting ingredients for synthesis of other polymers. It is shown that, the chemically recycled PET by esterifying the polyester with an excess of reactant such as Pentaerethrol in the presence of zinc acetate as a catalyst at 190-220 °C for 8 hrs. The produced oligoester from such glycolysis of PET waste was introduced as a starting material in the manufacturing of High Branched Poly(hydroxy ethylene terephthalate pentaerythritol bis-phenol A) resin, its happened through the reaction of oligoesters with bis phenol epoxy at 200 -220°C for 6hrs, the product of which is suitable to produce a high branched polyurethane coating. A possibility of new application of high branched Poly(hydroxy ethylene terephthalate pentaerythritol bis phenol A) resin and toluene di-isocyanate (TDI) as curing agent coatings are applied on the prepared surface of carbon steel specimen. The physical, mechanical and chemical characteristics of the obtained high branched polyurethane films were investigated. Corrosion resistivity based on salt spray and cathodic disbondment were evaluated for the formed dry films on carbon steel specimens, the obtained high branched polyurethane coating films can be reinforced with nanoparticles for increasing the film strength and durability.

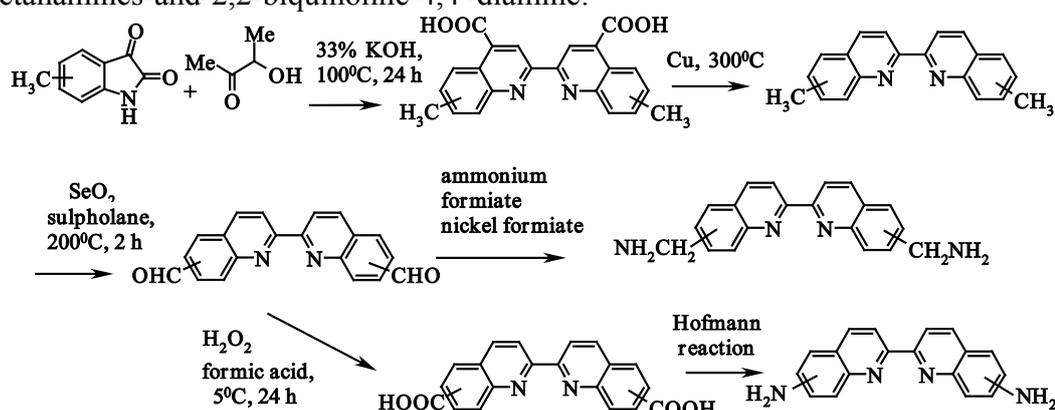
Synthesis and properties new co-polymers with biquinoline units in the main chain and metal-polymer complexes based on

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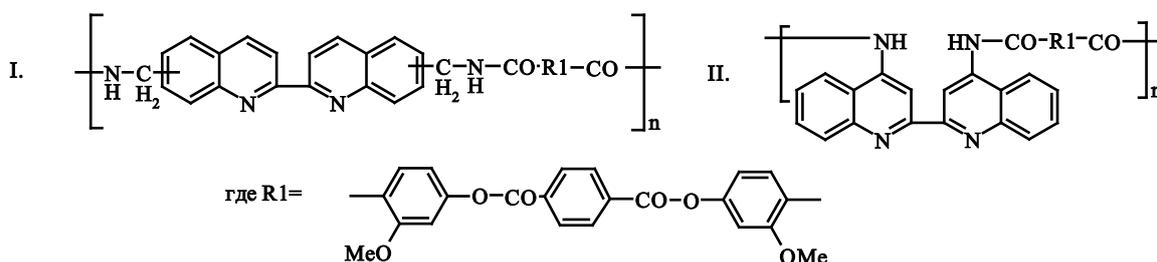
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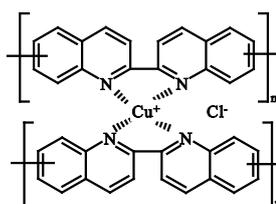
Macromolecular complexes of transition metals are promising compounds for the creation of high-performance electro-optic devices, sensors, photochemical, electrocatalytic systems, and gas separation and pervaporation membranes. The functionalization is achieved by introducing into the main copolymer chain units containing biquinoline group capable of forming coordination bonds with cuprous salts. The purpose of this study was to obtain new biquinoline containing monomers - diildimetanames and diamines, synthesis of heat-resistant functionalized polymers on therefrom, synthesis a metal-polymer complexes with CuCl and study their properties. Synthesis of monomers -6,6', 7,7', and 8,8'-2,2-bihinolin diildimetanamines-and-2,2-biquinoline-4,4'-diamine:



On the basis of these monomers, by low-temperature polycondensation, new polyamides with 10% biquinoline units and polymer-metal complexes with CuCl based on were synthesised. The structure of biquinoline-containing polymers:



The structure of metal polymer unit:



The spectral, molecular, deformation-strength, thermal and photophysical characteristics of the synthesized polymers were investigated.

Surface properties and chemical structure of polyethersulfone films treated by direct current discharge

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In this report we present a study of the DC discharge treatment on the contact properties, structure and surface morphology of PES films. PES of the Ultrason E brand (BASF) was used, films of ~50 μm in thickness were prepared by casting a 10% polymer solution in dimethylacetamide. The samples were modified by DC discharge, and the films were placed on the anode or cathode. The plasma gas was filtered air; plasma treatment was carried out at a pressure of ~20 Pa, discharge currents of 10–50 mA, and treatment times from 10 to 60 s.

The surface properties were characterized by contact angles (θ) of water (deionized) and glycerol. The values of the work of adhesion (W_a), total surface energy (γ), and its polar (γ^p) and dispersion (γ^d) components were calculated from the experimental θ values. The chemical structure of the films was studied by the XPS technique. The changing of the surface morphology of the films under the plasma action was studied by SEM and AFM.

Surface characteristics (θ_{water} , θ_{gluc} , W_a , γ , γ^p , and γ^d) for an initial PES film, the films treated at the anode and cathode by DC discharge ($I = 50\text{mA}$, 20 s), and the discharge-modified films after storage for 14 days under ambient conditions

Sample		θ , deg		W_a , mJ/m ²		γ , mJ/m ²		
		of water	of glycerol	of water	of glycerol	γ	γ^p	γ^d
Initial		90	87	72.8	66.7	18.3	11.4	6.9
Treated at the anode	After treatment	14	7	143.4	126.3	70.8	52.8	18.0
	Storage for 14 days	44	35	125.2	115.3	54.3	32.8	21.5
Treated at the cathode	After treatment	10	8	144.5	126.2	72.1	55.5	16.6
	Storage for 14 days	48	41	121.5	111.2	51.0	31.9	19.1

It can be seen that the plasma treatment leads to the hydrophilization of the surface of the polymer modified at the anode or cathode. After storage of the films for 14 days, θ_{water} and θ_{glyc} increased to a greater extent for the films modified at the cathode, although the films remained hydrophilic in both cases ($\theta_{\text{water}} < 60^\circ$).

By XPS it was shown that the film treatment at the anode and cathode seems to lead to partial degradation of the aromatic rings, elimination of SO₂ groups, and formation of carbonyl and carboxyl groups on the PES film surface. By SEM and AFM methods it was shown a noticeable change in the morphology of the PES film surface modified by plasma. The value of the mean-square roughness (R_q) of the initial film surface was 4 ± 0.3 nm. Modification by the DC discharge at the cathode resulting in a reduction to $R_q = 1.5 \pm 0.1$ nm, and to increasing to 7.2 ± 1.2 nm after treatment at the anode.

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Structural modification of polyimides for various applications

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Polyimides (PI) are ranked among the most heat-resistant polymers and are widely used in high temperature plastics, dielectrics, photoresistors, nonlinear optical materials, membrane materials, among others. In our work we research the possibility of expanding the application of polyimides in proton exchange membranes (PEM), insulation materials, sorption materials and composites with thermal stability and radiation resistance.

Polyimides are particularly attractive for PEM studies due to the large variety of possible chemical structures. However, PI themselves may not satisfy all the requirements for PEM, thus block copolymers where each repeating unit performs a specific function should be developed. We focus on a combination of polyimides with polysiloxanes and crown-ethers for high-efficient PEM.

Fluorine-containing polyimides possess low dielectric constants, high optical transparency, low refractive indices and remarkably low water absorption. A reduced dielectric constant in insulation materials allows higher signal-propagation speeds in miniaturized electronic devices and components. Fluorinated polyimides have been made with a broad range of chemical structures and possess an equally wide range of properties.

The thermal stability, good chemical and radiation resistance of PI with introduced fragments capable to complex with metal ions make them suitable materials for sorbents used to remove radioactive isotopes from waste waters. The crown-ethers and chelators are used in our research for complexation with metal ions.

The combination of carbon nanotubes and polyimides is expected to play an important role in the development of novel high-performance nanocomposites with enhanced mechanical properties, in addition, they may be able to achieve certain levels of electric conductivity through a percolation network for charge mitigation and electromagnetic shielding.

A new material based on polyimide and nanostructured SiC has been synthesized successfully, at short periods of time, the use of these particles improves thermal stability of the base polymer. The incorporation of nanosized boron carbide in polyimide matrix will allow to produce radiation shielding materials. Combined with ultra high molecular weight polyethylene filled with metal oxide it can be used in lightweight materials for radiation protection.

PI are suitable to be used as a matrix resin in fiber reinforced composites. Composites of carbon fibers and PI are fabricated by routing an poly(amic acid) solution followed by thermal curing. In fact polyimides exhibit excellent physico-mechanical properties in a broad temperature range and have exceptionally high radiation resistance and superior semiconductor properties. These characteristics allow polyimides to dominate the applications in many fields.

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Drugs Technology LLC (DrugsTech) is an innovative pharmaceutical corporation developing more than 100 Generic Drug formulations and 13 Innovative dosage forms in more than 12 therapeutic areas. The Brand Portfolio is notable for several Drug Candidates at various stages of Clinical Trials. The current Brand Portfolio includes drug delivery systems and new medicines created in conjunction with leading research universities in Russia and abroad, involving key scientific figures and organizations worldwide.

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ООО «Технология лекарств» — инновационная фармацевтическая компания, специализирующаяся на разработке и производстве современных лекарственных препаратов для лечения онкологических, инфекционных и других социально значимых заболеваний.

Компания разработала и производит портфель лекарственных препаратов, направленный на

импортозамещение дорогих зарубежных оригинальных лекарственных средств качественными отечественными аналогами.

В настоящее время коллектив компании Технологии лекарств ведёт разработки отечественных препаратов на основе различных инновационных систем доставки, а также новых оригинальных молекул. Данные разработки базируются на результатах многолетних исследований российских и международных научных коллективов. Разрабатываемые технологии являются передовыми и, в ряде случаев, не имеют аналогов в мире.

В настоящее время ряд инновационных препаратов компании рекомендован Министерством здравоохранения РФ к клиническим исследованиям I фазы. Совместно с ведущими научно-клиническими центрами России подготовлена программа клинических исследований на ближайшие три года. Ряд исследований стартовал в 2014 году.



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Bruno Visconti is one of the most popular trade marks of business accessories. The items are especially requested by companies with conservative manner. The majority of the diaries are made in classic style though there also can be found creative models.

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Bruno Visconti — один из самых популярных брендов деловых аксессуаров. Особенным спросом продукция бренда пользуется у компаний, предпочитающих консервативный подход. Выполнены ежедневники в строгом классическом стиле, хотя есть и креативные модели. Ежедневники Bruno Visconti — это всегда высокое качество и изысканный дизайн. Особое место ежедневники бренда Bruno Visconti занимают в подарочном сегменте, ведь это великолепный корпоративный подарок, который можно презентовать руководителю, клиентам или партнерам.

Кроме высокого качества материалов, ежедневники Bruno Visconti отличаются широким выбором оформления. Bruno Visconti предлагает как бюджетные варианты, так и дорогостоящие ежедневники с изысканной отделкой обложек.

Дизайнеры Bruno Visconti прикладывают немало усилий, чтобы разрабатывать самые привлекательные и оригинальные обложки, которые произведут впечатление на каждого. Ежедневники Bruno Visconti — идеальный деловой аксессуар и незаменимый помощник.



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CJSC "Donau Lab. Moscow / «Donau Lab. Moscow» specializes in the supply of laboratory and pilot equipment

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ЗАО «Донау Лаб. Москва/ «Donau Lab. Moscow» специализируется на поставках лабораторного и пилотного оборудования ведущих европейских производителей (таких как: **BUCHI Labortechnik AG, Binder GmbH, Martin Christ GmbH, Metrohm AG, Camag AG, Sartorius AG и т.д.**), лабораторном инжиниринге, лабораторных систем управления информацией на предприятии LIMS. Мы осуществляем установку и запуск оборудования, квалификацию и реквалификацию IQ/OQ/PQ в соответствии с требованиями GLP/GMP, методическую поддержку, постановку методик и обучение.



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ANALIT Ltd had been established in 1992 and celebrated its 20-th anniversary in 2012. At the present time ANALIT is the group of companies that has its representative offices in Saint-Petersburg (HQ), Moscow, Kazan, Nizhny Novgorod and Ufa and is one of the largest Russian suppliers of analytical and testing equipment.

ANALIT offers to its clients the complex lab solutions. We supply equipment, spare parts, consumables, reagents, furniture etc, provide methodical support and specialist training. ANALIT has its own accredited analytical lab that can perform the wide range of research works, develop different methods and train your specialists.

In 1996 ANALIT began the collaboration with the Japanese company SHIMADZU – world's leading manufacturer of analytical and testing equipment – and became its general distributor. Since 2004 SHIMADZU annually awards ANALIT as its best distributor.

ANALIT also collaborates with many other manufacturers of equipment and materials acting as the exclusive distributor in Russia for some of them (AntonPaar, Milestone, CEM, Sineo, Uniqsis, AntonPaar, Milestone, (Италия), CEM (США), Sineo (КНР), Uniqsis, Великобритания, Optical Activity и Index Instruments, Англия, LabTech, Millipore, Leco, Carl Zeiss, Retsch, Antec (Leyden), Polymer Standards Service (PSS), Markes International, BUCHI, EnSpectr, Pike, Glass Expansion, JTBaker, Sigma-Aldrich).

ANALIT is the only supplier in Russia that has its own accredited analytical lab with advanced SHIMADZU and other equipment allowing to perform any type of analysis.

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- Equipment for research of the mechanical characteristics: test machine for statistical and dynamic tests, hardness and ultra hardness testers

- Sample preparation equipment: microwave ovens and other thermal decomposition and evaporation systems, extractors, water purification systems, filtering systems, equipment for grinding, crushing, sieving, pressing etc.
- General laboratory equipment, consumables, reagents
- Laboratory furniture from the foreign and domestic manufacturers



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Группа компаний «Аналит», основанная в 1992 году, имеет представительства в Санкт-Петербурге, Москве, Казани, Нижнем Новгороде и Уфе и является одним из крупнейших в России поставщиков аналитического и испытательного оборудования.

АНАЛИТ предлагает своим клиентам комплексные решения для оснащения лабораторий, поставляя оборудование, расходные материалы, реагенты, мебель, осуществляет методическую поддержку и стажировку специалистов.

Наличие собственной аккредитованной аналитической лаборатории позволяет выполнять широкий спектр исследований, разработку методик и обучение специалистов.

АНАЛИТ производит дополнительное оборудование для следового спектрального анализа.

С 1996 года АНАЛИТ является генеральным дистрибьютором японской компании SHIMADZU - ведущего мирового производителя аналитического и испытательного оборудования. С 2004 года по настоящий момент компания «Аналит» признана лучшим дистрибьютором SHIMADZU в России и странах СНГ.

АНАЛИТ также сотрудничает с целым рядом компаний-производителей оборудования и материалов, являясь для некоторых из них эксклюзивным дистрибьютором в РФ: AntonPaar (Австрия), Milestone (Италия), СЕМ (США), Sineo (КНР), Uniqsis, Великобритания, AntonPaar (Австрия), Milestone (Италия), СЕМ (США), Sineo (КНР), Uniqsis, Великобритания, Optical Activity и Index Instruments, Англия, LabTech, Италия, Millipore, Франция, Leco, США, Carl Zeiss, Германия, Retsch, Германия, Antec (Leyden), Нидерланды, Polymer Standards Service (PSS), Германия, Markes International, Нидерланды, ВUСНI, Швейцария, EnSpectr, Россия, Pike, США, Glass Expansion, Австралия, JTBaker и Sigma-Aldrich и многие другие.



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For 20 years TECHNOCOMPLEKT IEPA JSC has been engaged in the development, production and supply of electrical products. Founded in 1996 in Dubna, the company was able to accumulate the unique intellectual potential of legendary national scientific expertise, create its high-tech manufacturing facilities and produce a dealer network.

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- Construction and reconstruction of power supply network facilities (construction-and-assembly operations and commissioning);
- Complex engineering production.

Our company has a great interest in the expansion of production and the introduction of new advanced technologies, especially in the area of solar energy and energy storage systems. The symbiosis of industry and science is very important in our time, so we are ready to cooperate with a view to industrial implementation.



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ЗАО «МПОТК «ТЕХНОКОМПЛЕКТ» 20 лет занимается разработкой, производством и поставкой электротехнического оборудования. Основанная в 1996 году в г. Дубна компания аккумулировала уникальный интеллектуальный потенциал легендарного наукограда страны, создала современное, высокотехнологичное производство, сформировала дилерскую сеть.

Основными направлениями нашей деятельности являются:

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- Научно-исследовательские и опытно-конструкторские изыскания в области силовых полупроводниковых технологий;
- Проектирование вновь сооружаемых и реконструируемых объектов энергетики;
- Строительство и реконструкция объектов электросетевого хозяйства (выполнение строительно-монтажных и пусконаладочных работ);
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JSC «Institute of Plastics» is a multipurpose research and production enterprise specializing on:

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In JSC «Institute of Plastics» there are research and development subdivision, technological subdivision, pilot production and commercial service. This potential of the company provides a full cycle of innovative products creation from the concept to commercialization.



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ОАО «Институт пластмасс» является многофункциональным научно-производственным предприятием, специализирующимся:

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- на создании, освоении и совершенствовании технологических процессов производства полимеров, синтетических смол, полимерных материалов и изделий, включая решение экологических проблем и ресурсосбережения;
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