SUNDAY, AUGUST 27

OPENING SESSION

18:00 to 20:00  Registration and Welcome Reception

20:00 to 20:10  Iskender Yilgör, Koc University, Istanbul, Turkey
Introduction, Overview and Objectives of the Workshop

20:10 to 20:25  Attila Askar, President, Koc University, Istanbul, Turkey
Welcoming Speech

20:25 to 20:30  Hans R. Kricheldorf, Hamburg Macromolecular Institute, Germany
Preview of Polycondensation 2008

20:30 to 21:00  Hans R. Kricheldorf, Hamburg Macromolecular Institute, Germany
Multicyclic Polymers by "a₂ + b₃ Polycondensations

MONDAY, AUGUST 28

INVITED LECTURE SESSION I
Discussion Leader - Kenneth J. Wynne

9:00 to 9:30  James Economy, University of Illinois, Urbana-Champaign, USA
Preparation of Low (Zero) Wear Surfaces Based on Specially Designed Polyesters

9:30 to 10:00  Dan Knauss, Colorado School of Mines, USA
Novel High Performance Condensation Polymers

10:00 to 10:30  Rikio Yokota, Hiroyuki Moriuchi, Yuichi Ishida Japan Aerospace Exploration Agency, Institute of Space and Astronautical Science
Thermoplastic-Thermosetting Polyimides Derived from Asymmetric a-BPDA and Aromatic Diamine with Pendent Phenylethynyl Groups

10:30 to 10:45  BREAK
INVITED LECTURE SESSION II
Discussion Leader - Dean C. Webster

10:45 to 11:15  Masa-Aki Kakimoto, Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Japan
Polysiloxyilsilane Hyperbranched Polymers

11:15 to 11:45  Tsutomu Yokozawa, Department of Applied Chemistry, Kanagawa University, Japan
Catalyst-Transfer Condensation Polymerization: Synthesis of Well-Defined π-Conjugated Polymers

11:45 to 12:15  Cor Koning, Eindhoven University of Technology, The Netherlands
Renewable Polyesters for Powder Coating Applications

12:15 to 13:30  LUNCH

INVITED LECTURE SESSION III
Discussion Leader - Hans R. Kricheldorf

13:30 to 14:00  Reinoud J. Gaymans, University of Twente, The Netherlands
High Tg Polymers with Monodisperse Crystallizable Segments

14:00 to 14:30  Kenneth R. Carter, University of Massachusetts, USA
Reactions of Functional Polymeric Surfaces

14:30 to 15:00  Yakov S. Vygodskii, Institute of Organoelement Compounds Russian Academy of Science, Moscow, Russia
Polycondensation Reactions in Ionic Liquids

15:00 to 15:30  Yasuharu Yamada, Nagoya Institute of Technology, Japan
Hyperbranched Polyimide-Silica Hybrids for Gas Separation Membranes

15:30 to 15:45  BREAK

INVITED LECTURE SESSION IV
Discussion Leader - Kenneth R. Carter

15:45 to 16:15  Jöns Hilborn, Materials Chemistry, Uppsala University, Sweden
Material - Living Tissue Adhesion Using Telechelic Isothiocyanate Functional PEG Block Copolymers with Siloxanes: Intraocular Lens Adhesion to the Capsular Bag

16:15 to 16:45  Javier de Abajo, Departamento de Quimica Macromolecular Instituto de Ciencia y Tecnologia de Polimeros, Madrid, Spain
Monomers Reactivity and Steric Factors Affecting the Synthesis of Aromatic Polyamides and Polyimides

16:45 - 19:30  RECEPTION AND POSTER PRESENTATION

20:00  DINNER AT A RESTAURANT ON THE BOSPHOROUS
# TUESDAY, AUGUST 29

## INVITED LECTURE SESSION V

**Discussion Leader - Masa-aki Kakimoto**

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<tr>
<td>9:00 to 9:30</td>
<td>Vasif N. Hasirci, Middle East Technical University, Ankara, Turkey</td>
<td>Polycondensation Polymers of Natural and Synthetic Origin as Biomedical Materials</td>
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<tr>
<td>9:30 to 10:00</td>
<td>Detlev Fritsch, GKSS, Institute for Polymer Research, Germany</td>
<td>Uncommon Sulfonated and Phosphonated Polymers Developed for Fuel Cell Membranes</td>
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<td>10:00 to 10:30</td>
<td>Alain Fradet, University of Pierre and Marie Curie, France</td>
<td>Recursive Probability Approach of the Average Degrees of Polymerization and Molar Masses of Hyperbranched Condensation Polymers</td>
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## INVITED LECTURE SESSION VI

**Discussion Leader - Mikhail Zolotukhin**

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<tr>
<td>10:45 to 11:15</td>
<td>Wolfgang Ziche, Wacher Chemie GmbH, Munich, Germany</td>
<td>GENIOMER®: Thermoplastic Silicone Elastomers</td>
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<td>11:15 to 11:45</td>
<td>Pavel V. Buzin, Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Science</td>
<td>Synthesis of Hyperbranched Polyimides in Active Medium</td>
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<td>11:45 to 12:15</td>
<td>Nesrin Hasirci, Middle East Technical University, Ankara, Turkey</td>
<td>Polyurethanes in Medical Applications</td>
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## INVITED LECTURE SESSION VII

**Discussion Leader - Maria Bruma**

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<td>Régis Mercier, CNRS, France</td>
<td>Polycondensation Via Microwave Reaction Conditions</td>
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<td>14:00 to 14:30</td>
<td>Alexander L. Rusanov, Institute of Organoelement Compounds, Russian Academy of Science</td>
<td>New Sulfonated Condensation Heterocyclic Polymers for Proton-Exchanging Membranes</td>
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<tr>
<td>14:30 to 15:00</td>
<td>Kenneth J. Wynne, Virginia Commonwealth University, USA</td>
<td>Polyurethanes with Novel Soft Blocks as Surface Modifiers</td>
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<td>15:00 to 15:30</td>
<td>Doris Pospiech, Department of Polymer Structures, Leibniz-Institute of Polymer Research Dresden, Germany</td>
<td>Melt Polycondensation of Polyesters: The Use of an Old Reaction to Develop New Materials</td>
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<td>15:45 - 16:15</td>
<td>Dennis W. Smith, Jr., Clemson University, USA</td>
<td>Advances in New Step-Growth Chemistry from Fluoroolefins and Diynyl Arenes</td>
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<td>16:15 - 16:45</td>
<td>Mikhail Zolotukhin, Universidad Nacional Autonoma de Mexico</td>
<td>Step Growth Polymerizations Involving Superelectrophiles</td>
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<td>16:45 - 17:15</td>
<td>Luc E. F. Leemans, Performance Materials - Chemistry &amp; Technology, DSM, The Netherlands</td>
<td>Influence of Titanium Catalyst on the Fate of Endgroups in the Melt Polymerization of Poly(butylene terephthalate)</td>
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<td>18:00</td>
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**WEDNESDAY, AUGUST 30**

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<tr>
<td>9:00 - 9:30</td>
<td>Dean Webster, Coatings &amp; Polymeric Materials, North Dakota State University</td>
<td>New Developments in Anti-Fouling Marine Coatings</td>
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<td>9:30 - 10:00</td>
<td>Ruud Rulkens, Performance Materials, The Netherlands</td>
<td>Polycondensates and Polycondensation Chemistry at DSM</td>
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<td>10:00 - 10:15</td>
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<td>10:15 - 10:45</td>
<td>Ramaz Katsarava, Georgian Technical University, Tbilisi, Georgia</td>
<td>New, Amino Acid Based Unsaturated Biodegradable Poly(Ester Amide)S with Double Bond Moieties in The Backbones</td>
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<td>10:45 - 11:15</td>
<td>Maria Bruma, Institute of Macromolecular Chemistry, Iasi, Romania</td>
<td>New Developments in Polyphenylquinoxalines</td>
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<td>12:00 - 13:30</td>
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<tr>
<td>13:30 - 14:00</td>
<td>Atila Gungor, Marmara University, Istanbul, Turkey</td>
<td>Phosphorous Containing Novel Sulfonated Polymides</td>
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<td>14:00 - 14:30</td>
<td>Yuji Shibasaki, Tokyo Institute of Technology, Japan</td>
<td>Oxidative Polymerization of Substituted Phenols with a Copper Amine Catalyst Within Mesoporous Silica</td>
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<td>14:30 - 15:00</td>
<td>Shadpour Mallakpour, Isfahan University of Technology, Isfahan, Iran</td>
<td>Ionic Liquids as Green Solvents and Catalysts for the Synthesis of Optically Active Poly(amide-Imide)</td>
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<td>15:00 - 15:15</td>
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<td>15:15 to 15:45</td>
<td><strong>Dildare Basalp, Izmir Institute of Technology, Turkey</strong>&lt;br&gt;Biodegradation of Poly-(L)-lactide and Poly-(L-lactide-co-D,L-lactide) in simulated body fluid (SBF)</td>
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<td>15:45 to 16:15</td>
<td><strong>Huseyin Deligoz and B. Tieke, Istanbul University, Turkey</strong>&lt;br&gt;Solvent Free Preparation of Conducting Polyurethane (PU)-Ionic Liquid (IL) Composites and Their Electric Properties</td>
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<tr>
<td>16:15</td>
<td><strong>CLOSING REMARKS</strong>&lt;br&gt;Masa-aki Kakimoto, Hans R. Kricheldorf, and Iskender Yilgör</td>
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1. Surface modification of polyimides containing moieties of aliphatic diamines in chain by the low temperature plasma  
Piskarev M.S., Gilman A.B., Yablokova M.Yu. and Kuznetsov A.A.

2. New phenoxy-substituted aromatic diamines and organosoluble polyimides therefrom  

3. Linear and four-arm multiblock copolymers by Ring Opening Polymerization in Supercritical Carbon Dioxide  
Burcu Saner, Nalan Bilgin and Yusuf Z. Menceloglu

4. Synthesis, melt-spinning and characterization of fully aromatic, thermotropic liquid crystalline copolyesters containing m-hydroxybenzoic acid units  
Erdal Bayramli, Zekeriya Yerlikaya and Serpil Aksoy

5. Synthesis and Characterization of new substituted polythiophenes  
Mariana-Dana Damaceanu, Silvia Destri and Maria Bruma

6. Polysilane-metal complexes for organic semiconductors  
Liviu Sacarescu, Rodinel Ardeleanu, Gabriela Sacarescu, Mihaela Simionescu and Ionel Mangalagiu

7. Crosslinkable polysilane-organometallic structure  
Liviu Sacarescu, Rodinel Ardeleanu, Gabriela Sacarescu and Mihaela Simionescu

8. N-Hydroxyphthalimide reactions with cyclic alkenes  
Sergiu Coseri and Bogdan Cr. Simionescu

9. New insights on the urethane reaction mechanism  
Sergiu Coseri and Adrian A. Caraculacu

10. Novel polyazomethines as photoluminescence sensors  
Danuta Sek, Agnieszka Iwan, Zbigniew Mazurak

11. Parabanic copolymers obtained by condensation or cyclocondensation reactions  
Elena Scotaranu, Elena Gabriela Hitruc and Adrian Caraculacu

12. Reactive Hot Melt Polyurethane Adhesives Modified by Macromer  
Han Mo Jeong, Jin Su Jung, Jin Hee An, Jae Hoon Kim, Min Seok Kim, Young Soo La, Dae Hoon Kim, Eun Hak Lee, Nam Ho Kim, Yong Sung Kim, Tae Kyoong Kim, Yang Lae Cho and Jeong Mi Hwang
13. **The Effect of Na-MMT Intercalated with PEG on the Properties of Reactive Hot Melt Polyurethane Adhesives**
   Han Mo Jeong, Dae Hoon Kim, Jin Su Jung, Jin Hee An, Jae Hoon Kim, Min Seok Kim, Young Soo La, Eun Hak Lee, Nam Ho Kim, Yong Sung Kim, Tae Kyoong Kim, Yang Lae Cho and Jeong Mi Hwang

14. **Semiinterpenetrating polymer networks containing polysaccharides. I. Xanthan/lignin networks**
   Irina Elena Raschip, Cornelia Vasile, Diana Ciolacu and Georgeta Cazacu

15. **Semiinterpenetrating polymer networks containing polysaccharides. II. Alginate/N-Isopropylacrylamide networks**
   Raluca Petronela Dumitriu and Cornelia Vasile

16. **Polysulfone-g-Poly(styrenesulfonic acid) Graft Copolymers for Proton Exchange Membranes**
   Young Cheol Park, Young Gyu You, and Chang Gi Cho

17. **Plasma-chemical synthesis of polyconjugated polymer from 1-amino-9,10-anthraquinone**
   Gilman A.B., Drachev A.I., Kuznetsov A.A.

18. **Self-organized lamellar nanostructures of wholly aromatic block co-oligomers: Oligo(ether-sulfone)-b-oligo(ether-ketone)**
   Teruaki Hayakawa, Raita Goseki, Masa-aki Kakimoto

19. **Synthesis and properties of highly soluble addition-type imide oligomers based on fluorenylidene diphenyl ether groups for matrices of carbon fiber composites**
   Yuichi Ishida, Toshio Ogasawara and Rikio Yokota

20. **Synthesis of hyperbranched polymers with penta(ethylene oxide) chains and core structure**
   Atsushi Kameyama and Eisuke Makino

21. **End group controlled cure of polyester powder coatings with a B-hydroxyalkylamide as crosslinker**
   Paul Buijsen

22. **Siloxane-organic polyesters by direct polycondensation**
   Carmen Racles, Maria Cazacu, Vasile Cozan and Daniela Filip

23. **Influence of chemical structure on processing and thermotropic properties of poly(siloxane-azomethine)**
   Carmen Racles and Vasile Cozan

24. **Novel thermal acid generators for low temperature cyclization of poly(o-hydroxyamide) and their application for photosensitive polymer**
   Tomohito Ogura, Kota Yamaguchi and Mitsuru Ueda

25. **Development of low-k materials based on poly(naphthylene ether)**
   Kousuke Tsuchiya, Yuji Shibasaki and Mitsuru Ueda

26. **Amide interchange reactions in polyamide blends: Influence of end-groups**
   P. Blondel, F.L.G. Malet, J.-J. Flat
27. **Morphology Control of Poly[2,2’-(p-phenylene)-5,5’-bibenzimidazole] by Using Crystallization of Oligomers during Solution Polymerization**
   Shin-ichiro Kohama, Jin Gong, Shinichi Yamazaki, Kunio Kimura, and Kaoru Shimamura

28. **Synthesis of Polyimides using Ionic Liquids as Condensation Agents and Medium**
   Masaru Yoneyama, Yuichi Matusi and Satosi Morizumi

29. **Facile synthesis of monodisperse oligoamides based on 4-(N-methylamino)benzoic acid using thionyl chloride as an activating agent**
   Isao Washio, Yuji Shibasaki and Mitsuru Ueda

30. **Synthesis and characterization of water-soluble poly(para-phenylene ethynylene) copolymer for bioconjugation**
   Moon Soo Choi and Taek Seung Lee

31. **Synthesis and characterization of fluorescent water-soluble conjugated poly(aryleneethynylene)**
   Hyung Jun Kim, Jung Hyo Lee and Taek Seung Lee

32. **Self-assembly of low molar mass molecule containing 2-(2’-hydroxylphenyl) benzoxazole units: Structural and optical properties of supramolecular structure**
   Tae Hyeon Kim, Won Ho Park and Taek Seung Lee

33. **Synthesis and functionalization of alkoxy-carboxylated water-soluble poly(para-phenylenes) for biosensors**
   Chan Kyu Kwak and Taek Seung Lee

34. **Crosslinked Siloxane-Polyurethane Coatings for Underwater Marine Applications Using Combinatorial High Throughput Experimentation**
   Abdullah Ekin, Dean C. Webster, Justin Daniels and Shane Stafslien

35. **Diels-Alder trapping of photochemically generated dienes with acrylic esters: A novel approach to photocured polymer film development**
   Faysal Ilhan, Daniel S. Tyson, La’Nita D. Ward, Deedee Smith, Mary Ann B. Meador, Baochau Nguyen and Michael A. Meador

36. **Polyurethane/clay nanocomposite based reactive hot melt adhesive(RHMA) : The effects of clay**
   TK Kim, YS Kim, YL Cho, JM Hwang and HM Jung

37. **Synthesis of Water-Soluble Poly(para-phenyleneethynylene) Copolymer Containing Blocked-Maleimide for Bioapplications.**
   Jung Hyo Lee, Moon Soo Choi, Taek Seung Lee*
38. New film-forming polymers containing in the main-chain dibenzo-18-crown-6, dibenzo-21-crown-7, dibenzo-24-crown-8, or dibenzo-30-crown-10 ether units alternating with aliphatic \((C_{10}-C_{16})\), aliphatic-aromatic spacers or oxindole fragments
Maria del Carmen G. Hernández, Mikhail G. Zolotukhin, Ana Maria Lopez, Gerardo Cedillo, Alberto Ruiz-Treviño

39. Comparison between telechelic and random sulfonated poly(butylene terephthalate) ionomers
C. Berti, M. Colonna, A. Celli, P. Marchese, M. Fiorini, E. Binassi and D.J. Brunelle

40. Polyarylates one-pot synthesis using diphenyl carbonate, aromatic diols and dicarboxylic aromatic acids
C. Berti, M. Colonna, M. Fiorini, E. Binassi and D.J. Brunelle

41. Nonstoichiometric polymerization of polyimide by means of reaction-induced crystallization of oligomers
Kanji Wakabayashi, Shinichi Yamazaki, Kunio Kimura

42. FTIR investigation of the influence of diisocyanate symmetry on the morphology development in model segmented polyurethanes
Iskender Yilgör, Emel Yilgör, I. Guclu Guler, Emre Unsal and Garth L. Wilkes

43. Mechano-optical properties of polyetherurethanes with a symmetrical hard segment of uniform length
I. Yilgör, E. Yilgör, E. Unsal, B. Erman, M. Cakmak

44. Luminescent Nd\(^{3+}\) doped thermoplastic silicone-urea copolymers
Iskender Yilgör, Emel Yilgör, Ozgul Tezgel, Umit Demirbas, Alphan Sennaroğlu, and Adnan Kurt

45. Structure-property relationships and melt rheology of segmented, non-chain extended polyureas: Effect of soft segment molecular weight
Bora Inci, Iskender Yilgör, Emel Yilgör, Sudipto Das, Frederick L. Beyer, Garth L. Wilkes

46. Highly branched polyurea elastomers through oligomeric A\(_2\) + B\(_3\) approach
Seda Cakir, Emel Yilgör, Iskender Yilgör

47. Conjugated Polymer Systems for Optical Sensing and Patterning
Taek Seung Lee, Tae Hyeon Kim, Tae Hoon Kim, Moon Soo Choi, Hyung Jun Kim, Chan Gyu Kwak, Jung Hyo Lee, Chi-Han Lee

48. Synthesis and Characterization of a Fullerene Based Copolymer
N. Marangoci, A. Farcaș, M. Pinteala, V. Harabagi, B. C. Simionescu
Lecture Abstracts
**Multicyclic polymers by “a₂ + b₃” polycondensations**

Hans R. Kricheldorf, Lali Vakhtangishvili, Nino Lomadze and Gert Schwarz

*Institut für Technische und Makromolekulare Chemie,*
*Bundesstr. 45, D-20146 Hamburg, Germany*  
*kricheld@chemie.uni-hamburg.de*

Various activated difluoroaromatics were polycondensed with triphenols with optimization of the reaction conditions, so that gelation was avoided. Analogous polycondensations were performed with various diphenols and aromatic trifluoroketones. Soluble multicyclic polyethers, or in other words, soluble nanogels having molar masses up to $10^8$ Da were obtained. Multicyclic poly(ether ester)s were prepared from trimesoyl chloride and monodisperse oligo(ethylene glycol)s. These poly(ether ester)s were found to dissolve all alkalimetal benzoates in contrast to the highly selective crown ethers.

**References**


Preparation of Low (Zero) Wear Surfaces Based on Specially Designed Polyesters

James Economy

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University of Illinois at Urbana-Champaign
1304 W. Green St.
Urbana, IL 61801
jeconomy@uiuc.edu

Wear arising from the sliding of objects represents a major cost factor in the manufacturing and consumer industries. For example, wear in large aircraft brakes amounts to a replacement cost of $0.5 billion/yr. This problem was discussed at the previous Polycondensation Conference in Roanoke. It was shown that replacing the currently used C/C composite with a C/BN composite greatly reduced wear by a factor of 10x, and the cost of preparing the new composite was comparable to the currently used system. More broadly, in the USA it is estimated that $170 billion is lost annually due to excessive wear problems. In China 800,000 tons of steel are lost annually due to wear in the mining industry. For the near future the success of nano-devices with moving parts will require that wear at the interface be reduced to the smallest amount possible. Considering this background, it is surprising how little work is being done to design new materials with greatly improved wear resistance. In this paper I describe the following three new systems developed recently in our laboratory, namely:

1. A Polyester Lubricant for Hard Disc Drives (HDD)
2. Self-lubricated Polyester (ATSP) and Polytetrafluorine (PTFE) Composites and
3. ATSP and Ultra-high Molecular Weight Polyethylene for Use in Hip Replacements

Lubricants for HDDs

For a number of years, the perfluoropolyethers have dominated the HDD industry. They do introduce several problems including; (1) severe stiction in stop-start operations, (2) potential for spin-off at higher spindle speeds > 10,000rpm, and (3) instability to contact with the \( \text{Al}_2\text{O}_3/\text{TiC} \) head material leading to fragmentation. We have designed a low MW aliphatic polyester which is stable to concerns with decarboxylation and hydrolysis and which remains fluid at temperatures as low as -38 degrees C. Problems associated with spin-off and stiction appear to be greatly reduced. The dynamic and static coefficient of friction values are very similar to the perfluoropolyethers.

ATSP/PTFE Composites with Outstanding Wear Characteristics

Teflon is known to have a very low coefficient of friction but tends to wear very rapidly. Consequently, it has been shown that addition of small amounts of polyimide, graphite or PEEK will greatly enhance the wear properties of Teflon. We have found that we can prepare composites of ATSP and Teflon over the entire composition range using temperatures and pressure well below the conditions required for processing the Teflon. Thus, at temperatures of 325 °C we can prepare well solidified articles where the bonding is achieved primarily by the interchain trans-esterification of the cured polyester with particles accompanied by some flow by the Teflon. Such composites display excellent wear resistance bordering on zero
wear in many cases. The existence of zero wear is interpreted to mean that the debris formed during wearing is efficiently reincorporated back into the wear surface. Data are presented to demonstrate the effect of compatibilizers on the properties of the blends.

**ATSP/UHMWPE for use in Hip Replacement**

UHMWPE has been the material of choice for the bearing surface in hip replacements in the USA. Major problems include formation of wear debris and in certain cases loss of adhesion. Debris formation is especially serious, because of the particles with dimensions of 1 micron and below. Radiation crosslinking of the UHMPE is now being routinely used but it is still too early to tell what the problems might be. We have shown that blends of ATSP with UHMWPE can display significantly reduced wear characteristics using a compatibilizer of polyethyleneacrylate (PEA). Such blends not only display greatly improved wear characteristics but the debris formed tends to be in the range of > 1 micron and hence, not as prone to stimulate phagocytosis with localized chronic inflammation. Wear results are presented which demonstrate the advantages of these blends using pin on disc and dynamometer evaluations.
Poly(aryl ether)s by Nucleophilic Aromatic Substitution Using Unconventional Activating Groups

Daniel M. Knauss

Chemistry Department, Colorado School of Mines, Golden, CO 80401
dknauss@mines.edu

Several new types of poly(aryl ether)s have been produced by nucleophilic aromatic substitution (S$_{N}$Ar) utilizing activating groups that are not considered to be strong electron withdrawing groups. Two different approaches have been applied for the activation of monomers to S$_{N}$Ar: electron accepting heteroatom activation, and ring-opening Meisenheimer stabilization.

We have found that sulfur and selenium effectively activate S$_{N}$Ar by phenoxides to quantitatively substitute arylfluorides. Bis(4-fluorophenyl)sulfide, 2,7-difluorothianthrene, and bis(4-fluorophenyl)selenide have been investigated as monomers (Figure 1) in reaction with bisphenol A and other bisphenols. Reaction conversions greater than 98 percent are observed under typical S$_{N}$Ar reaction conditions using DMPU as solvent. The reaction mechanism is being studied along with the properties of the polymers and will be discussed. In the case of 2,7-difluorothianthrene, number average molecular weights in excess of 30,000 are found. The poly(aryl ether thianthrene)s are flame resistant and self extinguish within 0.2 seconds upon removal from a flame source. TGA of the poly(aryl ether thianthrene)s in an inert atmosphere result in a char yield greater than 50% at 750 °C. The poly(aryl ether thianthrene)s are found to have high refractive index values, 1.61-1.70, depending on wavelength and bisphenol composition.

![Figure 1. Monomers for heteroatom activation of nucleophilic aromatic substitution](image1.png)

We have also investigated an alternative type of activating group, which is proposed to activate substitution of arylfluorides by the formation of a ring-opened Meisenheimer complex intermediate from phthalide ring containing monomers (Figure 2). For this case, the mechanism and the results of polymerizations will also be presented.

![Figure 2. Monomers for ring-opening activation of nucleophilic aromatic substitution](image2.png)
Thermoplastic-thermosetting polyimides derived from asymmetric a-BPDA and aromatic diamine with pendent phenylethynyl groups

Rikio YOKOTA, Hiroyuki MORIUCHI, Yuichi ISHIDA

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Abstract

In order to develop high performance/high temperature structural adhesives, thermoplastic (before curing) and thermosetting (after curing) polyimides consisting of asymmetric 2,3,3’,4’-biphenyltetracarboxylic dianhydride (a-BPDA), 4,4’-oxydianiline (4,4’-ODA)(80%) and 2,4-diamino-1-(4-phenyl ethynyl- phenoxy)benzene having phenylethynyl groups in the side chain (m-PDAp) (20%) were prepared. For understanding to curing mechanism, the corresponding oligomers with different degree of polymerization: n=4, 8, and 16 having equal amount of concentration of terminal and/or pendent phenylethynyl groups were also prepared (Figure 1). As shown in Figure 2, temperature dependence of dynamic tensile properties for uncured polyimide indicated rather high Tg (290°C) and thermoplasticity (E’ drop > 10³ at Tg). After curing reaction of pendent phenylethynyl group, the Tg of the polyimide was increased dramatically (385°C). Furthermore, the Tg cured at 430 °C increases with the increasing degree of polymerization of those oligomers as Tg= 343 °C: TriA n=4, Tg= 361 °C: TriA-P8 n=8, Tg= 364 °C: TriA-P16 n=16(Table 1). Although, absolute concentration of phenylethynyl groups in TriA n=4 oligomer is larger than that of PI-P, Tg of the polyimide: PI-P is 41 °C higher than Tg of TriA. It means that the cure reaction in imide oligomer TriA which contains phenylethynyl groups as the only terminal groups proceeds mainly to chain extension, while the pendent phenylethynyl groups in the side chain of PI-P may form inter- or intra-molecular crosslinking. Table 2 shows mechanical properties of the polyimide cured. This paper also will discuss the effect of flexibility of diamine structures with pendent phenylethynyl groups.

Figure1  Polyimide oligomer and polymers containing terminal and/or pendent phenylethynyl groups
Table 1. Tgs of thermoplastic-thermosetting polyimides and oligomers : TriA-PI

<table>
<thead>
<tr>
<th></th>
<th>Tg(℃) by DSC</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>uncured</td>
<td>370℃</td>
<td>400℃</td>
<td>430℃</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(250℃ )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TriA</td>
<td>220</td>
<td>339</td>
<td>340</td>
<td>343</td>
<td></td>
</tr>
<tr>
<td>TriA-P8</td>
<td>239</td>
<td>344</td>
<td>354</td>
<td>361</td>
<td></td>
</tr>
<tr>
<td>TriA-P16</td>
<td>ND(263℃)</td>
<td>349</td>
<td>362</td>
<td>364</td>
<td></td>
</tr>
<tr>
<td>PI-P</td>
<td>266(304℃)</td>
<td>355</td>
<td>371</td>
<td>385</td>
<td></td>
</tr>
<tr>
<td>PI</td>
<td>—</td>
<td>336</td>
<td>337</td>
<td>340</td>
<td></td>
</tr>
</tbody>
</table>

ND : not detected  a : +280℃/10min uncured  b : +300℃/10min uncured

Figure 2 DMA curves of polyimide films containing pendent phenylethynyl groups

Figure 3 DMA curves of polyimide and imide oligomer films containing pendent and/or terminal phenylethynyl groups

Table 2. Mechanical properties of cured polyimides and oligomers

<table>
<thead>
<tr>
<th></th>
<th>Modulus E (GPa)</th>
<th>Strength σ (MPa)</th>
<th>Elongation at break ε b (%)(max)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>430℃</td>
<td>430℃</td>
<td>370℃</td>
</tr>
<tr>
<td>TriA</td>
<td>2.69</td>
<td>107</td>
<td>21.6</td>
</tr>
<tr>
<td>TriA-P8</td>
<td>2.64</td>
<td>114</td>
<td>13.2</td>
</tr>
<tr>
<td>TriA-P16</td>
<td>2.73</td>
<td>119</td>
<td>10.5</td>
</tr>
<tr>
<td>PI-P</td>
<td>2.85</td>
<td>126</td>
<td>13.3</td>
</tr>
<tr>
<td>PI</td>
<td>2.64</td>
<td>103</td>
<td>89.0</td>
</tr>
</tbody>
</table>

1) R.Yokota et al, Polymer, 46, 6968-6975, 2005
Hyperbranched polymers have been paid attention because of their unique structure. Especially, they have many terminals whose number is the same of that of repeating units as far as they are synthesized from AB$_2$ type monomers. These characteristics of the hyperbranched polymers make them new functionalized polymers. Polysiloxanes have unique properties such as low Tg, high decomposition temperature, water repulsion, and good dielectric property. They are widely fabricated from liquid (oil) to solid (resin) by changing the extent of crosslinking. We have studied dendrimers and hyperbranched polymers possessing polysiloxane structure.

Hyperbranched polysiloxysilanes are easily synthesized as shown in eq. 1, and have the similar structure to hyperbranched polysiloxane. Hyperbranched polysiloxysilane (2) with a vinyl terminal was synthesized starting from AB$_2$ monomer (1) possessing one Si-H and two vinyls. The polymerization was carried out by the hydrosilylation reaction in the presence of platinum catalysts. The polymer was growing by the connection of silicon atom and a carbon of the vinyl group. Hyperbranched polysiloxysilane (2) was colorless liquid having the molecular weight of 6000. The terminal vinyl group of (2) can be converted to various functional groups as shown in Scheme 1. Especially, hyperbranched polysiloxysilane possessing carboxylic acid functional group was soluble in basic aqueous solution. It was interesting that polysiloxysilanes hyperbranched polymers had strong affinity to inorganic surface such as glass and silica gel surface. For instance, epoxy group terminated polysiloxysilane hyperbranched polymers act as a good dispersion reagent for inorganic particles. Furthermore, triethoxysilyl group was introduced at the focal point of polysiloxysilane hyperbranched polymers to increase ability for adhesion to the inorganic surface. This is a technique to control the molecular weight by adding mono-vinyl functionalized reagent to the polymerization system.
Polysiloxy silanes hyperbranched polymers having various functional terminal groups were synthesized. As they have good adhesive property with inorganic surface, they are good candidates for polymer brushes to modify the surface. In the lecture, recent results including POSS terminated polysiloxy silane hyperbranched polymers will be presented.
Catalyst-Transfer Condensation Polymerization: Synthesis of Well- Defined \(\pi\)-Conjugated Polymers

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We have reported that the polycondensation of 2-bromo-5-chloromagnesio3-hexylthiophene (1) with Ni(dppp)Cl\(_2\) proceeds in a chain polymerization manner to yield head-to-tail poly(3-hexylthiophene) (HT-PHT) with low polydispersities and that the \(M_n\) of HT-PHT is controlled by the feed ratio of 1 to Ni catalyst (Scheme 1). In this paper, we study the polymerization mechanism by analysis of the chain ends of HT-PHT.

![Scheme 1](image)

On the basis of MALDI TOF-MS analysis of the polymer obtained by quenching with 5M HCl, one of the chain ends was confirmed to be Br and the other was H. When 3,4-dimethylphenylmagnesium chloride was added to the reaction mixture before quenching the polymerization, the obtained polymer had the dimethylphenyl group at both ends. These results indicated that the propagating group of the polymer is a polymer-Ni-Br complex. The \(^1\)H NMR intensity ratio of the chain end groups to that of the repeating units revealed that one polymer chain formed per single Ni molecule. Consequently, we have proposed a catalyst-transfer polymerization mechanism (Scheme 2). As an initiation step, Ni(dppp)Cl\(_2\) reacts with 2 equivalents of 1, and the coupling reaction occurs with concomitant generation of a zero-valent Ni complex. Then the Ni(0) complex inserts the intramolecular C-Br bond without diffusion, and reacts with another 1. Growth would continue in such a way that the Ni catalyst moves to the terminal C-Br bond without diffusion after the coupling reaction of the polymer end group and monomer 1.

![Scheme 2](image)

Other monomers leading to well-defined \(\pi\)-conjugated polymers via the above mechanism will be also reported.
High Tg polymers with monodisperse crystallizable segments

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High Tg polymers are usually amorphous polymers with excellent mechanical properties but a poor solvent resistance. Sometimes these polymers can be made to crystallize but the melting temperatures are excessively high and due the high melt viscosity the crystallization rates very low. New is the modification of these polymers with monodisperse crystallizable segments. Monodisperse crystallizable segments crystallize extremely fast and to a large extend. For the crystallization of these segments the melting temperature need not to be very high and the Tg/Tm ratios can in the order of 0.75-0.85. For improvement in dimension stability and solvent resistance of the high Tg polymers the concentration of the mono disperse crystallizable segments need not be high, even a few wt% is already effective.

The unusual behavior of these mono disperse crystallizable segments is demonstrated on poly(phenylene ether) (PPE), a polymer with a Tg of 210°C.
Introduction

Polyfluorene is being considered by many research and industrial groups as a very promising blue light-emitting material due to the chemical and thermal stability, high photoluminescence quantum efficiency and ease of property tunability through structural modification of the 9-position of the fluorene ring\(^1\). Conventional manufacturing processes apply the active polymer layer by solvent deposition or evaporation, and achieve patterning via a number of complex low resolution (> 20 um) methods including, shadow masking, ink-jetting, photolithography, silk-screening, patterned sublimation source, microfluidics, and contact stamping techniques. Similar patterning schemes have been employed in the patterning of semiconducting polymers for electronic applications. Most of the aforementioned techniques are low resolution with minimum feature size possible ranging from in the tens of microns to hundreds of nanometers in the best cases. Many techniques rely on complex lithographic processes that limit the types of materials that can be employed. Non-traditional high-resolution contact patterning techniques including nanoimprint lithography and UV-Assisted imprint lithography have received continual attention. Additionally a number of surface-bound “living” polymerization techniques have been successfully employed to give surface-grafted polymers under controlled growth conditions.\(^2\)

Previously we have reported novel nano-contact molding techniques for the replication of nanometer-scale features on surfaces utilizing functional crosslinked polymeric materials.\(^3,4\) An advantage of this technique compared with other available methods is precise control of the chemistry of the patterned areas through surface modification and incorporation of reactive functionality into the crosslinked polymers. We have shown that complex functionality can be obtained by the covalent incorporation of functional inimers (having both an initiator and monomer fragment) for “living” free radical polymerization into the photopolymer matrix. Controlled “living” radical secondary brush polymerizations of styrene, acrylates and other vinyl monomers from embedded inimer sites yield a polymer brush surface that offers the ability to adjust imprinted feature size and chemical functionality in the nanometer-size regime.\(^4\) As a result the surface properties of the patterned substrate can be radically altered.
Recently we began to investigate the growth of other types of polymer brushes by utilizing metal-catalyzed polycondensations of aromatic bromides.\textsuperscript{5} Bromostyrene was incorporated into the crosslinked patterned surfaces and subsequently polyfluorene brushes were grown from the surface by the Ni(0)-mediated step-growth polymerization of 2,7-dibromo-9,9-di-n-hexylfluorene. These condensation polymerizations were performed primarily on patterned surfaces with feature sizes in the 100nm range. A range of surface analytic techniques, including UV and fluorescence spectroscopy, fluorescence microscopy, contact angle, surface profilometry, and AFM, confirmed surface growth of brushes. This is one of the few studies of surface initiated polycondensation reactions from functionalized polymer surfaces. The patterned areas displayed the expected UV absorption and fluorescence behaviour expected, though no in-depth study of the electroluminescent behaviour was made. We have also initiated preliminary work on the growth of polythiophene brushes utilizing a similar approach via Grignard metathesis polymerization (GRIM) of 2,5-dibromo-3-hexylthiophene from patterned surfaces.\textsuperscript{6}

We have recently completed studies showing the utility of microwave heating to promote the efficient attachment of polyfluorene grafts from functional surfaces.\textsuperscript{7} We are now able to graft polyfluorene layers up to 35 nm thick from patterned surfaces. The PL emission from a patterned film is shown in figure 1 and the emission spectra for a series of films are shown in Figure 2.

References


Polycondensation Reactions in Ionic liquids

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Ionic liquids (ILs) represent a class of neoteric solvents, having ionic structure [1]. They can be introduced as low melting organic salts and consist of bulky organic cations in combination with organic or inorganic anions. Typically ionic solvents are based on imidazolium cations:

\[ \text{C}(\text{R}_1\text{R}_2^+)\text{Y}^- \]

\( \text{Y}^- = \text{NO}_3^-, \text{NO}_2^-, \text{BF}_4^-, \text{PF}_6^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{ClO}_4^-, \text{SbF}_6^-, \text{CF}_3\text{COO}^-, \text{CF}_3\text{SO}_3^- \) (inorganic anions)

\( \text{CF}_3\text{COO}^-, \text{CF}_3\text{SO}_3^- \) (organic anions)

The ability of high molecular weight condensation polymers formulation in such media was shown[2-4].

The combination of IL’s with activating agent - triphenyl phosphite (TPP) allowed to carry out polyamide and polyhydrazide syntheses by direct polycondensation of diamines and dicarboxylic acids or their bis-hydrazides, respectively. It was found that this reaction is successfully occurred out without any extra components which commonly use in ordinary organic solvents.

Scheme 1

The combination of IL’s with activating agent - triphenyl phosphite (TPP) allowed to carry out polyamide and polyhydrazide syntheses by direct polycondensation of diamines and dicarboxylic acids or their bis-hydrazides, respectively. It was found that this reaction is successfully occurred out without any extra components which commonly use in ordinary organic solvents.
This paper describes also the study of a new, convenient synthesis of aromatic poly-(1,3,4-oxadiazole)s (PODs) from dicarboxylic acids and/or their bishydrazides or hydrazine’s salts (sulfate, phosphate) under influence of IL/TPP mixture:

\[
\begin{align*}
\text{Ionic Liquid, TPP} & \quad n \text{ HOOC—X—COOH} \\
\text{Ionic Liquid, TPP} & \quad n \text{ H}_2\text{NNH}_2 \ast \text{H}_3\text{PO}_4 \text{ or } \text{H}_2\text{SO}_4
\end{align*}
\]

The polycyclization occurred at sufficiently low temperature equal to 210°C for 2 - 5 hours and the resulting polymers were easily isolated from reaction solution without any hydrolytic degradation. Obtained polymers have inherent viscosities up to 0.9 dl/g and good thermal stability (400°C). Organosolubility and films properties of PODs synthesized in ionic media were thoroughly investigated. PODs containing cardo groups are amorphous and characterized by excellent solubility and film forming ability.

Thus suggested method allows convenient “one pot” preparation of aromatic PODs by using ecologically friendly media instead of significantly more toxic and corrosive solvents, such as oleum, PPA and PPMA.

Acknowledgments

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References

Hyperbranched polyimide-silica hybrids for gas separation membrane

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1. Introduction

Aromatic polyimides have been widely used in the microelectronics and aerospace fields due to their excellent properties. Organic-inorganic hybrids are attractive materials since they generally possess desirable organic and inorganic characteristics such as heat, mechanical, and electrical advantages. Polyimide-silica hybrid materials have also been studied to develop advanced materials with polyimide and silica characteristics. Almost of them, however, are based on linear polyimides. Recently, dendritic polymers (dendrimers) and hyperbranched polymers have been developed and drawn considerable attention as high performance materials because of their unique physical and chemical properties and multifunctionality. In this study, novel hyperbranched polyimide (HBPI)–silica hybrids and terminal-modified HBPI–silica hybrids were prepared by one-step polycondensation using a dianhydride (4,4’-(hexafluoroisopropylidene)diphthalic anhydride (6FDA)) and a triamine (1,3,5-tris(4-aminophenoxy)benzene (TAPOB)) followed by sol-gel reaction, and their physical and gas transport properties were investigated.

2. Experimental

2.1. Polymerization of 6FDA-TAPOB hyperbranched polyamic acid

6FDA was dissolved in DMAc in a 100 ml three-neck flask under N₂ flow at room temperature. To this solution, TAPOB dissolved in DMAc was added dropwise through a syringe with stirring. After that, 3-aminopropyltrimethoxysilane (APTrMOS) was added in the reaction mixture to afford 6FDA-TAPOB hyperbranched polyamic acid. The residual anhydride terminal groups were modified to react with 3,5-bis(trifluoromethyl)aniline (6FMA) or 1H,1H-heptadecafluorononylamine (17FN).

2.2. Membrane formation

Appropriate amounts of water and TMOS were added in the DMAc solution of the polyamic acid. The mixed solution was stirred for 24 h and cast on a PET sheet and dried at 80 ºC for 2 h. The prepared membrane was peeled off and subsequently imidized at 100 ºC for 1 h, 200 ºC for 1 h, and 300 ºC for 1 h in a heating oven under N₂ flow.

2.3. Measurements

Infrared (IR) spectra were recorded on a JASCO FT/IR-460 plus. Thermogravimetric-differential thermal analysis (TG-DTA) experiments were performed with a Seiko TG/DTA6300 at a heating rate of 10 ºC/min under airflow. Gas permeability coefficient, \( P \) [cm³(STP)cm/cm²sec.cmHg], was determined by the vacuum-pressure method. The permeability coefficient can be explained on the basis of the solution-diffusion mechanism, which is represented by the following equation;

\[
P = D \times S
\]

where \( D \) [cm²/sec.] is the diffusion coefficient and \( S \) [cm³(STP)/cm³polym.cmHg] is the solubility coefficient. The diffusion coefficient was calculated by the time-lag method.

3. Results and Discussion

Figure 1 shows the scheme of hyperbranched polyimide (HBPI)–silica hybrids. FT-IR measurements for the HBPI – silica hybrids were carried out to confirm progresses of thermal imidization and hybridization. The bands observed around 1784 cm⁻¹ (C=O asymmetrical stretching), 1725 cm⁻¹ (C=O symmetrical stretching), 1378 cm⁻¹ (C–N stretching), and 723...
cm\(^{-1}\) (C=O bending) are the characteristic absorption bands of polyimides [1]. It is also found that the band observed around 1080 cm\(^{-1}\) which is assigned to Si–O–Si vibration increases with increasing silica content in the hybrids, indicating sufficient formation of the three-dimensional Si–O–Si network.

The thermal properties of the hybrids were investigated by TG-DTA measurements. The thermal decomposition temperature (\(T_d\)) and glass transition temperature (\(T_g\)) considerably increase with increasing silica content. This fact suggests effective intermolecular crosslinking mediated by APTrMOS moiety is formed in the HBPI – silica hybrids.

The relationship of gas permeability coefficients and CO\(_2/\)CH\(_4\) selectivity (\((\text{CO}_2/\text{CH}_4)\)) are shown in Figure 2. It can be said that gas permeability coefficients of terminal-modified HBPIs are higher than those of original HBPI. This result can be attributed to the increase in the fractional free volume (FFV) by the introduction of bulky groups into molecular chain terminals. The gas permeability increases with increasing silica content. This fact suggests additional formation of free volume holes by the incorporation of silica [2].

CO\(_2/\)CH\(_4\) selectivity of the hybrids increased with increasing the silica content. The remarkable CO\(_2/\)CH\(_4\) separation behavior of the hybrids is considered to be due to characteristic distribution and interconnectivity of free volume holes created by the incorporation of silica.

6FDA-TAPOB HBPI – silica hybrids and the terminal-modified 6FDA-TAPOB HBPI – silica hybrids have good thermal stability, high gas permeability, and remarkable CO\(_2/\)CH\(_4\) selectivity, and are expected to apply to high-performance gas separation membranes.

![Figure 1](image1.png)

Figure 1 Scheme of hyperbranched polyimide-silica hybrids

References
Cataract extraction is among the most commonly performed operations in the world. In this operation the natural lens is removed and replaced with an artificial intraocular lens (IOL), which will mimic the transparency and the refractive function of a natural lens. The intraocular lens is implanted or inserted into the capsular bag using a simple surgical procedure. To further improve the technique of IOLs, the size of surgical incisions can be reduced below ca. 1.5 mm by using an injectable ophthalmic composition. Here the original lens material is removed from the capsular bag, then a low viscosity lens precursor is injected directly into the empty capsular bag, Figure 1, and cured \textit{in situ} as a part of the surgical procedure. The capsular bag is thus used as a mould to shape the lens. Therefore, the precursor material should be bio-inert, fast curable \textit{in vivo} and transparent. In addition a precursor polymer with a higher density than water would facilitate the complete refilling of the capsular bag by injection, thus avoiding surgical problems from flotation of material.

\textbf{Figure 1. Extraction of the opaque lens is followed by injection of the siloxane precursor that cures to the final synthetic lens using the capsular bag as the mould.}

Copolymerisation of different siloxane monomers gives silicone materials which can fulfil the above criteria for injectable IOL materials. In this paper we present the controlled synthesis of $\alpha,\omega$-dihydroxylhexyl-terminated poly(dimethyl-co-diphenyl-co-methyltrifluoropropyl-siloxane) terpolymers, Scheme 1, which are intermediates for the photocurable injectable IOLs. This synthesis allows preparation of polymers with refractive index in the range of the human eye and a density higher than one. Extraction of the old lens, injection of the new and curing can now be performed with minimal invasive techniques, i.e. through a syringe, within minutes.
Lens removal with an artificial lens implantation provides significant benefits to most cataract patients. However, it is estimated that up to fifty percent of all patients, who have implants placed within the capsular bag, will develop capsular opacification (CO), also known as secondary cataract or “after cataract”, within five years after surgery. CO is caused by unwanted growth of cells at the interface between the lens and the eye, which will cloud the vision. We therefore designed an amphiphilic block copolymer that adheres to the capsular bag and to the injectable siloxane lens to bridge the lens-capsular bag interface. This close connection prevents and/or reduces the unwanted growth of cells since there is no space for them to grow. Furthermore the amphiphilic block copolymers will improve the adhesion between the capsular bag and the intraocular lens, which may improve the accommodation of the lens and capsular bag.

The block-copolymer synthesis involves the preparation of \(\alpha,\omega\text{-isothiocyanate-poly(ethylene oxide)}\) and \(\alpha,\omega\text{-diamino-propyl-terminated poly(dimethyl-co-diphenyl-co-methyltrimfluoropropylsiloxane)}\) terpolymer as precursors followed by their polycondensation, Scheme 2. These bloc-copolymers terminated with isothiocyanate PEG were stable in water and could be reacted to modify surfaces of both collagen models and cadaver capsular bags to significantly improve interfacial adhesion between tissue and the siloxane.
Monomers reactivity and steric factors affecting the synthesis of aromatic polyamides and polyimides

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The most usual route to the preparation of wholly aromatic polyamides and polyimides is the low-temperature polycondensation in polar organic solvents of aromatic diamines with diacyl chlorides or dianhydrides respectively. Early works also demonstrated that aliphatic amides could be prepared in excellent yield from N-trimethylsilyl-substituted aliphatic amines and acid chlorides [1], and Katsarava et al demonstrated that the synthesis of aromatic polyamides could be improved on substituting aromatic diamines by the more reactive silylated diamines in 1985 [2]. With regards to polyimides, the first synthesis of aromatic polyimides by the “silylation” method was reported by Boldebuck and Klebe [3] in the patent literature in 1967 and later by Korshack and his group in the synthesis of aliphatic-aromatic polyimides [4].

The main disadvantage of using silylated diamines as condensation monomers is their great ability to hydrolyze, which makes it difficult the isolation and purification of these monomers. An approach to overcome this limitation is the in situ preparation of silylated diamines just by adding trimethylchlorosilane (TMSCl) to the diamine solutions. The method shows two additional advantages regarding the use of previously synthesised silylated diamines: 1) the presence of TMSCl ensures that small amounts of water do not hydrolyze the moisture-sensitive diacid chloride or dianhydride, and 2) the handling of silylated diamines is highly simplified and the polyamidation procedure too.

In the course of many works on aromatic polyamides and polyimides, we have found that there is not a general rule that applies for all the systems, and so, sometimes unexpected results have been attained on using the silylation method. These results prompted us to investigate the effect of some promoters of polycondensation through the activation of diamines. Very few modern examples show the use of organic bases, such as pyridine (Py) or the Py/TMSCl pair with this purpose, so that, a study was outlined to make clear the effect of these promoters on the polycondensation of a set of aromatic diamines of very different chemical nature.

Five diamines were used in this study: oxydianiline, with an electron donating hinge linkage; sulfonyledianiline and hexafluoroisopropylidenedianiline, with electron withdrawing groups; and 4M and DDM with similar reactivity to that of aniline but with very different geometry. They were combined with isophthaloyl chloride (polyamides) and with hexafluoroisopropylidene diphthalic anhydride (polyimides).

The molecular weight achieved in any case could be related with the effect of diamines reactivity and polycondensation promoters.

References

Renewable polyesters for powder coating applications

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Abstract

Polyester resins containing terephthalic and isophthalic acid residues are widely used in the powder coating industry. The monomers used in their synthesis originate from fossil feedstock. The objective of this work is the development of bio-based resins (and networks thereof) that can compete with the conventional materials with respect to mechanical properties and chemical stability.

From corn to coatings

Several renewable monomers were used, such as isosorbide and its isomers, affording the chain rigidity required for obtaining the desired relatively high glass transition temperatures for the targeted polyesters, even for relatively low molar masses. These dianhydrohexitols are aliphatic and are therefore expected to be less susceptible to discoloration by UV radiation than the classical aromatic systems. Other sustainable monomers used in this study are adipic acid, succinic acid, tartaric acid, 2,3-butanediol and 1,3-propanediol. Series of clear, slightly yellow polyesters were obtained through tetrabutyltitanate catalyzed polycondensation in bulk at 180 – 250 °C, with either acid or hydroxyl functionality.

Example of a renewable polyester
The glass transition temperatures of the synthesized polyesters strongly depend on the dianhydrohexitol content. The $T_g$ range from 40 up to 80 °C (for polyester number average molecular weights between 2500 and 5000 g/mol) is suitable for the envisioned application.

The linear polyester resins could also be end-capped with multifunctional monomers, such as citric acid, affording polymer chains with enhanced functionality. In this way, network formation with commercially available curing agents was improved significantly. The different resins were subsequently used to formulate and apply coatings from solution as well as by using the powder coating technique. Initially, several classical cross-linking agents, both for hydroxyl and carboxylic acid functionalized polyesters, were selected in order to compare the renewable systems with conventional (powder) coatings. The coatings were cured at 200 °C under $\text{N}_2$ flush, which led to slightly yellow transparent films with good solvent resistance, gloss, adhesion to aluminum and toughness. We are currently developing sustainable curing agents to create a fully renewable system.

This project is sponsored by the Dutch Polymer Institute.
Polycondensation polymers of natural and synthetic origin as biomedical materials

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Polymers used as biomedical materials are numerous. This is because the properties of the natural tissue and the polymers of synthetic and natural origin are quite similar, and modification of these polymers through a variety of routes helps us create the optimum biomaterials. A large fraction of these polymers are produced through condensation reactions. Among these are the synthetic polymers such as silicones, polyurethanes, polyglycolides, polylactides and their copolymers, polyanhydrides, polycaprolactone, and natural polymers such as polyhydroxalkanoates (polyhydroxybutyric acid (PHB), poly(hydroxybutyric acid-co-hydroxyvaleric acid) (PHBV), etc.), proteins (collagen, gelatin), and polysaccharides (alginites, hyaluronic acid, chondroitin sulfate, cellulose, starch). The main advantage of using these polymers in biomedical applications is their degradability in a reasonable duration (from weeks to a few months) and the compatibility of their degradation products. This property makes them ideal for the construction of controlled release systems, degradable sutures and similar applications and for tissue engineering.

In this paper two tissue engineering applications of polycondensation polymers will be described. In the first of the studies the effect of microscale topographical and chemical cues on the morphology, proliferation and differentiated phenotype expression level of osteoblasts derived from mesenchymal stem cells of rat bone marrow was investigated on poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV8). Silicon templates with parallel grooves (groove width: 2 µm, groove depth: 30 µm, ridge width: 10 µm) and micropits (ridge width: 10 µm x 10 µm and 20 µm x 20 µm alternating, groove width: 4 µm, groove depth: 5 µm) were prepared by photolithography, and PHBV films were prepared on these templates by solvent casting. Fibrinogen (Fb), was selected as a chemical cue for cell adhesion and was allowed to adsorb inside the grooves and pits of the films. Covalent immobilization of alkaline phosphatase (ALP), an important enzyme in bone remodeling and formation, in the grooves and pits of PHBV films was also done to induce natural calcium phosphate deposition on the films via ALP enzymatic activity. It was observed that untreated polymeric surfaces were not suitable for cell attachment. Chemical modification (Fb adsorption and calcium phosphate deposition via ALP activity) of film surfaces improved cell attachment, evenness of cell distribution and proliferation (close to tissue culture polystyrene). The cells on all Fb adsorbed and Ca-P deposited microgrooved films were aligned parallel to the groove axis, latter showing a higher deviation angle (Fig.1a). No particular cell confinement was detected on the micropitted films; cells were randomly distributed as on the unpatterned films. Collagen type I deposition (at 2 weeks) seemed to imitate the pattern on the film surface and was most intense on the Fb adsorbed PHBV films (Fig.1b). The highest ALP activity per
sample (2 weeks) was obtained on the Fb adsorbed microgrooved PHBV films, indicating that aligned morphology of osteoblasts improves their function.

Figure 1. Osteoblast morphology on (a) Fb-adsorbed, microgrooved PHBV films (Acridine Orange staining, x150), and (b) collagen type I deposited on Fb-adsorbed, microgrooved PHBV films (2 weeks post seeding) (indirect immunostaining, x 75).

In the second, nerve tissue engineering, application films of PHBV, PLLA and their blend were used to investigate the effect of protein adsorption and micropatterning on the morphology, alignment and proliferation of mouse neural stem cells (NSCs) (ATCC). SEM and MTS results showed that the presence of fibronectin on polymeric films enhanced the attachment and growth of NSCs and the presence of micropatterning affect the organization and growth of NSCs on polymeric surfaces (Fig.2). NSCs on the unpatterned surfaces were distributed randomly (Fig.2a), whereas on micropatterned polymeric films the cells were found in and at edges of the grooves and had a tendency of alignment along the grooves (Fig.2b). It was revealed that there was no significant difference in morphology and alignment of cells when different types of polymeric films were used; however, NSCs were higher in number on micropatterned PHBV-PLLA films.

Figure 2. SEM of NSCs on fibronectin adsorbed, PHBV films of (a) unpatterned, and (b) micropatterned surfaces (after 3 days in culture)

Acknowledgements

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Negatively charged polymers are dedicated to function as proton exchange membranes for polymeric fuel cells. In general, as higher the negative charge of the polymer per volume unit a higher conductivity should be generated. To abandon special effects, such as water channel forming with Nafion®, the upper limit of the amount of negative charge is given by its solubility in water. With hydrogen as fuel the water generated as by-product will significantly soften the membrane, and with methanol as fuel (typically diluted by water to ca. 3%) the membrane may even disintegrate. The task of this paper is to identify polymers as backbones to generate negative charges evenly distributed within the membrane volume.

A Mexican group [1] reported recently on polymers prepared by an uncommon route, promising polymers with good mechanical and oxidation stability as may be concluded by the structure. Following this route a variety of polymers are available as shown in Scheme 1. Sulfonation and phosphonation of selected polymers was performed and their proton conductivity detected. As a result at the same degree of sulfonation the more compact distribution of sulfonic acid groups of polymer 1a showed a higher proton conductivity compared to polymer 1b. The mechanical properties of the polymers at a sulfonation degree of 66% were excellent.

Recursive Probability Approach of the Average Degrees of Polymerization and Molar Masses of Hyperbranched Condensation Polymers

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In the early 50's, Stockmayer\(^1\) derived a general expression for the chain length distribution (CLD) of condensation polymers obtained by reacting mixtures of A\(_f\)-type monomers with B\(_g\)-type monomers, using a combinatorial and statistical approach that assumes the equal reactivity of all A- and B-groups and the absence of intramolecular reactions. Explicit expressions of average degrees of polymerization, average molar masses and polydispersity index \((I_p)\) were obtained from CLD statistical moments. However, this approach was not extended to mixtures of monomers bearing both A- and B-groups, as those used in hyperbranched polymer synthesis. At the same time, Flory\(^2\) calculated the CLD and average degrees of polymerization of AB\(_2\)-type condensation polymers by a similar approach, introducing the concept of hyperbranched polymers. Although some authors quite recently derived the CLD and average DP's of AB\(_2\)-type, AB\(_3\)-type and AB\(_2\)+B\(_3\)-type polymers using kinetic approaches or Monte-Carlo simulations\(^3,7\), only quite simple hyperbranched polymerizations have been examined so far, either by the combinatorial or the kinetic approaches. Applying these approaches to systems involving several types of monomers bearing both reactive A- and B-groups would obviously lead to complex expressions, difficult to generate and to apply to practical cases. This probably explains why explicit expressions of the theoretical mass-average degree of polymerization and polydispersity index of even very simple hyperbranched polymers, such as those obtained by reacting AB\(_2\)-type monomers with B\(_g\)-type core-molecules, have not yet been established.

In 1976, Macosko and Miller introduced the "in-out" recursive probability approach of nonlinear polycondensations and applied it to reactions involving monomers with reactive A-groups and monomers with reactive B-groups. They derived average degrees of polymerization and molar masses and other average properties in a quite simple way, but did not consider the case of monomers bearing both A- and B-groups.\(^8\)

Here, we extend this approach to the most general case, i.e. the polycondensation of mixtures of polyfunctional monomers bearing A- and/or B-groups, assuming equal reactivity of all A- and all B-groups and the absence of side reactions such as cyclizations (Flory's assumptions).

The recursive probability approach is based on the determination of the number of monomer units (i.e. the DP of the branch) "seen" by random A- and B-groups, either reacted or nonreacted ones, looking "out" and "into" the monomer unit to which they belong (Scheme 1).
Applying elementary statistical laws to the "in-out" equations relative to such systems, we derived a general explicit relationship between the mass-average degree of polymerization ($DP_w$), conversions $p_A$ and $p_B$ relative to A- and B-groups and various average functionalities relative to the initial monomer mixture. We present below the expressions giving the average degrees of polymerization of $AB_f + B_g$ polycondensation polymers. This case is important in practice, as most hyperbranched polymers are synthesized by polymerizing mixtures of $AB_f$ monomers (e.g. 2,2'-bis(hydroxymethyl)propanoic acid, $AB_2$) and multifunctional core molecules $B_g$ (e.g. pentaerythritol, $B_4$). If 1 mol $AB_f$ monomer and $x$ mol $B_g$ core molecule are reacted, the general relationships simplify to:

$$\frac{DP^P}{DP^W} = \frac{1 + x}{1 + x - p_A} \quad (1)$$

$$\frac{DP^P}{DP^W} = 1 + \frac{2p_A(f + gx)[f(1 - p_A) + gx] + p_A^2[f(f - 1) + gx(g - 1)]}{(1 + x)[f(1 - p_A) + gx]^2} \quad (2)$$

It is easy to check that equation (2) reduces to the well-known Flory equations in the case of $AB$ linear polycondensations ($x = 0, f = 1$) and $AB_f$ hyperbranched polycondensation ($x = 0$), and that the polydispersity index of "star" copolymers obtained by $AB + B_g$ polycondensations is close to $1 + 1/g$ when $p_A \rightarrow 1$ and $x \rightarrow 0$, another result of Flory. The variations of $I_p$ calculated from equations (1) and (2) versus conversion $p_A$ for some other model $AB_f + B_g$ polycondensations are plotted below (Fig. 1 and Fig. 2). The calculations of the average DP's and molar masses in the case of more complex polyadditions and polycondensations (taking into account the elimination of a condensation by-product) and the calculation of the conversion at the gel point in network polycondensations involving $AB_f$ monomers are also straightforward and will be discussed.

![Figure 1: Variation of polydispersity index $I_p$ versus conversion $p_A$ during the polymerization of 1 mol $AB_f$ with 0.02 mol $B_g$. $f = 1, 2, 3, 4, 6, 8$.](image1)

![Figure 2: Variation of polydispersity index $I_p$ versus conversion $p_A$ during the polymerization of 1 mol $AB_2$ with 0.02 mol $B_4$. $g = 1, 2, 3, 4, 5, 6, 20$.](image2)

**References**

In 1982 a paper on a novel type of siloxane copolymers was published [1]. Despite their interesting properties widespread commercialization was achieved only more than quarter of a century later by Wacker Chemie AG under the brand name of Geniomer® [2].

The key factor to large scale production was the synthesis of a novel cyclic silazane as building block for the synthesis of bis(aminopropyl) siloxanes [3].

The range of Geniomer® materials combines typical siloxane properties with thermoplastic processability [4].

Some applications of Geniomer® will be presented such as processing aid and modifier in thermoplastics or as injection molding material.

An outlook is given for new developments which comprise crosslinkable modifications as shown in the following scheme.


[4] EP 1,496,079 W. Ziche et al. (Wacker Chemie AG)
SYNTHESIS OF HYPERBRANCHED POLYIMIDES IN ACTIVE MEDIUM

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Hyperbranched polyimides are new kind of polymers, which are expected to combine the architecture and functionality of hyperbranched macromolecules and high thermostability of linear polymides. Recently, we have offered a simple approach for the synthesis of linear AB-type poly(ether imide)s (PEIs) based on aminophenoxyphthalic acids by the one-pot high temperature polycyclocondensation (HTPC) in “active medium” – molten benzoic acid [1]. “Active medium” plays the role of dehydration agent to form phthalic anhydride groups in situ, and a catalyst in acylation stage. Besides, molten benzoic acid is a non-toxic solvent.

Hyperbranched poly(ether imide) (PEI) and hyperbranched poly(thio imide) (PTI) have been prepared by the one-pot high temperature polycyclocondensation in benzoic acid medium at 140°C based on 4,5-bis-(3-aminophenoxy)phthalic acid (I) and 4,5-bis(4-aminophenylthio)phthalic acid (II). Hyperbranched PEI and PTI have weight average molecular weight $M_w=9000$ and 5000, logarithmic viscosity 0.12 dl/g and 0.11 dl/g, glass transition temperatures 230°C and 210°C accordingly.

PEIs and PTIs with different terminal groups were synthesized by the reaction between corresponding hyperbranched PEI and PTI (amino terminated) with maleic, phthalic and acetic anhydrides.

HB PEI thus obtained was found to form only brittle films, similar to other hyperbranched polymers because of the lack of chain entanglement. Combination of linear and hyperbranched macromolecules is a tool to obtain hyperbranched polymers with improved mechanical properties.

In this work, a series of hyperbranched co-PEIs and co-PTIs with controlled ratio of linear and branched units were prepared by copolycyclocondensation of monomers I and II under conditions mentioned above. 4-(3-aminophenoxy)phthalic acid (III) was used as AB monomer. Structure of co-PEIs was examined by FTIR, DSC, viscosimetry, turbidimetry, potentiometric analysis of amino groups. According to turbidimetry data, coPEIs have random distribution of AB and AB$_2$ fragments in macromolecule.

Polyurethanes in Medical Applications

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Polyurethanes are the most widely used materials in the design and production of blood contacting devices because of their inherent non-thrombogenic properties. They are known as a class of polymers which have ‘urethane linkage’ in their structure and are commonly prepared by the addition of a polyglycol to an isocyanate. In general, isocyanate components are aromatic molecules which give rigidity and hardness while polyglycol components form less rigid and soft parts. These segments are distributed in the polymer structure and create nano-domains which lead to elastomeric property. Polyurethanes can be tailored for many applications either by changing the chemicals used or by changing the molecular weight of the polyglycols or extender chains used to make the polymer.

In medical applications polyurethanes can be used in various forms such as tubing (catheters, parenteral solution tubing), films (dialysis membranes, skin dressings, tapes), fibers (suture material), coatings (cardiac pacemaker coatings) and foams (surgical sponges). Due to their excellent mechanical and flexure properties they are preferred especially in the production of cardiovascular devices. Polyglycol parts can be either ester or ether based polymers and generally ether based are preferred in medical applications since ester based ones are not hydrolytically stable. In general high molecular weight polymers -if not enzymatically degraded- are stable in biological media. Presence of catalysts, diluents, solvents, fillers, extenders, monomers etc. decrease biocompatibility since these molecules may leach out from the structure and cause severe allergic toxic or carcinogenic responses. Although it is accepted that polyurethanes are biocompatible and non-thrombogenic, still an intense research is going on alter the surface properties and increase biocompatibility. One very effective method used in surface modification is glow-discharge plasma technique, in which generally radiofrequency energy is applied at low pressures in the presence of a certain gas (which can also be a monomer gas) atmosphere.

In these studies, various polyurethanes were prepared by using different types of diisocyanates and glycols without addition of any ingredient such as chain extender, solvent or catalysts. Some of them were modified with oxygen or argon plasma application and their chemical, mechanical, thermal properties as well as their biocompatibilities were examined. It was observed that oxygen permeability increased as the soft segment content increased. The adsorbed protein levels decreased upon modification with plasma and protein adsorption was the lowest for oxygen plasma treated ones where albumin levels were higher than fibrinogen and gammaglobulin. Films prepared from toluene-diisocyanate and poly (propylene-ethylene) glycol did not cause any cell aggregation or fibrin formation except the ones which contained high amount of glycol. When the samples prepared by diphenylmethane-diisocyanate or hexamethylene-diisocyanate were brought in contact with blood no clotting was observed even after one hour of contact. Aging and accelerated aging did not cause any change in mechanical properties.
POLYCONDENSATION VIA MICROWAVE REACTION CONDITIONS

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Over the past 25 years, Microwave irradiation has found increasing interest as a powerful technique for the synthesis of number organic chemicals (1). If the main advantage of the synthesis under microwave is the short reaction time, better selectivity and yield are also often observed over the conventional heating conditions.

Concerning the synthesis of polymers the growing number of publications related to microwave-assisted synthesis includes polyaddition (2), step-growth polymerization (3) as well as metal-catalyzed polymerization (4).

In our efforts to develop a new approach for the preparation of aromatic and or heterocyclic polymers we have investigated the synthesis of poly aryl ethers and polyimides via microwave-assisted polymerisation. This presentation will address our recent advances.

References

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Macromolecules, 38, 687, (2005)
Abstract

New sulfonated condensation heterocyclic polymers – polyimides and polyphenylquinoxalines – for proton-exchanging membranes were prepared on the basis of new sulfonated monomers based on 2,4,6-trinitrotoluene (trotyl, TNT) derivatives.

Alternatively sulfonated polyphenylquinoxalines were prepared by the post-sulfonation of polyphenylquinoxalines prepared on the basis of TNT derivatives.

Along with the above-mentioned approaches sulfonated polyphenylquinoxalines were prepared via the branching reactions using poly-(4-fluorophenyl)-quinoxalines as starting polymers.

This work was supported by Russian Fundamental Investigations Foundation (Grants RFFI № 05-03-33181 and RFFI-OFI-a № 05-03-08164) and NATO (Grant № 981762)
Unusual Surface Properties Resulting from New Polyurethane Soft Blocks

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In well phase separated polyurethanes, the soft block occupies the surface. A strategy has been devised to leverage this thermodynamically driven surface concentration by creating unusual soft-blocks that provide novel surface properties.

A series of polyurethanes with novel copolymer soft blocks display a new surface phenomenon, contraphilic wetting: the dry surface is hydrophilic while the wetted surface is hydrophobic. A precursor polymer was prepared with copolymer soft blocks containing semifluorinated (trifluoroethoxy, 3FOx, or pentafluoropropoxy, 5FOx) and bromomethyl functional pendant groups with 2:1, 1:1, and 1:2 semifluorinated / bromomethyl ratios. The conventional hard block consists of isophorone diisocyanate (IPDI) and 1,4-butanediol (BD). A difference (\(\Delta C\)) between dry (68°) and wet (108°) contact angles of as much as 38° has been observed. Drying the coating (50°C) reversibly restores hydrophilic character. A model is proposed according to which contraphilic wetting is driven enthalpically by hydrogen bonding.

In a second area, new soft blocks containing alkylammonium side chains have been designed to mimic naturally occurring antimicrobial peptides. The biocidal action of new alkylammonium-functionalized soft blocks is under investigation. Thus far, the new compositions have been used as polyurethane polymer surface modifiers (PSMs) that are molecularly designed to surface-concentrate when added at low levels to conventional polyurethanes. The PSM modified polyurethanes are highly effective in killing the pathogenic bacteria Pseudomonas aeruginosa.

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Polycondensation of polyethylene terephthalate – a tool to design new materials

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Polyethylene terephthalate (PET) is one of the oldest and most important synthetic polymers, widely used for fibres and textiles, increasingly for packaging applications as bottles or films, but also as engineering plastic with high property level. Therefore, the synthesis of PET by direct or transesterification polycondensation in the melt has been intensively studied before (see, e.g. [1,2]).

We could follow the two-step transesterification process in the melt using dimethyl terephthalate (DMT) and ethylene glycol (EG) and different catalysts in a 2 L-stirring autoclave by using the ATR-FTIR in-line monitoring technique, described by Long [3]. We could show the start and the progress of the PET polycondensation by the reaction between DMT and EG and later we could clearly show the start of the transesterification reaction. However we cannot yet detect any of the known side reaction by this method.

The polycondensation of DMT and EG was also performed in the presence of high concentrations of layered silicates (sodium montmorillonite (MMT) and organically modified MMT) in order to succeed in an in-situ formation of a PET/MMT nanocomposite, which could afterwards be used as masterbatch for the preparation of polyester nanocomposites by melt compounding.

The transesterification polycondensation was furthermore used to incorporate special comonomer units which introduce functionality to the polyester chain. Two examples will be discussed in the lecture:

1. Substitution of DMT by a semifluorinated isophthalic acid methylester to generate a family of new semifluorinated polyesters and copolyesters:

   \[
   \begin{align*}
   &\text{O} \\
   &\begin{array}{c}
   \text{C} \\
   \text{O} \\
   \text{O} \\
   \text{C} \\
   \text{O} \\
   \text{(CH}_2\text{)}_n \text{O} \\
   \text{O(CH}_2\text{)}_{10}\text{(CF}_2\text{)}_9\text{CF}_3
   \end{array}
   \end{align*}
   \]

   \[p\]

2. Substitution of ethylene glycol by P-diols to create new phosphorous-containing polyesters for the improvement of flame retardance of polyesters:

   \[
   \begin{align*}
   &\text{O} \\
   &\begin{array}{c}
   \text{O} \\
   \text{O} \text{-(CH}_2\text{)}_n \text{O} \\
   \text{O} \text{-(CH}_2\text{)}_n \text{O} \\
   \text{O} \text{-(CH}_2\text{)}_n \text{O}
   \end{array}
   \end{align*}
   \]

   \[n\]

In the lecture the synthesis results achieved as well as the resulting properties of the new polymers will be discussed.
References
Perfluorocyclobutyl (PFCB) polymers are prepared from step-growth, free-radical thermal \([2+2]\) cyclodimerization of trifluorovinyl ethers (TFVE) (Scheme 1). The polymerization event produces a stereorandom, amorphous polymer possessing excellent processability. We have developed these fluoropolymers for a multitude of material applications. Our recent efforts have focused on preparing fluorinated aryl ether polymers from nucleophilic additions of functionalized bisphenols to TFVEs. This approach is modeled from a field of organofluorine chemistry that continues to be intensely studied. These fluoroelastomers exhibit low surface energy, thermal stability, chemical resistance, and the ability to thermally crosslink. Our recent efforts focus on PFCB and fluorinated aryl ether polymers that address limitations in optical, PLED, and fuel cell applications.

Bis-ortho-diynyl arene (BODA) monomers are tetrafunctional and therefore produce highly crosslinked networks via Bergman-like cycloaddition. Recent work has focused on preparing BODA fullerene composites, including the first radial addition to carbon nanoonions (CNOs), rendering soluble and processable materials. This added functionality is useful for producing organic charge transfer materials for photovoltaic applications.

Friedel-Crafts aromatic substitution reactions – alkylation and acylation are some of the most fundamental reactions in organic chemistry. Beyond this, they are widely used in polymer chemistry. Recent progress in the chemistry of electrophilic intermediates, especially the major contribution to this field by group of Nobel Prize Winner G. A. Olah, led to the superelectrophilic hydroxylation reactions, in which carboxonium intermediates react with Lewis or Bronsted acids to give extremely reactive dications.\(^1\) Recently, for the first time we reported applications of superelectrophilic chemistry for the preparations of novel, linear, high-molecular-weight polymers by reaction of carbonyl-containing compounds with non-activated aromatic hydrocarbons in a medium of trifluoromethane sulfonic acids.\(^2\) Calculations have shown that (i) involvement of superelectrophiles reduces activation and total reaction energies of the aromatic electrophilic substitution reaction, and (ii) that significant enhancement of the reactivity of carbonyl compounds can be achieved by the presence of electron withdrawing substituents, adjacent or relatively close to a carbocation center.\(^3,4\)

Exploration of these findings has allowed for the variety of superelectrophilic polymer-forming reactions to be performed.\(^5-7\)

The report presents a general overview of novel, superacids catalyzed polymer syntheses based on carbonyl containing compounds and non-activated aromatics. Examples of new polymer preparations and the properties of the polymers obtained are presented.

One-pot syntheses, cheaply available monomers and the promising properties of the new polymers that might be obtained will make superelectrophilic reactions a powerful tool in polymer chemistry.

References


Titanium alkoxides are catalysts of choice for the industrial melt condensation of poly(butylene terephthalate). Strict control on endgroup distribution for polyesters is utterly important, i.e. Influence of carboxylic endgroup concentration on hydrolytic stability.

Melt polymerization of poly(butylene terephthalate) as catalyzed by Ti (IV) butoxide and its influence on the endgroup distribution will be discussed. Within the maintained experimental conditions for melt polymerization a linear dependence of carboxylic endgroups in poly(butylene terephthalate) with Ti (IV) butoxide concentration is observed. As polymerization times to constant molecular weight become shorter with increasing concentration of Ti (IV) butoxide, thermal degradation processes should become more important. Selectivity of the Ti (IV) butoxide catalyst towards endgroup distribution in melt polymerization is observed to be very different when synthesizing poly (butylene terephthalate) to identical molecular weight starting either from terephthalic acid or from dimethyl terephthalate. This may indicate that different catalytic species having different selectivity are at the origin of this phenomenon.
New Developments in Anti-Fouling Marine Coatings

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Abstract

Fouling of underwater structures by marine organisms is a persistent problem. In the case of oceangoing vessels, fouling can create severe drag penalties resulting in decreased or impaired ship performance and increased fuel consumption. Since shipping is a global operation, hull fouling can also lead to the transport of organisms from one ecosystem to another, introducing invasive species. Current technology for deterring fouling involves the use of coatings containing poisons for the fouling organisms. Tributyl tin and copper oxide have been the most effective deterrent chemicals used to date. While highly effective, these chemicals diffuse out of the coating to create a pollution problem and can persist in the environment for long periods of time, harming non-targeted organisms. Thus, new non-toxic, non-leaching methods to mitigating fouling are being sought.

One promising concept is that of fouling-release coatings. These coatings do not deter fouling through chemical means; rather, they do not permit the fouling organisms to create a strong adhesive bond to the coating surface. Thus, fouling organisms that are able to attach to the coating surface are easily removed through the application of low levels of shear. Silicone elastomer coatings have been shown to function effectively for a wide variety of marine organisms, however, have low toughness and poor adhesion to typical epoxy primers.

We have been exploring the concept of crosslinked siloxane-urethane coatings. These coatings are prepared from a combination of organofunctional poly(dimethyl siloxane) (PDMS) oligomers, an organic polyol, and a polyisocyanate. The coating formulation also includes organic solvents, a curing catalyst and a pot life extender. After the formulation is mixed and coated on the substrate, the solvent evaporates and crosslinking occurs. Due to the low surface energy of the PDMS component, it is expected to preferentially stratify to the coating surface, providing a low surface energy, mobile surface that organisms cannot readily adhere to. Crosslinking will prevent rearrangement of the coating under water immersion so that the coating can retain its low surface energy surface. In addition, the polyurethane will provide a tough coating system that has good adhesion to the epoxy primer or other substrate.

Figure 1. Schematic diagram of stratified siloxane-urethane coating.

Since a large number of variables may affect the exact coating morphology, and since the optimum morphology for minimizing organism adhesion is not known, we use high throughput screening methods to systematically investigate the effect of coating composition on several key performance properties. For example, in one set of experiments, we explored...
the effect of PDMS molecular weight, poly(caprolactone)-PDMS triblock copolymers and PCL segment length, and PDMS polymer amount in 192 polyurethane coating formulations. Coatings were screened for their surface energy and “pseudo-barnacle adhesion” both before and after immersion in water for 30 days (see Figure 2).

Figure 2. Water contact angle and pseudo-barnacle adhesion after water immersion as a function of caprolactone units in the PDMS polymer.

The results of the screening experiments are then used to downselect coatings compositions for additional detailed analysis. The downselected coatings are characterized using DSC, DMTA, AFM, TEM, and XPS. Coatings are also screened for their interaction with biological organisms such as bacteria, algae and diatoms. From these experiments coatings have been identified that provide easy release properties.
Polycondensates and Polycondensation Chemistry at DSM

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Polycondensates and step growth polymers are produced in large quantities as specialty products and therefore play a central role in the performance materials of the chemical company DSM. It is explained how the company promotes synergy between the different areas and business groups by sharing research knowledge in the polycondensates competence group and how DSM interacts with the academic world. Examples of the many different polycondensates products and their research are given for engineering plastics i.e. polyamides, thermoplastic polyesters and polyester elastomers, and for resins i.e. powder and solvent based (un)saturated polyester resins.

Some of the topics addressed are:

- PA46 (Stanyl) with increased melt temperature of by using isomorphous monomers
- Hyperbranched polyesteramides (Hybrane) and applications
- Multi block poly-ether esters used as thermoplastic elastomers
- Enzymatic polycondensation
NEW, AMINO ACID BASED UNSATURATED BIODEGRADABLE POLY(ESTER AMIDE)S WITH DOUBLE BOND MOIETIES IN THE BACKBONES

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α-Amino acids-based poly(ester-amide)s (AAB-PEAs) belong to the class of AA-BB type heterochain polymers obtained by solution active polycondensation. These polymers showed a high potential for various biomedical applications. The most of AAB-PEAs obtained to date don’t contain any pendant functional groups, with the exception of end groups, presumably one nucleophilic and one electrophilic end groups. At high conversions these functional end groups are very low in concentrations, especially taking into account the formation, during the polycondensation, of significant amount of cyclic macromolecules which do not have functional end groups at all; hence they are too low to be useful for covalent linkage of any biologically active compounds like drugs. Therefore, it is desirable to design new functional PEAs that could have pendant lateral functional groups along the backbones.

One of the most convenient ways to functional polymers is the incorporation into the polymeric backbone unsaturated double bonds that could easily be derivatized. We have developed several approaches to the synthesis of AAB-PEAs with unsaturated moieties (UPEAs) in the polymeric backbones.

In one approach the unsaturated UPEAs were synthesized using in solution active polycondensation di-p-nitrophenyl fumurate as a bis-electrophilic partner of di-p-toluenesulfonic acid salts of bis-(α-amino acid)-α,ω-alkylene diesters - key monomers for preparing AAB-PEAs. We have obtained the unsaturated dicarboxylic acids were obtained by interaction of maleic anhydride (2 moles) with α,ω-alkylene diols. These unsaturated diester-diacids were subsequently transformed into di-p-nitrophenyl esters – active bis-electrophilic monomers we normally use for synthesizing AAB-PEAs. The goal UPEAs were obtained by solution active polycondensation of these new bis-electrophiles with di-p-toluenesulfonic acid salts of bis-(α-amino acid)-α,ω-alkylene diesters.

In another approach new unsaturated dicarboxylic acids were synthesized by interaction of diacyl (adipoyl, sebacoyl) chlorides with hydroxyl-(o,m,p)-cinnamic acids interfacially according to Shotten-Baumann procedure. The obtained o,o’-diacyl-bis-hydroxycinnamic acids were transformed into corresponding di-p-nitrophenyl esters which were polycondensed with di-p-toluenesulfonic acid salts of bis-(α-amino acid)-α,ω-alkylene diesters resulting in UPEAs containing at the same time rigid (o,m,p)-phenylene in the polymeric backbones.
References:
New developments in polyphenylquinoxalines

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Various polymers (I, II) containing phenylquinoxaline rings and silicon bridges in the main chain were synthesized by polycondensation reactions of aromatic diamines having phenylquinoxaline rings with diacid chlorides containing diphenyl- or dimethylsilane units, or with a dianhydride having dimethylsilane groups. Due to the presence of voluminous phenylquinoxaline rings and silicon bridges, these polymers are soluble in polar amicid solvents and chloroform, and can be processed into thin films from such solutions. Freestanding films, prepared by casting onto glass plates, having the thickness of 20-30 µm, were tough and flexible, and showed a low dielectric constant, below 3.5, similar to that of polyimide H Film which is one of the most preferred dielectrics in high performance applications (Table I). Very thin films with the thickness of 30-50 nm which were deposited on silicon wafers by a spin-coating technique had a strong adhesion to the silicon substrate and exhibited compact and homogeneous surface in atomic force microscopy investigations. These polymers are highly thermostable, their decomposition temperature (Td) being above 450°C and glass transition (Tg) around 250°C, with a large interval between glass transition and decomposition which may be advantageous for their processing by a thermoforming technique. The thermal stability of these polymers is very similar to that of related wholly aromatic/heteroaromatic polymers which do not contain any flexible bridges, while their processing is significantly improved. After thermal treatment up to 400°C, the polymer films became completely insoluble and lost their glass transition, while maintaining their flexibility and high thermal stability. This behaviour is explained by some crosslinking being induced through phenylquinoxaline rings during heating up to 400°C, although the IR spectra did not reveal any changes of the absorption peaks.

Table 1. Properties of Polyphenylquinoxaline-amides I.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ar</th>
<th>Elongation (%)</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (MPa)</th>
<th>Dielectric constant</th>
<th>Td (°C)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td></td>
<td>38</td>
<td>101</td>
<td>386</td>
<td>3.48</td>
<td>455</td>
<td>253</td>
</tr>
<tr>
<td>Ib</td>
<td></td>
<td>61</td>
<td>100</td>
<td>180</td>
<td>3.49</td>
<td>460</td>
<td>255</td>
</tr>
</tbody>
</table>

The UV absorption spectra of some polymers in solution showed maxima in the range of 363 nm – 374 nm and their behaviour did not differ very much from each other although an
aromatic radical with different extent of conjugation was introduced between the two phenylquinoxaline rings. Therefore the absorption properties of the polymers were mainly determined by the phenylquinoxaline units. The films of these polymers showed absorption maxima in the range of 372 nm–382 nm, being slightly red-shifted compared to those of the polymer solution (Table 2).

Some of these polymers exhibited blue fluorescence both in solution and in film form, with a maximum in the range of 415 nm–425 nm, the fluorescence intensities of different polymers being comparable to each other (Figure 1). Such behavior can be important for the use of some of them in the manufacture of blue light-emitting devices.

Table 2. UV absorption and fluorescence properties of polyphenylquinoxaline-imides II.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ar</th>
<th>Absorption (nm)</th>
<th>Fluorescence (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Solution</td>
<td>Film</td>
</tr>
<tr>
<td>IIa</td>
<td></td>
<td>374</td>
<td>374</td>
</tr>
<tr>
<td>IIb</td>
<td></td>
<td>369</td>
<td>374</td>
</tr>
<tr>
<td>IIc</td>
<td></td>
<td>374</td>
<td>380</td>
</tr>
<tr>
<td>IIId</td>
<td></td>
<td>363</td>
<td>372</td>
</tr>
</tbody>
</table>

Figure 1. The absorption and fluorescence spectra of the polymer IIa in solution and as spin-coated film (solution; film).

All these properties associated with easy processability make the present polymers attractive for high performance applications in microelectronics, optoelectronics or other related advanced fields.

Acknowledgements: It is a great pleasure to acknowledge the financial support for a part of this work provided through the projects CEEX/29/2005 and INTAS /2006.
References
ACTIVITY LEVELING OF THE HIGH AND THE LOW BASIC DIAMINES IN SYNTHESIS OF RANDOM COPOLYIMIDES

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It is known that reactivity of aromatic diamines in a low temperature polycondensation with tetracarboxylic acids dianhydrides is in a strong correlation with their basicity. For example, changing the type of bridge substituent in a row –O--; -CH2--; -SO2-- in bridged dianilines (DAO, DAM, DAS correspondingly) leads to about 3 orders of magnitude decrease of the polycondensation rate constant with pyromellitic dianhydride [1]. Such a large difference in reactivity between DAO and DAS makes impossible obtaining copolymides containing both types moieties in chain. Recently, we have found that homopolyimides of with intrinsic viscosity $\eta=0.5-1.0$ dl/g can be prepared easily from low basic diamines as well as from high basic ones when molten benzoic acid (BA) is used as reactive medium at 140-160$^0$C[2,3]. In this work, copolymides were prepared in from 2,2-bis-[(3,4-dicarboxyphenoxy]—phenyl)-propane dianhydride (BPADA) and the DAO/DAS mixtures (one-portion loading). The DAO/DAS ratio was varied (0,25: 0,75; 0,5: 0,5; 0,75: 0,25); DPADA/(DAO+DAS)=1. Microstructure of polymer chain was analyzed by $^1$H and $^{13}$C NMR. Three types of diads (DAO-DAO, DAO-DAS and DAS-DAS) were found in $^{13}$C NMR spectra. On the basis of data of $^{13}$C NMR and turbidimetry it was concluded that DAO/DAS copolymides have random distribution of DAO and DAS moieties in chain.

To explain small difference in activity between the low and the high basic diamines, three hypothesis were offered: 1) Stronger specific solvatation of high basic diamine compensates catalytic action of acid medium; 2) Difference in temperature coefficients of the reaction rate for the high and the low basic diamines ; 3) Polycondensation is not the rate-determining stage.

To check this hypothesis, we investigated the kinetics of model reaction - acylation of DAS, DAM and DAO by phthalic anhydride (PhA) in glacial AcOH at16-50$^0$C. Kinetic experiments were carried out just in a cell of automatic potentiometer. Current content of amino groups was measured by titration with solution of HClO$_4$ in AcOH. Obvious reversible character of acylation in AcOH has been established. The values of equilibrium constants, enthalpy as well as the rate constants and activation energy for direct and back reactions were determined in a range of 16-50$^0$C. Corresponding kinetic parameters were calculated for 140$^0$C by extrapolation using Arrhenius and Vant-Hoff equations (table).

The second order acylation rate constants were found to be much higher than that in amic solvent at about similar conditions (see table below). Such a high rate constants values are obviously caused by catalysis of polycondensation by BA medium. It can be seen that the rate constants of DAO in AcOH at 22$^0$C as well as at 140$^0$C are much higher than that of DAS. This means that hypothesis 1 and 2 should be refused. In the same time, both the $K_e$ values for DAS and DAO decrease considerably at 140$^0$C, and the difference in $K_e$ between DAS and DAO becomes low.

On the basis of results obtained for the model acylation reaction in AcOH (table), it should be suggested that the rates of direct and the reverse polycondensation stage in molten BA at
140°C are also very high. On the other hand, due to low equilibrium constant, polymerization degree of amic acid oligomer is not more than \( P=3-5 \). Because \( k_2<<k_{-1} \), chain growth of formerly formed oligomer proceeds only due to the consumption of amino acid moieties by imidization reaction. This results in shift of equilibrium of the polycondensation stage.

### Table. Kinetic parameters of acylation of bridged dianilines by phthalic anhydride

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Temperature, °C</th>
<th>Substituent in diamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 ), l/mole*min</td>
<td>22</td>
<td>-SO(_2)-</td>
</tr>
<tr>
<td>( K_p ), l/mole</td>
<td>22</td>
<td>-CH(_2)-</td>
</tr>
<tr>
<td>( \Delta H ), kcal/mole</td>
<td></td>
<td>-O-</td>
</tr>
<tr>
<td>( E_a ), kcal/mole</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 ), l/mole*min</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>( k_{-1} ), min(^{-1})</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>( K_p ), l/min</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>( k_3 ), min(^{-1})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Experimental data; for comparison: \( k_1=5.1 \) l/mole*min for 4-diamino diphenyloxide in DMAA at 30°C **extrapolated data/

Imidization of amic acids must have low sensitivity to changing the bridged substituent. Indeed, according to our (table), the ratio of imidization rate constants \( k_2 \) of corresponding DAO- and DAS-based bis-phalamic acids in model experiment in AcOH at 140°C is equal to 3.5. On the basis of the fact that imidization is the rate-determining stage, the phenomena of apparent leveling the “activity” of the high and the low basicity dianines can be easily explained in following way. Apparent activity \( k_{app} \) of diamine in copolycondensation in BA at 140-160°C should be nearly proportional to the product of the acylation equilibrium constant and imidization rate constant: \( k_{app} = K_p \cdot k_2 \). Because both the members, \( K_p \) and \( k_2 \) don’t differ much for the low and high dianines, \( k_{app} \) values are of the same order of magnitude. Hence, formation of random copolymer is available, which conclusion is in accordance with experimental data.


**Acknowledgements.**

The work was supported by RFBR (Grant #05-03-32998)
Aromatic polyimides are one of the most significant classes of high performance polymers, in view of excellent electrical, thermal and high-temperature mechanical features. They have been used in variety of applications such as; high-temperature insulators and dielectrics, coatings, adhesives and matrices for composites. Nonetheless, aromatic polyimides have good thermal stability; they are not highly flame resistance. Therefore, they are inexpedient for some applications. In order to enhance their flame retardant behavior, the introduction of phosphorus, either as a constituent part in the polymer chain or as an additive is preferred. Polyimides based on phosphine oxide exhibit good flame resistance, high thermal oxidative stability, enhanced solubility and improved miscibility and adhesion, due to the fact that phosphine oxide moieties are oxidatively and hydrolytically stable\textsuperscript{1,2}. Besides that, sulfonated polyimides are a sub-class of polyaromatic materials that have attracted attention as proton exchange membranes for fuel cell applications.

In recent years, proton exchange membranes have been investigated intensively. NAFION (by Dupont) is by far the leading membrane in all types of PEM fuel cells. Although NAFION has excellent chemical and mechanical stability, high proton conductivity, it has some disadvantages that restrict its industrial applications and include high cost, low running temperature (about 80°C) and high methanol permeability. Therefore, lower cost polymers with high performance are strongly desired as alternative materials.\textsuperscript{3} Over the last decade, several new classes of proton-conducting polymer electrolytes have been formed into membranes and their properties investigated. These membranes include based on partially fluorinated polymers, composites, and aromatic polymers. The major approach has been the attachment of sulfonic acid groups onto highly stable aromatic polymers such as; sulfonated poly(ether ether ketone)s, sulfonated polysulfones, sulfonated poly(arylene ether sulfone)s, sulfonated poly benzimidazole, sulfonated poly(styrene)s, sulfonated poly(phenylene sulfide)s and sulfonated polyimides.\textsuperscript{4} The introduction of sulfonic acid groups is achieved either by direct sulfonation of the parent polymers or by polymerization of sulfonated monomers.

Sulfonated polyimides are reported to possess high proton conductivity, comparable to, or greater than, NAFION at elevated temperatures. In addition, sulfonated polyimides based on phosphine oxide are flame retardant. In view of the fact that phosphine oxide moieties have properties of strong hydrogen bonding and miscibility in many systems, they have excellent thermal and chemical durability\textsuperscript{5}.

The present study describes the synthesis and characterization of the novel sulfonated (m-diaminophenyl)phosphine oxide monomer and the use of this monomer in the synthesis of a new phosphine oxide based sulfonated polyimides as a potential candidate for proton exchange membrane. FTIR, mass spectroscopy, NMR spectroscopy were used to obtain the chemical structure of the monomer synthesized. Benzophenone tetracarboxylic dianhydride (BTDA), 4,4\textsuperscript{'}-hexafluoropropylene bis(phthalic anhydride) (6FDA) and 3,3\textsuperscript{'}-diamino
diphenyl sulfone (DDS) were used as monomers in polyimide synthesis. Sulfonated polyimide membranes were obtained by solution thermal imidization method. Thermal behavior of polymers was investigated by performing both differential scanning calorimetry and thermal gravimetric analysis. The ion-exchange capacity (IEC) was measured by classical titration. The swelling in water was determined by measuring the uptake of water at room temperature using the weight difference of the swollen to the dry membrane, relative to the dry weight. Further, characterization studies such as ion-conductivity of the membranes are in progress.

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Oxidative polymerization of substituted phenols with a copper amine catalyst within mesoporous silica

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A well-characterized SBA-15 supported CuCl catalyst was prepared and applied for the regio-controlled oxidative coupling polymerization of substituted phenols. The catalyst provided the regio-controlled poly(2,5-dimethylphenol) in 1 and 4 linkage, and the resulting poly(2,5-dimethyl-1,4-phenylene ether) showed melting point at 320 °C, while regio-uncontrolled poly(2,5-dimethylphenol) doesn’t show melting point in DSC measurement.

Introduction
Poly(phenylene ether)s (PPEs) are attractive materials for engineering plastics, and are produced by oxidative coupling polycondensation catalyzed by a copper-amine complex under oxygen.¹ Substituent groups both on 2 and 6 positions of phenolic OH moiety are necessary to prevent the formation of unfavorable branching polymers, limiting the availability of phenols as the monomer.² Here, We present a new method to control regio-regularity of the oxidative coupling polymerization of 2,5-dimethylphenol and o-cresol utilizing a copper-amine catalyst immobilized on mesoporous material, which prevents the formation of branching and crosslinking in the polymerization.

Results and Discussion
Copper ion was incorporated into SBA-15 silica materials by functionalization of SBA-15 with N,N,N’-trimethyl-N’-trimethoxysilylpropyl ethylenediamine.

The molar ratio of diamine and Si in SBA-15 with a diamine functionality (without Cu) was determined by elemental analysis to be 0.9:13. After immobilization of Cu ions, the ratio of Cu to Si was estimated by inductively coupled plasma atomic emission spectroscopy (ICP) and elemental analysis as 1.0 : 13, indicating similar formation of copper and diamine. X-ray diffraction (XRD) analysis of SBA-15 before and after the modification showed second and third peaks in addition to the first strong peak, indicating that a regular nano-structure was maintained during the modification. Pore diameter before and after the modification was 8.20 and 6.00 nm, respectively, as estimated
by the Barrett-Joyner-Halenda (BJH) method. In addition, BET surface areas decreased from 813 to 344 m$^2$/g, respectively. These results revealed that copper ions are immobilized homogeneously on the internal surface of the SBA-15 material.

The oxidative polymerization was carried out using the mesoporous supported CuCl and CuCl-pyridine catalyst as a reference. The polymer with a high molecular weight ($M_n = 7,400, M_w/M_n = 2.5$) was obtained when the mesoporous supported CuCl (2 mol%) was used in conjunction with 2,6-lutidine as an additive. The regio-regularity was affected by the additive and the polymerization temperature. Figure 1 shows the $^{13}$C NMR spectra of the polymers obtained with (a) CuCl-pyridine and (b) the mesoporous catalyst with 2-propylpyridine as an additive. The mesoporous catalyst provided the regio-controlled polymer, while such regularity cannot be achieved with the conventional catalyst. Furthermore, the regio-controlled polymer showed its melting point at 320 °C by DSC analysis. Regio-controlled oxidative coupling polymerization of o-cresol using this mesoporous supported CuCl catalyst will also be discussed in this paper.

This study was supported by Industrial Technology Research Grant in 2003 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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Ionic Liquids as Green Solvents and Catalysts for the Synthesis of Optically Active Poly(amide-Imide)

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Almost all solution polycondensation techniques for the preparation of polyesters, polyamides, polyimides and other functional polymers are carried out in volatile organic solvents (VOS) such as $N,N$-dimethylformamide, $N,N$-dimethylacetamide, $N$-methylpyrrolidine, chlorinated hydrocarbons and so on. These solvents are volatile, most of them flammable, toxic, and harmful. Thus, removing organic solvents in polymer synthesis is very important in the drive towards environmentally green technologies. Ionic liquids (ILs) are salts melting at temperature below 100 °C. They have unique properties such as nonvolatility, inflammability, high ionic conductivity, high thermal stability, high ion concentration, etc. and are reported to have applications in many different scientific fields. In recent years, ILs have attracted considerable attention as environmentally safe solvents and catalysts. Therefore replacement of VOS by ILs as reaction media and catalysts in polymer chemistry would be a proper choice towards environmentally benign technologies. Although ILs as solvents have been widely used in organic and inorganic synthesis, but, their application in polymer synthesis is still limited. In this investigation we wish to report direct polycondensation of an optically active monomer containing imide preformed ring and amino acid linkages with different aromatic diamines in ILs as solvents and catalysts. The polymerization reactions were carried out in ILs media based on the dialkylimidazolium cations and triphenyl phosphate (as condensing agent) and lead to the formation of optically active poly(amide-imide)s with high yields and inherent viscosities. The influence of various reaction parameters including the nature of the IL cations and anions, the monomer structures, the reaction temperature, and the reaction time, on the yields and inherent viscosities of the resulting optically active poly(amide-imide)s will be reported. It is interesting to mention that, in this method extra components, such as pyridine, CaCl$_2$ (LiCl), which are used in similar reactions in conventional molecular solvents, are not required. Thus, ILs can act as both solvents and catalysts, in a safe and green process.

Literature:
Polylactide (PLA), a polymer produced from condensation or ring opening polymerization of lactide, is one of the attractive biodegradable polymers due to the derivation from renewable resources and a non-toxic polymer for the human body. [1-5]. PLAs derived from the three different lactide stereoisomers (L-lactide, D-lactide and meso-lactide) have different physical and chemical properties such as crystal structure, mechanical and degradation properties and also used for biomedical and pharmaceutical applications such as resorbable sutures, medical implants, scaffolds for tissue regeneration and drug delivery systems [3,6-15].

In this study, the biodegradation and apatite formation of PLLA and PDLA films prepared by using solvent casting method were analyzed as a function of immersion time in simulated body fluid (SBF). The specimens (3cmx3cm) were immersed in SBF at 37 °C and pH of 7.4 for up to 120 days in dynamic mode. Surface topography and apatite formation were evaluated by atomic force microscopy (AFM), scanning electron microscopy (SEM), Wide angle X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) analyses. SEM-EDX analysis of the depositions formed on the biodegradable film surfaces was performed to investigate the changes in ion concentrations. Molecular weights of the films were measured with Gel Permeation Chromatography (GPC).

AFM studies indicated that surface topography of polymer films was dependent on immersion time in SBF and polymer type. The surface roughness of PLLA was increased from 0.255 nm to 328 .8 nm after 120 day. However, initial surface roughness of PDLA film measured as 0.555 nm were found as 308.63 nm after 120 day. XRD, FTIR and SEM analyses also demonstrated the apatite formation on PLLA and PDLA films. XRD results demonstrated that crystallinity index values of the films increased with Ca/P precipitation. The characteristic peaks of apatite at 600 and 562 cm⁻¹ were also observed from FTIR analyses. GPC analyses indicated that the molecular weights of the PLLA and PDLA films decreased with immersion time in SBF due to the biodegradation of the films. The number average molecular weights decreased from 90817 to 45488 Da for PLLA and from 149394 to 100053 Da for PDLA films, respectively after 120 days. In conclusion, biodegradation and apatite formation of PLLA and PDLA films were confirmed by the results of AFM, SEM, XRD, FTIR and GPC analyses.

References
Solvent Free Preparation of Conducting Polyurethane (PU)-Ionic Liquid (IL) Composites and Their Electrical Properties

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Polyurethane resins (PUR) are unique polymers combining high elasticity with low abrasion. Among others, they are used in special applications such as rollers in electronic imaging and printing machines [1,2]. For these applications, an antistatic equipment is required to prevent the PUR from electrostatic charging. Antistatic properties are usually introduced by mixing the network-forming monomer components with electrically conducting additives such as carbon black, ion conducting salts. Up to present, the use of PUR as non-conducting polymer matrix has scarcely been described [3,4]. Ionic liquids (ILs) are organic salts with melting points under 100°C, often even lower than room temperature [5]. They offer interesting chemical and physical properties that have attracted the attention of many researchers, trying to redesign chemical processes to reduce, or eliminate, losses of solvents, particularly volatile organic compounds (VOCs). In chemistry, they acted in different roles such as solvent, catalyst and conductive additives. A typical example of ILs has been depicted in Figure 1. The anion shown here is tetrafluoroborate. The R group of the cation is also variable (e.g., methyl, ethyl, etc.). The variability of anion and R group may be used to fine-tune the properties of the ionic liquids.

![Figure 1: Structure of 1-methyl 3-ethylimidazolium tetrafluoroborate.](image)

In this study, the method of solvent-free preparation of conducting composites of PUR and IL (imidazolium salts) was described. Furthermore, the effects of IL addition, IL amount (w/w), IL type and humidity on the electrical and mechanical properties of the PUR-IL composites were investigated. In all cases, PUR was prepared by condensation reaction of isocyanate terminated prepolymer or toluene diisocyanate (TDI) and Hydroxol 15-W (E.W.:933 g/mole) as polyol cross-linker. Subsequently, IL was added to the PUR. As IL compounds, different types of anion containing (BF$_4^-$, PF$_6^-$, tosylate-, Cl$^-$ and Br$^-$) imidazolium based salts were used. In other set of experiments, the effect of length of alkyl chains (from methyl to dodecyl) was investigated.

Our studies indicate that solvent free procedures are readily applicable for preparation of composites of PUR and IL. Prepared composite products were obtained with specific conductivity $\sigma$ of $10^{-6}$-$10^{-7}$ S.cm$^{-1}$ while only 0.1 % (wt) of 1-methyl 3-ethylimidazolium tetrafluoroborate was added. For comparison, same amount of polypyrrole (PPy) effect was checked [6] and it was found the better conductivity value (nearly an increase of four orders of magnitude) in the case of adding Ionic Liquid. On the other side, the Shore A hardness
values of the composites were in the range of 30 and 50. Presence of moisture increased the $\sigma$ value with increasing time while no change in the hardness value of the composites.

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Poster Abstracts
Surface modification of polyimides containing moieties of aliphatic diamines in chain by the low temperature plasma

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In this work we studied the surface properties of 3 new polyimides on the basis of aromatic tetracarboxylic acid dianhydrides and 1,3-bis-(2-aminoethylaminoethyl)-adamantane (Ad).

\[ \text{CH}_2 \text{CH}_2 \text{N} \text{O} X \text{N} \text{O} \text{CH}_3 \text{CH}_3 \]

(Ad-DA)

(Ad-DO)

(Ad-DD)

New polyimides containing Ad moieties possess termoplastic behavior. Samples of polyimide films were obtained by melt pressing. Then, films were treated by the glow low-frequency discharge (50 Hz) in vacuum during 60 s. The wettability contact angle \( \theta \) was measured by the goniometric technique using distilled water and glycerol as test liquids. The \( \theta \) values measured experimentally were used to calculate the surface energy (\( \gamma \)) and its polar (\( \gamma^p \)) and dispersion (\( \gamma^d \)) components by the conventional procedure [1]. Experimental data are presented in a table. For comparison, the data from our early work concerning known aromatic polyimide films [2] treated by plasma also are given.

<table>
<thead>
<tr>
<th>Polyimide</th>
<th>Plasma treatment</th>
<th>( \theta ), degree</th>
<th>( \gamma ), mJ/m(^2)</th>
</tr>
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<tr>
<td></td>
<td></td>
<td>( \theta_{\text{water}} )</td>
<td>( \theta_{\text{glyc.}} )</td>
</tr>
<tr>
<td>Ad–DA</td>
<td>initial</td>
<td>61</td>
<td>58</td>
</tr>
<tr>
<td></td>
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<tr>
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<td>initial</td>
<td>59</td>
<td>53</td>
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<tr>
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<td>plasma treated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ad–DD</td>
<td>initial</td>
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<td>plasma treated</td>
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<td></td>
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<tr>
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<td>initial</td>
<td>76</td>
<td>64</td>
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<td>Kapton–H</td>
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<tr>
<td>Upilex–S</td>
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<tr>
<td>Upilex–R</td>
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<td>plasma treated</td>
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</tbody>
</table>

It is seen, that adamantane-containing polyimide film before treatment possess lower wettability angle in comparison with completely aromatic polyimides. Substantial decrease in a contact angle was observed for all the samples after plasma treatment. The final level of the total surface energy \( \gamma \) after treatment is about of the same value both for aromatic and Ad-containing polyimides. It should be concluded that chemical structure of polyimides has only
small influence on their capability to change surface properties under low temperature plasma
treatment.

References


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New phenoxy-substituted aromatic diamines and organosoluble polyimides therefrom

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Abstract

New phenoxy-substituted aromatic diamines – 3,4’-diamino-4-phenoxybezophenone and 3,4’-diamino-4-(p-chlorophenoxy-)benzophenone – were prepared using 4-step synthesis starting with p-nitrobenzoyl chloride and chlorobenzene.

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{O} \quad \text{Cl} & \quad + & \quad \text{Ph} \quad \text{Cl} \quad \xrightarrow{\text{AlCl}_3} & \quad \text{O}_2\text{N} & \quad \text{O} \quad \text{Cl} \quad \xrightarrow{\text{KNO}_3, \text{H}_2\text{SO}_4} \\
\text{O}_2\text{N} & \quad \text{O} \quad \text{Cl} & \quad \xrightarrow{\text{K}_2\text{CO}_3, \text{DMFA}} & \quad \text{O}_2\text{N} & \quad \text{O} \quad \text{Cl} \\
\text{SnCl}_2/\text{HCl} & \\
\xrightarrow{-\text{H}, -\text{Cl}}
\end{align*}
\]

Interaction of the diamines thus obtained with aromatic tetracarboxylic acid dianhydrides under the conditions of high-temperature solution polycyclocondensation in m-cresol led to the formation of new highmolecular weight organosoluble polyimides.
Linear and four-arm multiblock copolymers by Ring Opening Polymerization in Supercritical Carbon Dioxide

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² Institute of Environmental Sciences, Environmental Science Division, Bosphorus University, Bebek 34342, Istanbul, Turkey

Supercritical carbon dioxide (sc-CO₂) is an environmentally friendlier alternative to conventional organic solvents; it is inexpensive, non-toxic, non-flammable and has an easily accessible critical point (31.1°C and 73.8 bar). Sc-CO₂ is highly available, recyclable and biocompatible as well. Especially this last feature of sc-CO₂ is the major drive that accounts for increased research in the synthesis of biodegradable and biocompatible materials, since it can be removed almost 100% from the material after polymerization [1]. In the field of biomedicine, degradable polyester materials based on lactone monomers including L-lactide and ε-caprolactone became increasingly essential and this orients the understanding of the kinetics and mechanism of their polymerization [2,3]. Utilization of sc-CO₂ as a solvent requires the use and thus the careful design of fluorinated surfactants [4].

This study involves the synthesis of fluorinated poly-ε-caprolactone as a prepolymer by using different fluorinated diols (Fluorolink-D, Fluorolink D10, Fluorolink-E, and Fluorolink-T) in bulk. Sn(Oct)₂, a catalyst approved by the FDA, is used to catalyze the reactions [5]. Poly(L-lactide-co-ε-caprolactone) is synthesized by ring opening polymerization again with Sn(Oct)₂ catalyst in sc-CO₂ with the aid of the fluorinated surfactant. The polymers are characterized by ¹H-NMR, ¹³C-NMR, Differential Scanning Calorimetry (DSC), Gel Permeation Chromatography (GPC) and Scanning Electron Microscopy (SEM).

References

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SYNTHESIS, MELT-SPINNING AND CHARACTERIZATION OF FULLY AROMATIC THERMOTROPIC LIQUID CRYSTALLINE COPOLYESTERS CONTAINING m-HYDROXYBENZOIC ACID UNITS

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Abstract

A series of fully aromatic copolyesters based on p-acetoxybenzoic acid (p-ABA), hydroquinone diacetate (HQDA), terephthalic acid (TPA), and m-acetoxybenzoic acid (m-ABA) were prepared by a modified melt polycondensation reaction. The fibers from copolyesters showing thermotropic liquid crystalline properties were prepared by high-temperature melt-spinning technique. The copolyesters were characterized by DSC, TGA, 1H-NMR, polarized optical microscopy, X-ray diffraction, and intrinsic viscosity measurements. The mechanical properties and the morphology of the fibers were determined by WAXD, tensile testing and scanning electron microscopy (SEM). It was found that, the copolyesters exhibited nematic liquid crystalline phases in a broad temperature range of about 150°C, when the content of linear (p-ABA, HQDA, and TPA) units over 67 mol %. DSC analysis of the anisotropic copolyesters revealed broad endotherms associated with the nematic phases and the melting and spinning temperatures were found to be in processable region. The melting or flow temperatures, crystal-to-nematic and nematic-to-isotropic transitions depend on the type of the linear monomer units. When the content of p-ABA units increased, compared to other linear units (HQDA and TPA), the intrinsic viscosity and the degree of crystallinity of the copolyesters also increased. The aromatic region in 1H-NMR spectra of the copolyesters containing equal molar compositions of p-ABA, HQDA, and TPA units was found to be sensitive to the sequence distribution of aromatic rings. Fibers exhibited well-developed fibrillar structure parallel to the fiber axis. The highly oriented morphology of fibrils is slightly dependent on the type of the linear monomer.

Keywords: Aromatic; thermotropic; liquid crystalline; copolyester synthesis; degree of crystallinity; fibers; morphology.
Poly[3-(6'-bromo-n-hexyl)thiophene]s were synthesized by Grignard methathesis method of 2,5-dibromo-3-(6'-bromo-n-hexyl)-thiophene, using methylmagnesium bromide in the presence of 1,3-bis(diphenylphosphino)propanedichloronickel (II) [Ni(dpdp)Cl₂] as catalyst. The polymers were obtained with two degree of regioregularity: 83% head-to-tail (HT-HT) in a mixture with 7% HH-TT, 5% HT-HH and 5% TT-HT isomers and as 98% HT-HT regioregular poly[3-(6'-bromo-n-hexyl)thiophene], depending by the time of the catalyst adding. The starting monomer (6) was approached via nickel-catalyzed Grignard coupling of 3-bromothiophene (3) with 1-(p-methoxyphenoxy)-6-bromomagnesium-hexane (2), followed by hydrolysis and bromination (Scheme 1).

The substitution of the terminal bromine atom of the 98% HT-HT regioregular poly[3-(6'-bromo-n-hexyl)thiophene] (Scheme 2) with two aromatic units, phenyl and anthracenyl,
afforded poly[3-(6'-phenyl-\(n\)-hexyl)thiophene] (9) and poly[3-(6'-anthracenyl-\(n\)-hexyl)thiophene] (10), respectively (Scheme 3).

The structure, the degree of regioregularity and the degree of substitution of the polymers were proved by \(^1\)H-NMR, FTIR, gas-chromatography (GC) and UV-vis spectroscopy. Molecular modeling and UV-vis spectra of the phenyl- and anthracenyl-substituted poly(3-hexylthiophene)s evidenced the closely packed \(\pi\)-stacking arrangements in ordered cast films, with the formation of a double channel for the charge carrier transport. This additional channel for the charge carrier transport could account for some increasing in field effect-mobility of the polymers.

Acknowledgements
The financial support provided through the European Project, Research Training Network "EUROFET", contract no. HPRN-CT-2002-00327, and the Projects CEEX/29/2005 and INTAS/2006 is gratefully acknowledged.

References
New polysilane-metal complexes structures were obtained by the polycondensation reaction of \( \alpha,\omega \)-bis(chloromethyl)-polymethylphenyl-silane with various bis(salicylidene)diamines. The chloro-functionalized polysilane was obtained by a modified Wurtz coupling procedure at low temperatures. To obtain the polymer–metal complex the resulted macroligand was complexed with metal cations. This structure is characterized by a highly localized electroactivity in the redox moiety combined with a specific \( \sigma \) conjugative effect in the polysilane chain.

IR, \(^1\)H-NMR and UV-VIS spectral analyses as well as GPC and TGA were used to investigate the new chemical structures.

**Acknowledgements:** to Romanian Ministry of Research and Education-MATNANTECH program, grant no. 36/2005, for financial support

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CROSSLINKABLE POLYSILANE–ORGANOMETALLIC STRUCTURE

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Institute of Macromolecular Chemistry “Petru Poni”,
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Abstract

Starting from a poly(methyl-co-diphenylsilane) with pendant iodopropyl groups, a crosslinked polysilane has been prepared by a polycondensation reaction with hydroxi-functionalized bis(salicylidenimine). IR, $^1$H-NMR, SEC and TGA analyses were used to investigate both of the chemical structures and the evolution of the crosslinking process. The resulted network was doped with Cu$^{2+}$ cations by the complexation reaction of the pendant bis(salicylidenimine) segments with metal salt. The influence of the metal complex electronic transitions onto the $\sigma$-electrons delocalisation has been studied through UV-VIS spectral analysis of the polymer.

Acknowledgements: to Romanian Ministry of Research and Education-MATNANTECH program, grant no. 42/2005, for financial support
N-Hydroxyphthalimide reactions with cyclic alkenes

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It is commonly assumed that reaction between free radicals, $X^\cdot$, and cycloalkenes occur by an initial H-atom abstraction to give an allylic radical to which a second $X^\cdot$ adds, according to the equation:

$$
X^\cdot + \text{cycloalkene} \rightarrow X - \text{H} + \text{allylic radical}
$$

However, the reaction of excess 2,2,6,6-tetramethylpiperidin-N-oxyl (TEMPO) with unactivated alkenes is consistent with a low-energy pathway involving the addition of the nitroxyl radical to the double bond, followed by H-atom abstraction from the intermediate by another equivalent of nitroxyl radical, equation:

$$
X^\cdot + \text{cycloalkene} \rightarrow X - \text{H} + \text{new allylic radical}
$$

An unambiguous method for distinguishing between abstraction-addition and addition-abstraction mechanisms (and mixtures thereof) in the reaction of 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl ($R_2NO^\cdot$) with a specifically deuterated cyclohexene, 1,2-dideuterocyclohexene, is demonstrated, equation:

$$
D-D + R_2NO^\cdot \rightarrow D-D-R_2NOH
$$

Present work extends our preliminary studies, using other dideuterated alkenes and other nitroxyl radicals. By analysis of the reaction products and $^2$HNMR spectra, we were able to estimate the ratio between the H-atom abstraction mechanisms versus addition mechanism that occurred during the reaction.

The PINO radical was generated in situ, starting from its parent hydroxy amino, N-hydroxyphthalimide, namely, using two ways (Scheme 1):

a) by using a t-butylnitrite
b) by using lead tetraacetate
The reaction between dideuterated alkenes and PINO can be represented by the scheme 2:

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REFERENCES
New insights on the urethane reaction mechanism

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Abstract

The kinetics and mechanism of the uncatalysed reaction between phenylisocyanate and alcohols have been evaluated. An alternative reaction mechanism as a special case of second order reaction is proposed for reactions performed in unpolar media. In the first step of the process, the isocyanate group is activated through a rapid and reversible process by the mobile and polarized form of the hydroxyl hydrogen from the alcohol-alcohol or alcohol-urethane hydrogen bond associate. The final product appears in the next step, through a secondary order reaction as a result of the nucleophilic attack of the hydroxyl oxygen to the activated isocyanate group.

The reaction rate is governed by two factors:

- the hydrogen bond association degree, which influence especially the –NCO activation
- the nucleophily of the hydroxyl oxygen

Both together determining the second order constant magnitude, especially in the range of the low hydrogen bond association degree when the inactive alcoholic form have a significant share.

The reaction between isocyanates and alcohols begins in the first step of reaction through a polarization of the –NCO group by the polar mobile hydrogen $H^{\delta+}_{\text{mobil}}$ from the alcohol and (or) urethane associate through a rapid equilibrium reaction:

$$
\text{NC}O \quad \overset{H^{\delta+}_{\text{mobil}}}{\overset{\text{fast}}{\leftrightarrow}} \quad \text{N}^{\delta-}_{\text{mobil}} \quad \overset{\text{fast}}{\rightarrow} \quad \text{NC}O \quad \overset{\delta^+}{\text{C}}\overset{\delta^-}{\text{H}}_{\text{mobil}}
$$

Or even:

$$
\text{N}^{\delta-} \quad \overset{\delta^+}{\text{C}}\overset{\delta^-}{\text{H}}_{\text{mobil}} \quad \overset{H^{\delta+}_{\text{mobil}}}{\overset{\text{fast}}{\leftrightarrow}} \quad \text{N}^{\delta-} \quad \overset{\delta^+}{\text{C}}\overset{\delta^-}{\text{O}} \quad \overset{\delta^-}{\text{H}}_{\text{mobil}}
$$

82
The activating role of urethane was demonstrated by the addition of urethane (CEE) in the reaction mixture.\textsuperscript{1,2,3}

The second step of the reaction, between alcohol and isocyanate, take place the nucleophylic attack of the hydroxyllic oxygen to the positivated carbon atom from the \textendash\text{NCO} group. This process, comparatively slower and therefore rate determinant submit to the second order kinetics and lead to the whole process the second order character:

\[
\text{C and (or) D} \xrightarrow{\text{RO}_{\text{mobil}}^\delta-} \text{K' slow} \xrightarrow{} \begin{array}{c}
\text{N} \quad \text{C} \quad \text{O} \\
\text{R}
\end{array}
\]

REFERENCES
NOVEL POLYAZOMETHINES AS PHOTOLUMINESCENCE SENSORS

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In the last two decades conjugated polymers have attracted considerable attention because of their various applications in optoelectronic devices. Much works have been devoted to light emitting polymers being the basic materials for construction polymeric light emitting diodes (PLED). It should be stressed that especially important and desired are polymers emitting blue light because blue light can be converted to green or red with proper dyes. It means that blue PLED alone may generate all colours while green or red can not be converted to blue by the same method. Therefore many works have been concerned of synthesis of blue light emitting polymers [1].

Conjugated polymers are also reliable candidates for the sensory materials because of the sensing ability of the conjugated polymer which can be enhanced via interactions such as hydrogen bonding and π-π aromatic stacking between the receptor and the neutral guest molecule. The fluorescent sensors are one of the most desirable techniques to detect chemicals because the guest binding results in the increase, decrease and the wavelength shift of the emission peak. The acid-base chemistry plays an important role in the sensor system. The introduction of the aromatic unit including the nitrogen atom into the conjugated polymer provides the sensory materials to probe acids [2-4].

In this communication, we will report photoluminescence properties of novel undoped and doped polyazomethines having triphenylamine moieties for the field of optoelectronics. The polyazomethines obtained emitted blue light and intensity of their photoluminescence was tuned by supramolecular modification on a way of doping with phenolic type compounds being able to form H-bonds with lone electron pair of nitrogen atoms in imine group (Fig. 1).

Acknowledgements: The authors are grateful to the Scientific Research Committee for financial support (grant No. 1T09B 088 30).

References:
PARABANIC COPOLYMERS OBTAINED BY CONDENSATION OR CYCLOCONDENSATION REACTIONS

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¹The Romanian Academy's Institute of Macromolecular Chemistry "Petru Poni", Grigore Ghica Voda Alley, No. 41 A, 700487, Iasi, Romania

The polymers containing 1,3-imidazolidine-2,4,5-trione rings on the macromolecular backbone are known as poly(parabanic acid)s. There are known a few methods to obtain this kind of polymers starting from diisocyanates: by polyaddition reaction of diisocyanates with hydrogen cyanide followed by hydrolysis [1], or by polyaddition-polycondensation reaction between diisocyanates and bisesteroxalamides [2].

Parabanic copolymers based on cyclocondensation of polyureas with oxalyl chloride

New methods of parabanic polymer synthesis were developed in our laboratory (by Caraculacu and coworkers) and we already have reported an original synthetic method to obtain poly(parabanic acids) by a cyclocondensation reaction with oxalyl chloride on polyureas (Scheme 1) [3-4].

The reaction between polyureas and oxalyl chloride takes place quantitatively only if one of two radicals has an aliphatic or a non-symmetrical aromatic structure, for example 2,6-pyridyl structure. Polyureas containing only p-substituted aromatic radicals suffer partially the cyclocondensation reaction as observed from IR absorption spectra. Based on the IR spectral data, we calculated the transformation degree using an earlier reported method [5]. All polymers show a good thermal stability Td = 285-360°C (TGA) and Tg = 137-255°C (DSC), solubility, inherent viscosity between 0.18-0.53 dl/g. Parabanic polymers showed an electrical conductivity of 0.38-4.0 x 10⁻¹⁶ ohm⁻¹.cm⁻¹ which means that all polymers have good electrical insulator properties. The majority of polyureas presented a crystalline character, while almost all parabanic polymers tested by X-ray diffraction measurements appeared to be amorphous. Two polyparabanates showed a semicrystalline character: poly (hexylene-1,3-imidazolidinetrione), and poly(hexylene-1,3-imidazolidinetrione-p,p'-diben-zyl-diyl-1,3-imidazolidinetrione) with crystallinity degrees of 72% and, respective, 45%.

Parabanic copolymers based on monomers with preformed parabanic rings

Copolymers obtained from 1,3-bis(3-isocyanato-4-tolyl) parabanic acid (DITP)

Polyamides, polyamid-imides and polyimides [6] with parabanic structure were synthesized by polycondensation reaction between DITP and isophthalic acid, trimellitic anhydride, pyromellitic anhydride and benzophenontetraacarboxylic dianhydride. Syntheses were carried out in amide solvents at 90-130°C with carbon dioxide evolving. Thermal stability of polymers ranged between 330-400°C and they have good solubility in amide solvents.

Copolymers based on 1,3-bis(4-chloroformyl-phenylene) parabanic acid (DCPP)

A series of parabanic polyhydrazides was prepared based on this monomer obtained in our laboratory for the first time. All parabanic polyhydrazides were prepared by polycondensation reaction of dihydrazides [7] or aromatic dihydrazines [8] and DCPP. Polyhydrazides based on
Dihydrazides can be thermally or chemically cyclodehydrated to polyoxadiazoles; they can be also transformed in polychelates with metal salts producing diverse colored precipitates. Polyhydrazides based on dihydrazides can be further chemically transformed by using different reactive compounds such as aliphatic or aromatic mono-isocyanates that can be attached to NH hydrazide groups on polymer.

\[
\begin{align*}
\text{OCN-R-NCO} & \quad \text{HOOC-COOH} \quad \text{NMP} \quad \text{100°C} \quad \text{R-NHCO-CONH} \quad n \\
\text{OCN-R-NCO} & \quad \text{OC-OC-COOH} \quad \text{NMP} \quad \text{120°C} \quad \text{R-NHCO-CON} \quad n \\
\text{OCN-R-NCO} & \quad \text{OC-OC-COOH} \quad \text{DMF} \quad \text{40°C} \quad \text{R-NHCO-CON} \quad \text{130°C} \quad \text{R-NHCO-CON} \quad n
\end{align*}
\]

where \( R = \text{H}_2\text{C}, \text{Ar} = \text{PARABANIC POLYAMIDE, POLYAMID-IME AND POLYMIDES}

**Parabanic polyhydrazides and polyoxadiazoles**

\[
\begin{align*}
\text{ClCO-NN-OC} & \quad \text{H}_2\text{NNH-CR-CONH}_2 \quad \text{HCl} \quad \text{H}_2\text{O} \quad \text{Δ} \quad \text{R} = \quad \text{-(CH}_2)_4 \quad , \quad \text{-(CH}_2)_8 \quad , \quad \text{Ar}
\end{align*}
\]

REFERENCES
1. Patton T.L., Polymer Preprints, 1971, 12, 163;
Reactive Hot Melt Polyurethane Adhesives Modified by Macromer

Han Mo Jeong1, Jin Su Jung1, Jin Hee An1, Jae Hoon Kim1, Min Seok Kim1, Young Soo La1, Dae Hoon Kim1, Eun Hak Lee1, Nam Ho Kim1, Yong Sung Kim2, Tae Kyoong Kim2, Yang Lae Cho3, Jeong Mi Hwang3

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2Research Center, Hwaseung T&C Corp., Korea
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Reactive hot melt adhesives are applied in molten form, cool to solidity and subsequently cure by a chemical crosslinking reaction. An advantage of hot melt curable adhesives over traditional liquid curing adhesives is their ability to provide “green strength” upon cooling prior to cure. The majority of reactive hot melts are moisture-curing polyurethane adhesives. Substantial improvement of green strength can be obtained by the incorporation of acrylic polymers into conventional polyurethane adhesives. However the increase of viscosity by acrylic polymer can cause some troubles in the application process of adhesive.

The basic recipe for the preparation of reactive hot melt polyurethane adhesive (Sample 1), whose terminal NCO content is 3 wt%, is shown in Table 1. Additional 14.7 part of acrylic polymer (Elvacite 2013, produced by Ineos) was used in the preparation of Sample 2, and the same amount of polystyrene (PS) macromer, which has terminal diol group and whose molecular weight is 6000, produced by Toagosei, Japan, was used in the preparation of Sample 3, which is tentative sample tried before the main experiment utilizing acrylic macromer.

In Table 2, we can see that initial green strength developed between ABS and PET by Sample 2 is enhanced by Elvacite 2013 compared to Sample 1, however, the increase of viscosity is high. Whereas, although the enhancement of green strength is not so high in Sample 3 compared to Sample 2, the viscosity increase is relatively low, when PS macromer is used.

We can anticipate that the increase of green strength will be better than PS macromer, if we use acrylic macromer which has better compatibility with the components in adhesive, and that relatively low increase in viscosity will be observed. So, in order to get high green strength with relatively low increase of viscosity, we utilized in this study acrylic macromer which has terminal diol group and whose molecular weight is several thousands. The results will be presented at poster session.

---

**Table 1. Recipe for the preparation of Sample 1**

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount (by weight)</th>
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<tr>
<td>PPG 3000</td>
<td>76.8</td>
</tr>
<tr>
<td>PPG 1000</td>
<td>76.8</td>
</tr>
<tr>
<td>MDI</td>
<td>79.1</td>
</tr>
<tr>
<td>Polyester polyl (Dynacoll 7360)</td>
<td>76.8</td>
</tr>
<tr>
<td>Tackifier (terpene phenol)</td>
<td>76.8</td>
</tr>
<tr>
<td>Modaflow</td>
<td>4.0</td>
</tr>
<tr>
<td>Catalyst</td>
<td>0.1</td>
</tr>
</tbody>
</table>

---

**Table 2. Characteristics of reactive hot melt polyurethane adhesives**

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Green strength (kgf/cm) after 2 min</th>
<th>Viscosity (cps) at 100°C</th>
<th>120°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>0.16</td>
<td>2,325</td>
<td>1,012</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1.02</td>
<td>7,362</td>
<td>2,750</td>
</tr>
<tr>
<td>Sample 3</td>
<td>0.68</td>
<td>5,400</td>
<td>2,300</td>
</tr>
</tbody>
</table>
The Effect of Na-MMT Intercalated with PEG on the Properties of Reactive Hot Melt Polyurethane Adhesives

Han Mo Jeong\(^1\), Dae Hoon Kim\(^1\), Jin Su Jung\(^1\), Jin Hee An\(^1\), Jae Hoon Kim\(^1\), Min Seok Kim\(^1\), Young Soo La\(^1\), Eun Hak Lee\(^1\), Nam Ho Kim\(^1\), Yong Sung Kim\(^2\), Tae Kyoon Kim\(^2\), Yang Lae Cho\(^3\), Jeong Mi Hwang\(^3\)

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\(^2\)Research Center, Hwaseung T&C Corp., Korea
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In recent years, polymer / silicate nanocomposites have attracted considerable attention as advanced materials, because many physical properties of matrix polymers such as their mechanical, barrier, and flame retarding properties can be substantially enhanced with small amounts of silicate compared to conventional composites. Because these unique properties of polymer / silicate nanocomposites come from their high surface-to-volume ratio of fillers, layered silicate such as montmorillonite, which are composed of stacks of parallel lamellae with a 1nm thickness and a high aspect ratio, are most commonly utilized as a filler.

In this study, we prepared Na-MMT / PEG, sodium montmorillonite (Na-MMT) intercalated with poly(ethylene glycol) (PEG), where the content of PEG is 22 wt% and molecular weight of PEG is 2000. We utilized this Na-MMT / PEG to modify the reactive hot melt polyurethane adhesive. Table 1 shows the recipe of reference adhesive. In Table 2, we can see that initial green strength and final bond strength between ABS and PET generally increase when Na-MMT / PEG is added in the adhesive, much higher when higher amount of Na-MMT / PEG is used.

In addition to this adhesion property, we examined the effect of Na-MMT / PEG on the rheological and mechanical properties of adhesive. XRD and TEM morphology were also observed to explain our results.

<table>
<thead>
<tr>
<th>Table 1. Recipe for the preparation of reference adhesive sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
</tr>
<tr>
<td>PPG 3000</td>
</tr>
<tr>
<td>PPG 1000</td>
</tr>
<tr>
<td>MDI</td>
</tr>
<tr>
<td>Polyester polyol (Dyacoll 7360)</td>
</tr>
<tr>
<td>Tackifier (terpene phenol)</td>
</tr>
<tr>
<td>Modaflow</td>
</tr>
<tr>
<td>Catalyst</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2. Effect of modification by Na-MMT / PEG on bond strength between ABS and PET</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesive</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>Reference</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>C</td>
</tr>
</tbody>
</table>
The polysaccharides are important materials in food, pharmaceutical, cosmetic and related biomedical applications.

Xanthan gum is a microbial polysaccharide of great commercial significance. It is well known as one of the best thickening polymers due to its high intrinsic stiffness related to the helical conformation stabilized in the presence of excess salt. It is used in a wide variety of foods for a number of important reasons, including emulsion stabilization, temperature stability, compatibility with food ingredients, and its pseudoplastic rheological properties. Because of its properties in thickening aqueous solutions, as a dispersing agent, and stabilizer of emulsions and suspensions, xanthan gum is used in pharmaceutical formulations, cosmetics, and agricultural products, as well as in textile printing pastes, ceramic glazes, slurry explosive formulations, and rust removers. [1]

In this work the crosslinking of xanthan and lignins mixture in the presence of the epichlorohydrin, leading to superabsorbant hydrogels with high swelling rate in aqueous mediums, has been studied.

The swelling properties of these composite hydrogels were investigated. Three different types of lignin have been used namely: aspen wood lignin (lign.), annual fiber crops lignin (GL) and lignin epoxy-modified resin (LER). The sIPN hydrogels in various ratios were prepared. The influence of gravimetric ratio between components of the sIPN, as well as the kinetics of water sorption will be discussed.

The maximum swelling degree of the hydrogels and the swelling rate constant were determined as a function of the hydrogel’s composition.

It has been established that the lignin nature significantly influences swelling process, the chemical modified lignin having a particular behavior.
Swelling behavior of (a) xanthan/aspen wood lignin and (b) xanthan/annual fiber crops lignin hydrogels

References:
Hydrogels are polymeric materials with a great potential for applications in various fields, like biotechnology, medicine or pharmacy for biosensors, bioseparators, bioreactors, in tissue engineering, or as drug delivery systems, due to their excellent biocompatibility. [1]

Recently, a variety of natural or synthetic polymers employed to fabricate pH-sensitive hydrogels attracted increasing attention. Among them, alginate is one of those commonly used. Alginate, a natural polysaccharide composed of D-mannuronic acid and D-guluronic acid is derived from brown seaweeds, is a biodegradable polymer and has been widely used in biomedical applications. [2]

N-isopropylacrylamide (NIPAM) gels is one of the most commonly studied thermoreversible systems, with a lower critical solution temperature (LCST) in water of 34°C.[3] They swell below and collapse above the LCST.

In this paper, new semiinterpenetrating (sIPN) polymer networks containing N-isopropylacrylamide (NIPAM) and alginate (Alg) were obtained by radical crosslinking copolymerization at 25°C, using N,N’-methylenbisacrylamide (MBA) as crosslinking agent.

The swelling behavior of a series of NIPAM/Alg sIPN samples with different mixing ratios was studied in response to temperature and pH value of the external media.

The progress of the swelling was also followed with the variation of the crosslinking agent amount.

The maximum swelling degree of the hydrogels and the swelling rate constant were determined as a function of the hydrogel’s composition.

It has been established that the swelling degree values of the investigated sIPNs with different compositions increased with the alginate content. In the case of NIPAM gels the swelling degree decreases by increasing the amount of crosslinking agent.
Swelling behavior of NIPAM/Alg sIPN at 20°C
(A) NIPAM/Alg in different mixing ratios
(B) NIPAM/Alg with various amounts of crosslinking agent (MBA)

References
Polysulfone-g-Poly(styrenesulfonic acid) Graft Copolymers for Proton Exchange Membranes
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Polysulfones with pendant acid groups are very attractive materials for proton exchange membranes, and other possible applications. The polymer backbone possesses excellent thermal and mechanical properties, as well as resistance to oxidation and acid catalyzed hydrolysis. The polymers with sulfonic acid side groups show very promising characteristics towards an ideal proton exchange membrane, exhibiting high ionic conductivity and low reactant permeability [1,2]. But random copolymeric structure makes these copolymers poor in ionic domain connectivity at low acid content, and poor mechanical strength at high ionic contents and at high humidity conditions. To improve this situation, we synthesized new polysulfone graft copolymers containing polystyrenesulfonic acid grafts (PSF-g-PSSA). Number of grafts and the lengths of grafts were controlled. The graft copolymers were characterized by various methods, and their properties for proton exchange membrane were studied. Table 1 shows the molecular structure and the membrane characteristics of the obtained graft copolymers. Detailed results will be presented at the meeting.

Table 1. Molecular characteristics and properties of graft copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Structures of polymers</th>
<th># of SSA units / PSSA chain</th>
<th>Water uptake, %</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSF 3-g-PSSA</td>
<td>3 1 2</td>
<td>15</td>
<td>17</td>
<td>2.65×10^{-2}</td>
</tr>
<tr>
<td>PSF15-g-PSSA</td>
<td>15 1 5</td>
<td>3.67</td>
<td>18</td>
<td>5.40×10^{-3}</td>
</tr>
<tr>
<td>PSF29-g-PSSA</td>
<td>29 1 10</td>
<td>1.6</td>
<td>15</td>
<td>3.80×10^{-3}</td>
</tr>
</tbody>
</table>

References
Plasma-chemical synthesis of polyconjugated polymer from 1-amino-9,10-anthraquinone
Gilman A.B., Drachev A.I., Kuznetsov A.A.

Enikolopov Institute of Synthetic Polymer Materials Russian Academy of Sciences
plasma@ispm.ru

Basically, polymers obtained by plasma polymerization of aromatic compounds having fused rings possess specific conductivity of $10^{-14} – 10^{-16}\Omega^{-1}\mathrm{cm}^{-1}$ at $20^\circ\mathrm{C}$ [1], the level typical for dielectrics. Polymeric films with semiconductive properties ($\sigma=10^{-7} – 10^{-13}\Omega^{-1}\mathrm{cm}^{-1}$) can be obtained by plasma polymerization of heteroaromatic compounds, such as thiophene, aniline, pyridine, pyrrole, etc [2]. Doping these polymer by iodine and HCl increases conductivity up to $\sim10^{-4}\Omega^{-1}\mathrm{cm}^{-1}$. Formation of quinoid-benzoid type $\pi$–conjugated structure with participation of the electron pair of nitrogen atoms is postulated to explain semiconductive properties of polymer obtained by plasma polymerization of aniline [3].

In this work, the process of plasma polymerization of 1–amino–9,10–anthraquinone (AAQ) in DC discharge was investigated. Plasma polymerization process in DC discharge is non-symmetrical as regards direction of electric field. The layers deposited on the anode and cathode during plasma polymerization was found to differ essentially from each other. The former was yellow oligomer with poor mechanical properties. It had specific conductivity of $10^{-16}\Omega^{-1}\mathrm{cm}^{-1}(20^\circ\mathrm{C})$, a value typical for majority of polymers obtained by plasma polymerization [1, 2]. Contrast to that, strong black polymer layer having typical metal-like luster deposited on the cathode with the volume conductivity of $\sigma = 10^{-4} – 10^{-5}\Omega^{-1}\mathrm{cm}^{-1}$ (20$^\circ$C), i.e. higher by 11–12 orders of magnitude. The thickness of the layer can be controlled by duration of experiment. Semi-conductive polymeric layers with thickness up to 10 $\mu$m were obtained. The surface conductivity of the layer deposited on the cathode was found to be equal to $3.7 \times 10^{-16}\Omega^{-1}$, i.e. value typical for dielectrics. So, the polymer deposited on the cathode possesses pronounced electrical anisotropy. On the basis of FTIR data, it should be suggested that polymer film obtained has a polyconjugated structure close to that of polyaniline. Chain growth is thought to proceed as a result of migration of AAQ cation radicals generated in a gas phase to the cathode followed by electron transfer reaction between cation radical with poly-AAQ end fragment to give polyconjugated chain. Contrast to electropolymerization of aniline, cation radical is formed not due to electrochemical oxidation of neutral molecule, but due to direct ionization in low temperature plasma. The second stage – cation radical addition reaction to p-position of benzene ring is similar to polymerization of aniline.

References
Self-Organized Lamellar Nanostructures of Wholly Aromatic Block Co-Oligomers: Oligo(ether-sulfone)-b-Oligo(ether-ketone)

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A variety of nanodomains or supramolecular structures of block copolymers are of great interest in use directly or as templates especially for nanomaterials in a wide range of electronic, optic, or magnetic devices. A large variety of coil-coil type and rod-coil type block copolymers have been widely studied, however very few attempts have been made at study of wholly aromatic rigid-rod block copolymers, namely, rod-rod type block copolymers. The rod-rod type block copolymers are expected as a new class of nanomaterials with excellent thermal and mechanical properties. Herein, we report synthesis and self-organized nanostructure of wholly aromatic block co-oligomers, oligo(ether-sulfone)-b-oligo(ether-ketone)s (OES-b-OEK). The nanostructure characterization of OES-b-OEKs was carried out by using wide & small angle x-ray scattering (WAXS, SAXS) and transmission electron microscopy (TEM).

The well-defined diblock and triblock OES-b-OEKs were prepared by a stepwise synthesis via an aromatic nucleophilic substitution reaction. Infrared, 1H NMR, and MALDI-ToF MS spectra showed that the desired OES-b-OEKs were successfully obtained. Molecular weights of the diblock and triblock OES-b-OEKs were 1712.9 and 2236.7, respectively. In differential scanning calorimetry (DSC) curve of the diblock OES-b-OEK, the baseline shift observed at 120 °C correspond to the glass transition (Tg) of the OES block. Above the Tg temperature, an endothermic peak was observed at 202 °C, and a phase transition to an isotropic phase was found to occur around this temperature by means of a polarized optical microscope (POM) observation. The TEM image confirmed that the diblock OES-b-OEK formed lamellar structure with a periodicity of approximately 99 Å. This layer spacing was good agreement with that of the SAXS characterization of 91 Å. The intermolecular spacing of the block copolymer was found to be 4.7 Å from WAXS data.

Figure 1. TEM image of diblock OES-b-OEK.
Synthesis and Properties of Highly Soluble Addition-Type Imide Oligomers Based on Fluorenylidene Diphenyl Ether Groups for Matrices of Carbon Fiber Composites

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Introduction
Usually, composites of carbon fibers and thermosetting polyimides are fabricated by routing an amide acid solution prepreg, because an uncured imide oligomer’s solubility of more than 30 wt% is required to produce a prepreg. In this route, water generated as a by-product of imidization in the curing process may cause the generation of voids in the composites. In previous works, in order to improve the solubility of the imide oligomer while maintaining high thermal resistance, fluorenylidene groups were introduced to asymmetric thermosetting polyimide “TriA-PI”¹, ²). In this work, an imide oligomer based on symmetric 4,4’-biphenyltetrahydroxylic dianhydride (s-BPDA) and a diamine containing fluorenylidene diphenyl ether group (9,9-bis(4-(4-aminophenoxy)phenyl)fluorene, BAOFL) was synthesized. Solubility, processability of the imide oligomer, and the thermal and mechanical properties of the cured resin were evaluated.

Experimental
BAOFL (2.663 g, 5 mmol) and NMP (8.8 ml) were placed in a three-necked flask, equipped with a magnetic stirrer and nitrogen inlets. s-BPDA (1.177 g, 4 mmol) was added to the solution. The reaction was allowed to stir for 2.5 h at room temperature, for 1.5 h at 60°C, and then for 1 h at room temperature under nitrogen flow. Subsequently, PEPA (0.497 g, 2 mmol) was added to the solution; the solution was stirred for 18 h at room temperature and then for 5 h at 175°C. The solution was then poured into water (150 ml). The product was washed with methanol (60 ml), filtered, then dried at 60°C in vacuo.

Cured resin films were prepared in a polyimide film frame (80 mm × 50 mm × 75 µm) using a hot press. The imide oligomer (ca. 0.5 g) was heated at 310°C for 20 min on a hot plate. It was then cured at 370°C for 1 h under 2 MPa.

Results and Discussion
The imide oligomer was synthesized from the reaction of s-BPDA, BAOFL, and 4-phenylethynylphthalic anhydride (PEPA) through thermal imidization in NMP. The calculated degrees of polymerization of the imide oligomer were 4. After imidization, the reaction solution maintained homogeneity without precipitation. The imide oligomer had
excellent solubility of more than 33 wt% in aprotic polar solvents. The solubility is sufficient to prepare the imide solution prepreg. The minimum melt viscosity was 326 Pa·s, measured by a rheometer. The imide oligomer could be molded easily by using a hot press. The glass transition temperature \( T_g \) of the cured resin exhibited 321 °C, judged by DSC. The 5% weight loss temperature \( T_{d5} \) was 551 °C. The tensile modulus, tensile strength, and elongations-at-break of the cured resin film were 2.78 GPa, 110 MPa, and 10.2 %, respectively. Properties of the imide oligomers and cured resins prepared from s-BPDA and several diamines are summarized in Table 1. The imide oligomer based on BAOFL has high solubility and good processability as compared with other diamines. Furthermore, \( T_g \) was higher than that of other cured resins. It suggested that fluorenylidene groups affect solubility and heat resistance, and ether linkages affect low viscosity and processability.

### Table 1 Properties of the imide oligomers and cured resins based on s-BPDA and several diamines

<table>
<thead>
<tr>
<th>Diamines</th>
<th>Imide Oligomers</th>
<th>Cured Resins</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solubility in NMP</td>
<td>Processability</td>
</tr>
<tr>
<td>PI resin-1</td>
<td>BAOFL</td>
<td>soluble (33 wt%)</td>
</tr>
<tr>
<td>PI resin-2</td>
<td>4,4'-ODA</td>
<td>insoluble</td>
</tr>
<tr>
<td>PI resin-3</td>
<td>1,3,4-APB</td>
<td>insoluble</td>
</tr>
</tbody>
</table>

- a) BAOFL: 9,9-bis(4-(4-aminophenoxy)phenyl)fluorene, 4,4'-ODA: 4,4'-diamidodiphenyl ether, 1,3,4-APB: 1,3-bis(4-aminophenoxy)benzene
- b) Measured in NMP at r.t.
- c) Cured at 370°C for 1h.
- d) Determined by DSC at a heating rate of 10°C/min under argon.
- e) Determined by TGA at a heating rate of 10°C/min under argon.

**Conclusions**

Novel soluble addition-type imide oligomer and its cured resin were developed. The introduction of BAOFL resulted in an increase in solubility of imide oligomers prepared from not only asymmetric BPDA but also s-BPDA. A highly concentrated solution of the imide oligomer has the potential of avoiding voids in composites when routing solution prepreg because of the fact that there is no water volatility in the curing process.

**References**

Synthesis of Hyperbranched Polymers with Penta(ethylene oxide) Chains and Core Structure

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Hyperbranched polymers with oligo(ethylene oxide) chains have potential on various applications as well as liner poly((ethylene oxide)s. Our group has studied on the synthesis of hyperbranched polymers with oligo(ethylene oxide) chains by polycondensation of cyanomethylphenyl-type AB2 monomers.1) The obtained hyperbranched polymers with penta- or hexa(ethylene oxide) chains were not soluble in water. A purpose of our study is to prepare water-soluble hyperbranched polymers applicable for the formation of nanoparticles by self-organizations. This paper describes the synthesis of water-soluble hyperbranched polymers with penta(ethylene oxide) chain and a core structure by the polycondensation under mild reaction conditions.

Active methylene type AB2 monomer with penta(ethylene oxide) 5EM and core molecule 5EC4 were respectively prepared. Polycondensation of 5EM and 5EC4 (5-30 mol%) were carried out with NaOH in DMSO at room temperature. The structures of the obtained polymers were confirmed by FT-IR, 1H NMR, 13C NMR spectra, and GPC. The molecular weight \( M_n \) and \( M_w/M_n \) (PS standards) of the hyperbranched polymers obtained from the polymerization with 5 mol% of 5EC4 was ca. 9000 and 1.50, respectively. The molecular weights of the hyperbranched polymers decreased with increasing 5EC4 feed ratios on the polycondensation. The degree of branching (DB) of the polymers were 0.45-0.49. The solubility of the polymers in common organic solvents improved with 5EC4 ratios. The obtained polymers consist of methanol-insoluble and methanol-soluble polymers. The methanol-soluble parts were easily dissolved in water at room temperature. (1) A. Kameyama, S. Komine, D. Takeshita, The 8th SPSJ International Polymer Conference, Preprints, p560 (2005).
End group controlled cure of polyester powder coatings with a β-hydroxyalkylamide as crosslinker.

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Abstract

Acid functional polyester powder coatings can be cured with a β-hydroxyalkylamide (Primid®) as crosslinker. The condensation reaction occurs through an oxazoliniumcarboxylate ion pair intermediate and cannot be controlled by the use of a catalyst. For application purposes the crosslinking is sometimes too fast resulting in coating defects like pinholing due to e.g. degassing problems and bad flow. Research showed that the rate of the crosslinking reaction can be controlled by changing aromatic acid end groups (terephtalic or isophtalic acid) with aliphatic acid end groups like adipic acid. This gives the opportunity to obtain powder coatings with improved appearance.
SILOXANE-ORGANIC POLYESTERS BY DIRECT POLYCONDENSATION

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As a result of the increased bulkiness and flexibility of the siloxane groups, their use in copolymers with different architectures provides good solubility, film forming abilities, lower transition temperatures, which implies an increased processability. Due to the great versatility of their chemistry, by reacting siloxanes and different organic compounds, a large variety of improved materials can be obtained. Continuous efforts are focused nowadays to find new synthetic routes for siloxane-organic copolymers or to obtain new structures by „classical” methods, to investigate their properties and find applications according to the most up-to-date knowledge. Synthetic techniques have advanced to the point where almost any conceivable copolymer design can be made and the chemical composition of each block can be selected as desired.

We present the synthesis and properties of two classes of polyesters having either azomethine internal linkages or pendant azobenzene chromophores, and siloxane-organic backbone. Direct polycondensation in solution, at ambient temperature using dicyclohexylcarbodiimide as activating agent and 4-(N,N-dimethylamino)pyridinium-p-toluenesulfonate (DPTS) as catalyst proved to be an effective reaction path, which afforded azomethine and azobenzene-containing polyesters in good yields [1].

Azo-containing compounds are known for their interesting optical applications such as holographic information storage, photoswitching, sensors, surface relief gratings, and also for their behavior as calamitic mesogens. On the other hand, poly(azomethine)s exhibit excellent thermal stability, good mechanical strength and environmental resistance. They are thermotropic polymers and have potential as high performance fibers, opto-electronics and semiconducting materials, but the insolubility of aromatic poly(azomethines) is a rather common problem. One solution might be the introduction of siloxane linkages into their chain [1 - 4]

In our study, the starting compounds were siloxane-organic diacids and organic bisphenols or diols, having mesogenic structure. The method proved to be suitable for siloxane-organic synthesis, due to mild reaction conditions, avoiding acid chlorides and high temperatures, and providing a neutral medium, which preserved siloxane linkages.
The chemical structures of the obtained polymers were confirmed by spectroscopic techniques (IR, NMR). The molecular weights of the polyesters, determined by gel permeation chromatography, were in the range of $10^4$ g/mol.

The polyesters exhibited good thermal stability and were soluble in many common organic solvents.

The liquid crystalline behavior has been investigated by polarizing optical microscopy, differential scanning calorimetry, thermo-optical analysis and X-ray diffraction. The influence of siloxane segments’ length and polymers’ structure over the thermotropic, photochemical and surface properties has been studied.

**References**


**Acknowledgements**

The financial support from Romanian Ministry of Education and Research, under Grant CNCSIS No. 32952 / 22 VI 2004 is gratefully acknowledged.
Poly(azomethine)s are an important class of thermotropic polymers that have potential as high performance fibers and opto-electronic materials. They are also of great interest for their semiconducting properties and their ability in forming chelates.

The wholly aromatic poly(azomethine)s have high melting or softening temperatures and low solubility. Their processability may be improved by incorporating flexible aliphatic units into the main chain, by introducing pendent alkyl groups along the backbone, and/or by copolymerizing various dialdehydes and diamines.

Siloxanes as flexible segments have been used in different polymeric structures in order to ameliorate the processing properties, due to their ability to lower the transition temperatures and enhance the solubility. The same effect has been reported for poly(azomethine)s containing siloxane units [1-4].

By solution polycondensation, starting from bis(formyl-p-phenoxymethyl)-tetramethyldisiloxane and different organic diamines, new poly(azomethine)s have been obtained:

\[
\text{ArN} = \text{Si} \bigg(\text{ArN} = \text{Si}\bigg) + \text{H} \cdot \text{Ar} \cdot \text{NH}_{2} \rightarrow \left[\text{ArN} = \text{Si} \bigg(\text{ArN} = \text{Si}\bigg) \right]
\]

In the case of aromatic diamines with high rigidity, which gave insoluble polymers, different approaches were tested in order to improve the solubility: the use of a dialdehyde having longer siloxane chain, or of a siloxane diamine in a copolycondensation reaction.

The polymers’ structures were confirmed by IR and \(^1\)H-NMR spectroscopy and by elemental analysis. The structure-properties relationship was studied in terms of solubility, thermal and thermotropic behavior. Most of the obtained poly(azomethines) have mesomorphic properties, which were studied by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The influence of aromatic diamines’ chemical structure on the processability of the siloxane-organic poly(azomethine)s was emphasized.

References
Novel thermal acid generators for low temperature cyclization of poly(o-hydroxyamide) and their application for photosensitive polymer

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A novel high transparent and low-temperature curable photosensitive poly(benzoxazole) (PSPBO) consisting of poly(o-hydroxyamide) (PHA), a photo-acid generator, (5-propylsulfonyloxyimino-5H-thiophene-2-ylidene) - (2-methylphenyl) acetonitrile (PTMA), and a thermal acid generator, isopropyl p-toluenesulfonate or isopropyl methanesulfonate, has been developed. This PSPBO is transparent at 365 nm, thus is applicable to a thick film formulation.

Introduction

Photosensitive polybenzoxazoles (PSPBOs) have been used as buffer coatings to protect bare chips from stresses induced by fillers or thermal mismatches between a passivation layer and molding materials. This material, however, needs high curing temperature as high as 350 °C to transform PHA into PBO, which could damages the other components on the device. Recently, we reported a novel PSPBO that can transform PHA into PBO at 250 °C for 10 min, where (5-propylsulfonyloxyimino-5H-thiophene-2-ylidene)-2-(methylphenyl)-acetonitrile (PTMA) was used as a photoacid generator (PAG). This method, however, requires 10 wt% of PTMA that is expensive, thus the amount of PTMA should be reduced for practical applications of this method. Here, we report a latent thermo-sensitive acid generator (TAG), which promotes a low temperature cyclization of PHA, and formulation of PSPBO on the basis of PHA, a TAG, and PTMA.

Results and Discussion

(i) Low temperature cyclization of PHA with TAG

Isopropyl p-toluenesulfonate (1) and isopropyl methanesulfonate (2) as the TAG were prepared from isopropyl alcohol and the corresponding sulfonyl chloride. Two TAG are transparent at 365 nm (Scheme 1). Then, the cyclization of PHA film containing 10 wt% of TAG 2 was investigated at 250 °C for 15 min. The IR spectrum of the cured PHA film was identical with that of the PBO film obtained by the thermal treatment of PHA at 350 °C for 1 h, indicating TAG 2 decomposed at this temperature and released methanesulfonic acid, which promoted the cyclization of PHA.

(ii) PSPBO with TAG

PSPBO consisting of PHA (73 wt%), 9,9-bis(4-tert-butoxycarbonyloxyphenyl)-fluorene as a dissolution inhibitor (18.2 wt%), ¹ 1 (7.3 wt%), and PTMA (1.5 wt%)

Scheme 1. Structure of TAG

Figure 1. SEM image of PHA pattern.
as a PAG was formulated. The dissolution contrast between the exposed and unexposed areas with 365 nm light in an industrial standard developer 2.38 wt% tetramethylammonium hydroxide reached around 500 times. This PSPBO showed the excellent sensitivity of 33 mJ/cm\(^2\) and contrast of 5.8, and a 10 µm resolution pattern was easily obtained using a 5.6 µm-thick film (Figure 1). The IR spectrum of the patterned film heated at 250 °C for 15 min showed complete cyclization of PHA, indicating the TAG acted as the promoter for low temperature cyclization of PHA. The newly developed TAG is very useful to reduce the amount of an expensive PAG in the formulation of low temperature curable PSPBO.

References
A high molecular weight poly(binaphthylene ether) containing 2,2'-dimethylbiphenyl moiety as a matrix of low-κ materials was prepared by oxidative coupling polymerization using iron (III) chloride as an oxidant. The obtained polymer showed good solubility in various solvents to give self-standing, flexible and robust film. The polymer solution with a porogen in toluene was cast to make porous film by thermal treatment.

Introduction

Organic polymers have an advantage for low-κ materials because the inherent dielectric constant ($\varepsilon$) values of these materials are relatively lower than that of inorganic materials. However, the low-κ dielectrics require sufficient thermal and mechanical properties to endure the manufacturing process of electric devices, causing the limitation of available polymers for dielectrics only such as poly(imide)s. Recently we have discovered that poly(binaphthylene ether) showed low $\varepsilon$ value without sacrificing high thermal stability. This finding may be attributed to its kinked binaphthyl structure involving much free volume to decrease molecular density. Unfortunately, its bulky rigid backbone as well as the low molecular weight rendered the polymer film to be brittle. On the other hand, incorporation of pores in the polymer films, which requires possessing high mechanical strength, can significantly decrease the $\varepsilon$ value. Here, we report the synthesis of high molecular weight poly(binaphthylene ether) by oxidative coupling polymerization, and its application to porous films to achieve lower $\varepsilon$ value.

Results and discussion

In a previous work, the oxidative coupling polycondensation of binaphthyl ether containing 2,2'- (trifluoromethyl)biphenyl group gave the corresponding high molecular weight polymer enough to make flexible and robust films. Although this polymer showed excellent properties for low-κ dielectrics, incorporation of trifluoromethyl groups is costly undesirable. Therefore, 4,4'-bis(1-naphthyloxy)-2,2'-dimethylbiphenyl (1) which is an inexpensive analogue to the fluorine containing monomer was synthesized by Ullmann reaction using 2,2'-dimethyl-4,4'-biphenol and 1-bromonaphthalene.

The polymerization of monomer 1 was conducted with 2.5 equiv. of iron (III) chloride as an oxidant in nitrobenzene at room temperature. Table 1 shows the number average molecular weight ($M_n$), which was monitored by GPC as the polymerization time. The white fibrous polymer was obtained with high $M_n$ of 81,000, when the polymerization was carried out for 8 h. The polymer structure was confirmed by IR, $^1$H and $^{13}$C NMR spectra, and the coupling reaction completely occurred at para-position of 1-naphthyloxy moieties, resulting in the linear polymer.

The obtained polymer 2 showed good solubility in such as toluene, tetrahydrofuran and chloroform, and the film
obtained from toluene solution was self-standing, transparent and flexible. To the formation of porous film of 2, the polymer solution with 10 wt% of various porogens in toluene was prepared, then cast to make transparent film that is subject to thermal treatment.

References
Amide interchange reactions in polyamide blends: Influence of end-groups

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Polyamides are chemically reactive during melt processing, giving rise to interchange reactions. When polymer blends are processed, interchange reactions generate copolymers, consisting of sequences of the blend components. The sequence length and the degree of randomness of final copolymers are functions of blend composition, mixing temperature and residence time in the melt. Using such processes, therefore, one can design copolyamides of different degrees of randomness and compositions.\textsuperscript{1-3}

Although some authors did not detect any influence of the nature of end-groups on the properties of final polyamide blends,\textsuperscript{2} other authors found that COOH end-groups play a predominant role.\textsuperscript{4} In order to get information on the possible influence of end-groups and catalysts on amide interchange reactions, a series of model amides (aromatic, cycloaliphatic and aliphatic) were synthesized. The reaction of these amides with model acids, amines and amides were carried out at 220-270\textdegree{}C under nitrogen. Similar reactions were carried out between model amides and high molecular weight PA12 and between model amides and carboxy- or amine-terminated PA12. These reactions were followed by SEC. The influence of possible amide interchange catalysts was also studied using the model molecules.

From the set of interchange reactions, the following conclusions can be drawn:

- Amide-amide and amide-amine reactions do not take place either with or without catalysts, in the temperature range studied,
- Carboxy-amide reactions on model molecules can take place without catalyst. Carboxy-amide interchanges were also observed with model oligoamides and high molar mass PA12,
  - Aliphatic acids are more reactive than aromatic acids,
  - Some catalysts can increase the initial carboxy-amide reaction rate to ca. twice its value without catalyst; therefore a significant, though moderate, catalytic efficiency.

The interchange process leading to the random distribution is relatively slow. However, it must be underlined that mixtures of homopolymers are converted into block-copolymers after only one interchange reaction per chain i.e. at very low conversions. The existence of carboxy-amide interchange reactions can, therefore, lead to important consequences on the properties of final, processed blends.

References
Morphology Control of Poly[2,2’-(p-phenylene)-5,5’-bibenzimidazole] by Using Crystallization of Oligomers during Solution Polymerization

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² Graduate School of Natural Science, Okayama University, Okayama 700-8530, Japan

Nanotechnology has led to the fabrication of polymer fibers on the nano- and micrometer scale. Among them, aromatic polymer nanofibers have been attracting much interest as high-performance materials. However, they show neither solubility nor meltability and this intractability makes them inaccessible to process as materials. Under these circumstances, we have been studying the morphology control of aromatic condensation polymers by means of reaction-induced crystallization of oligomers. This paper deals with our new finding on the fabrication of poly[2,2’-(p-phenylene)-5,5’-bibenzimidazole] (PBI) nanofibers by using the crystallization of oligomers during solution polymerization.

Polymerizations of 3,3’-diaminobenzidine and diphenyl terephthalate were carried out at 320 and 350 °C for 6 hours in solvents in order to induce the crystallization of oligomers. The solvents used in this study were liquid paraffin (LPF), Barrel Therm 400 (BT4, Matsumura Oil Co., Ltd.), which is the mixture of dibenzyl toluene, and diphenyl sulfone (DPS). The polymerization results were summarized in Table. In the polymerizations in LPF, plate-like crystals of PBI were obtained in good yield. The inherent viscosity (ηinh) was 0.21 – 0.27 dL/g. On the other hand, in the polymerization in BT4, the bundle-like aggregates of PBI nanofibers were prepared with quantitative yields as shown in Figure. The diameter of each nanofiber was averagely 52 nm. The ηinh of PBI prepared in BT4 were 0.35 – 0.58 dL/g and they were higher than those in LPF. The ηinh of PBI prepared in DPS was 0.75 dL/g and it was higher than those in LPF and BT4. The nanofibers possessed high crystallinity measured on WAXS and

<table>
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<th>Polymerization condition</th>
<th>Conc (wt% vol%)</th>
<th>Temp (°C)</th>
<th>Yield (%)</th>
<th>ηinh (dL/g)</th>
<th>Morphology of crystals</th>
<th>Tg (°C)</th>
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</thead>
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<td>69</td>
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<td>plate</td>
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<tr>
<td>BT4</td>
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<tr>
<td></td>
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<td>84</td>
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<td>NF</td>
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<td>93</td>
<td>0.75</td>
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</tbody>
</table>

a) Inherent viscosity (ηinh) was measured in concentrated H2SO4 at 0.2 g/dL and 30 °C. b) 5% weight loss temperature measured at the rate of 10 °C/min in N2. c) NF stands for the aggregates of PBI nanofibers. d) Concentration (wt%) = (weight of PBI) / (weight of DPS) × 100.
good thermal stability. The morphology was drastically changed by the solvent, and the control of miscibility is of great importance for the fabrication of PBI nanofibers.

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Synthesis of Polyimides using Ionic Liquids as Condensation Agents and Medium

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Wholly aromatic polyimides are well-known as thermal-stable engineering polymers and applied as protection and insulation layers in manufacturing semiconductors [1]. In general, polyimides are prepared via poly(amic acid)s from aromatic diamines and dianhydrides. By the way, we have found previously that polyamides could be synthesized from diamines and diacids in ionic liquids (ILs). In this reaction, ILs acted as condensation agents. Here, it is discussed that polyimides are prepared from diamines and non-active tetra-acids in ILs. Cyclodehydration of poly(amic acid)s using ILs is also determined.

The condensation reaction of aniline with phthalic acid in 1-butyl-3-methylimidazolium bromide ([bmim][Br]) at 150°C for 12 h provided only N-phenylphthalimide in 73% without N-phenylphthalamic acid. It was thought that [bmim][Br] has high catalytic and condensation ability to activate carboxylic acids. The polycondensation of 1,3-bis(4-aminophenoxy)benzene and 3,4,3',4'-diphenylsulfonetetracarboxylic acid were carried out in various conditions such as four ILs containing imidazolium cation ([bmim][Cl], [bmim][Br], [bmim][BF4], [bmim][PF6]), temperature, time. Polyimides could be obtained in high yields using [bmim][Br] at 180 °C for 24h, while polymerization proceeded heterogeneously. Lower temperature gave polyimides with poly(amic acid) structure. The cyclodehydration of poly(amic acid)s in [bmim][Br] were also studied at lower temperature than conventional thermal cyclodehydration temperature (250-400°C). The treatment of poly(amic acid)s in [bmim][Br] at 150°C for only 30 min provided the complete transfer to polyimides.

References

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Facile Synthesis of Monodisperse Oligoamides Based on 4-(N-Methylamino)benzoic Acid Using Thionyl Chloride as an Activating Agent

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Introduction

In step-growth polymerization, $M_n$ as well as $M_w/M_n$ of the polymer is difficult to control due to the statistical nature in its mechanism. Recently, the control of $M_n$ and $M_w/M_n$ was achieved in the polyamide synthesis via chain growth manner using 4-(N-octylamino)benzoic acid phenylester as an AB monomer. Although such polymers have great interests for the building blocks of self-assembly architectures because of relatively uniform length and functionalities in their backbone, the preparation of the corresponding monodisperse aromatic $N$-alkyl amide oligomers has not been described so far. The $N$-alkyl oligoamides with a precise length is attractive for not only building units of supramolecular architectures but also useful models for their corresponding polydisperse macromolecular analogs.

Here, we describe a facile synthesis of monodisperse oligoamides based on 4-(N-methylamino)benzoic acid using thionyl chloride as an activating agent. In this method, the number of amide units doubles only through every two reactions, deprotection and condensation.

Results and Discussion

The protection reaction of 4-(N-methylamino)benzoic acid with excess amount of trifluoroacetic anhydride was first conducted to produce protected-monomer 2. The coupling reaction was carried out by the one-pot method involving activation of carboxylic acid in a protected-AB compound using thionyl chloride, followed by condensation with an unprotected-AB compound. The protected-dimer 3 was successfully prepared from 2 (protected) and 1 (unprotected) in 93% yield. The end trifluoroacetamide group was easily hydrolyzed using $K_2CO_3$ in $H_2O/MeOH$ at r.t. only for 30 min to unprotected-dimer 4 in quantitative yield due to the strong electron withdrawing effect of trifluoroacetyl group. Then, the carboxylic acid of protected-dimer 3 was activated using thionyl chloride and reacted with unprotected-dimer 4 to give protected-tetramer 5 in one-
pot. The resulting protected-tetramer 5 was quantitatively converted to unprotected-tetramer 6 by selective hydrolysis of the end group using $K_2CO_3$. We performed reactions in the same manner using protected and unprotected-tetramers to synthesize protected-octamer 7. As the protected-octamer is insoluble in H$_2$O/MeOH even under alkaline condition, the hydrolysis reaction of the end amide group in 7 was carried out in NMP using DBU as a base with small amount of water at 100 °C. All products were purified only using recrystalization or precipitation in quantitative yields. The $^1$H-NMR, $^{13}$C-NMR, IR, and MALDI-TOF MS spectrum indicates the formation and isolation of the each desired oligoamides.

References

Synthesis and Characterization of Water-Soluble Poly(para-phenyleneethynylene) Copolymer for Bioconjugation

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Recently, water-soluble conjugated polymer has attracted much attention because of their detection applications, such as DNA, proteins, and biological agents. Conjugated polymers, especially, were used for sensory materials due to large signal amplification by trace amount of analytes. Conventional conjugated polymers, however, are only soluble in organic solvents, because they have commonly a hydrophobic and rigid main chain. This resulted in a poor solubility in water and subsequent fluorescent quenching by micelle formation in an aqueous phase. Herein, we synthesized water-soluble poly(para-phenyleneethynylene) copolymer containing polyelectrolytes. Furthermore for bio-applications, water-soluble poly(para-phenyleneethynylene) copolymer include maleimide as a receptor in a main chain connected covalently. Widely utilized in bioconjugation, maleimides are often used to tag sulfhydryls in biomolecules by a facile Michael addition of the thiol across the maleimidyl double bond.
Synthesis and Characterization of Fluorescent Water-Soluble Conjugated Poly(aryleneethynylene)s

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In recent years, synthesis and application of water soluble conjugated poly(para-phenyleneethynylene) to sense chemical and biological analytes (ions, peptides, proteins, nucleic acids) has received much attention for many researchers. Until now, most of the attention has focused upon the dialkyl- and dialkoxy-PPEs, and only very few heteroaromatic poly(aryleneethynylene)s (PAE) have been reported. We herein describe the synthesis and photochemical properties of P1 and P2 with aryl moiety in the polymer backbone. These polymers have water soluble group (sulfonate and ethylene glycol group) in a symmetric fashion. By reduction of P1, phenylenediamine moiety could be introduced into the polymer backbone, which was expected to bind with anions. These polymers were soluble in water and showed strong fluorescence. Significant quenching of fluorescence of P2 upon addition of anions was observed. Fluorescence quenching was showed that P2 have selectivity for fluoride anion over other anions.

\[
\text{P1} \xrightarrow{[H]} \text{P2}
\]

\[ R = -\text{C}_4\text{H}_9\text{SO}_3\text{Na}, -\text{(CH}_2\text{CH}_2\text{O)}_3\text{H} \]
Supersructures, which are composed of low molar mass molecule, have attracted much interest due to their unique characteristics and potential applications as templates for nano-scale inorganic materials\(^1,^2\), organic soft materials\(^3\), and optical sensors\(^4\). These low molar mass molecules create a three-dimentional network structure by the entanglement of nanofibers or nanoribbons formed by self-assembly through noncovalent interactions such as hydrogen bonding, van der Waals force, \(\pi\)-stacking, and coordination.

2-(2’-Hydroxyphenyl)benzoxazole has been widely studied from the view point of photophysics due to its two emissions through the excited state intramolecular proton transfer (ESIPT) (Scheme 1). Urea bonds acting as hydrogen bonding sites enables the covalent link between 2-(2’-hydroxyphenyl)benzoxazole and long alkyl chain, which played crucial roles in \(\pi\)-stacking and van der Waals interactions, respectively, for superstructure formation. Dramatical increase in fluorescence intensity was observed after self-assembly process, implying that emission intensity of enol form was quenched and that of keto form considerably increased.

A low molar mass molecule for superstructure was synthesized by the reaction with 2-(2’-hydroxyphenyl)benzoxazole and alkyl isocyanate in THF at room temperature. The self-assembly of low molar mass molecule containing 2-(2’-hydroxyphenyl)benzoxazole units into supramolecular structure was performed in a DMF/toluene mixture by cooling to room temperature after heating. The supramolecular structure was confirmed with XRD, FE-SEM and TEM. The optical properties of the superstructure were investigated with UV-vis and fluorescence spectrometers. A fibrous nanostructure of which thickness and length were estimated near 30 nm and a few \(\mu\)m, respectively, was observed by FE-SEM and TEM, which obtained after freeze-drying (Figure 1). The diffraction peaks which were determined by SAXS indicated that the fibrous nanostructure was formed from hexagonal structures with a width of about 3 nm, which corresponds to be similar to the molecular length of a fully extended molecule. The self-assembly mechanism was comprised in hydrogen bond between amine unit and carbonyl units in urea groups and by van der Waals interaction between long alkyl chains.
Scheme 1. ESIPT process of 2-(2'-hydroxyphenyl)benzoxazole.

Figure 1. FE-SEM photograph of supramolecular structure from self-assembly of low molar mass molecule.

References
Application of fluorescent conjugated polymers to “amplified” sensing of chemical and biological analytes has received considerable attention. Recently, synthesis and application of water-soluble poly(para-phenylenes) via Suzuki cross coupling reaction has received attention for many researchers. We have attempted to synthesize water-soluble polymer composed of dialkoxy-carboxylate and benzaldehyde moiety in the polymer backbone. We developed a method to introduce a benzaldehyde group, a versatile functional group for bioconjugation, at the end of PPPs chain. The synthesis polymer was soluble in water. The polymer containing benzaldehyde end-group had binding capacity for biological analytes showing fluorescence quenching.
Crosslinked Siloxane-Polyurethane Coatings for Underwater Marine Applications Using Combinatorial High Throughput Experimentation

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Abstract

Crosslinked siloxane-polyurethane coatings were designed, synthesized, formulated, applied, characterized using high-throughput methods and eight coatings were selected as candidates for further characterization. First, 72 novel alkyl carbamate-linked PDMS oligomers and their block copolymers with PCL blocks were synthesized using a high-throughput synthesis robot. These siloxane oligomers and block copolymers were characterized for their molecular weight using Rapid-GPC. The 72 oligomers were incorporated into siloxane-polyurethane coatings at four different levels resulting in 288 siloxane-polyurethane coatings. After initial screening of these 288 coatings, eight coatings were down-selected for further characterization. DSC, DMA and XPS and surface energy analysis demonstrate the presence of PDMS on top layer and polyurethane underlayer. Bacteria tests for biofilm retention, redistribution and percent removal with C. lytica and H. pacifica show good agreement with pseudo-barnacle adhesion.
Diels-Alder Trapping of Photochemically Generated Dienes with Acrylic Esters: A Novel Approach to Photocured Polymer Film Development

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Diels-Alder cycloadditions have often been utilized in polymer synthesis as an alternative to condensation reactions.1 These methods are attractive for use in the preparation of high performance polymers, such as polyimides, because they utilize monomers that have less environmental, health and safety risks. In addition, they have the potential to be adapted to low cost processing techniques. Future NASA Human and Robotic Exploration missions will require polymers and adhesives that may be cured in ambient space environments for in-space repairs, large deployable, rigidizable arrays and inflatable habitats and rovers. On earth, lower cure temperatures are desirable to reduce tooling costs and processing induced thermal stresses. In addition, thermal processing conditions may be too severe to use with certain functional groups, such as nonlinear optically active or antimicrobial units. For these reasons, we have been pursuing the development of high performance polymers that can be cured at low temperatures with ultraviolet radiation.

Our approach to exploiting Diels-Alder cycloaddition reactions has focused on bis(o-quinodimethanes),2 which are generated in situ by a classical photochemical reaction: the photoenolization of o-methylphenyl ketones.3 As depicted in Scheme 1, photolysis of o-methylbenzophenone (1) produces a pair of hydroxy-o-quinodimethane isomers (3Z and 3E) via a 1,4-biradical intermediate (2). The quinodimethane isomer, 3Z, is unstable and reverts to the starting material with high efficiency. However, 3E can be trapped by Diels-Alder cycloaddition with dienophiles, including dimethyl acetylenedicarboxylate (3d), to produce the corresponding cycloadducts.4 We discuss herein our use of this chemistry toward the development of high performance polyimides.

Our initial work in the area of Diels-Alder trapping of photochemically generated dienes used a bis(o-methylbenzophenone) diene (5) and a rigid maleimide dienophile (6).5 The physical properties of the resulting polymers were evaluated for the polyadduct, the dehydrated
polyimide, and the fully aromatized polymer. Dehydrated polyimides had higher $T_g$'s than their precursors. This is a result of the increased chain stiffness brought about by the formation of more rigid tetrahydroanthracene units within the polyimide backbone. Further stiffening of the polyimide backbone in the anthrnyl polyimides (fully aromatized) is reflected in the still higher $T_g$'s for these systems. Higher $T_d$ values were also observed for tetrahydroanthryl polyimides and anthrnyl polyimides than those of the polyadducts. This is consistent with the presence of more thermally and thermo-oxidatively stable tetrahydroanthracene and anthrancene units within these polyimides. Attempts to prepare films from more concentrated cyclohexanone solutions produced films which adhere well to various substrates (glass, aluminum) but are brittle.

Subsequent work in this area made use of a bis(o-methylbenzophenone) diene (7) and a flexible acrylate dienophile (8). Here, in an attempt to produce polymer films with greater ductility and flexibility, a series of six new bis(o-methylphenyl ketone) monomers were prepared and irradiated in the presence of diacrylates and triacrylates to produce polymer films. A statistically derived screening study was carried out to examine the effects of photocuring conditions on glass transition temperature, decomposition temperature, and extent of reaction. The resulting empirical models provided significant insight into the relationship between the reaction variables.

Recently, we have designed and synthesized a new system based on the results of our previous work. Here, a bis(o-methylbenzophenone) diene (9) has been prepared with an ethylene oxide subunit to increase the flexibility of the resulting polymer. The dienophile (10) was chosen to include maleimide units to limit competing reactions and an ethylene oxide chain to improve flexibility. Interestingly, 9 is a viscous oil at room temperature, allowing the photoactive blend to be film cast with or without solvent. The latter makes use of 9 to dissolve 10, creating a photoactive gel. Initial studies indicate the resulting polyimide thin films have high $T_g$'s and are fairly strong, flexible, and elastometric. Additionally, polymerization was completed in the presence of oxygen, suggesting improved reaction rates. This is likely due to the inherently high concentration of a solventless system.
References
5. This is a representative example, for complete study details please see reference 2.
Polyurethane/clay nanocomposite based reactive hot melt adhesive (RHMA) were synthesized by intercalative polymerization technology. RHMAs with different clay contents were characterized by differential scanning calorimeter (DSC), transmission electron microscope (TEM), wide angle X-ray diffraction (WAXD), and stress-strain testing. Adhesion strength was measured by T-peel tests of ABS/PET fabric adhesive joints.

The added nano-size clay improved the initial adhesion strength and reduced the setting time of RHMA. As the content of clay in the RHMA was increased, tensile strength was enhanced and melt viscosity was decreased.

Table 1. Recipe for the preparation of reference adhesive sample

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<td>PTMG 2000</td>
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Table 2. Effect of modification by Na-MMT / PEG(Mw=2,000) on bond strength

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Synthesis of Water-Soluble Poly(para-phenyleneethynylene) Copolymer Containing Blocked-Maleimide for Bioapplications.

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During the past two decades, conjugated polymers have attracted much attention because of their potential applications such as organic light emitting diodes, organic field effect transistor, organic photovoltaic cell, and chemical sensors. Recently, most people were more concerned about healthcare than any other days. For approach to pulse ultimate applications, biotechnology needs much more developments in analytical tools such as DNA, proteins, and biological agents. The detection of biological analytes can be achieved in high sensitivity using sensory materials based on organic conjugated polymer due to their large signal amplification even more trace amount of analytes. However, the conjugated polymers are not easy to dissolve in aqueous media because, by their nature, they have a hydrophobic and rigid main chain. In this report, we will show newly designed water-soluble poly(para-phenyleneethynylene) copolymer containing blocked-maleimide in the side chain. Cysteine conjugation reactions can be attained employing maleimides, vinyl sulfones, iodoacetamides, and orthopyridyl disulfide units as functional groups. We have targeted the maleimide group due to the easy conjugate formation with thiols.
New film-forming polymers containing in the main-chain dibenzo-18-crown-6, dibenzo-21-crown-7, dibenzo-24-crown-8, or dibenzo-30-crown-10 ether units alternating with aliphatic (C_{10}-C_{16}), aliphatic-aromatic spacers or oxindole fragments

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Abstract.

Novel, linear, soluble, high-molecular-weight, film-forming polymers and copolymers in which main-chain crown-ether units alternate with aliphatic (C_{10}-C_{16}) units have been obtained for the first time from aromatic electrophilic substitution reactions of crown-ethers by aliphatic dicarboxylic acids followed by reduction of the carbonyl groups. The crown ether unit is dibenzo-18-crown-6, dibenzo-21-crown-7, dibenzo-24-crown-8, or dibenzo-30-crown-10; the aliphatic spacer is derived from a dicarboxylic acid (sebacic, 1,12-dodecanedicarboxylic, hexadecanedicarboxylic or 1,4-phenylenedicarboxylic acids). The reactions were performed at 35 °C in a mixture of methanesulfonic acid (MSA) with phosphorus pentoxide, 12:1 (w/w), (Eaton’s reagent). The carbonyl groups in the polyketones obtained were completely reduced to methylene linkages by treatment at room temperature with triethylsilane in a mixture of trifluoroacetic acid and dichloromethane. Polymers containing in the main chain crown-ethers alternating with oxindole fragments were prepared by one-pot condensation of crown ethers with isatin in a medium of Eaton’s reagent. A possible reaction mechanism is suggested. According to IR and NMR analyses the polyacylation reactions lead to the formation of isomeric (syn/anti-substituted) crown-ether units in the main chain. The polymers obtained were soluble in the common organic solvents, and flexible transparent films could be cast from the solutions. DSC and X-ray studies of the polymers with “symmetrical” crown-ethers reveal the presence of the endotherms corresponding to the supramolecular assemblies.
Comparison between telechelic and random sulfonated poly(butylene terephthalate) ionomers

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Introduction

The presence of low concentrations of covalently bonded ionic substituents in organic polymers is well known to produce a consistent effect on their physical and rheological properties\textsuperscript{1}. Indeed, ionomers (polymers containing less than 10 mol % of ionic groups) have been shown to exhibit considerably higher moduli and higher glass transition temperatures compared to those of their non-ionic analogues. Improvements in mechanical and thermal performance are generally attributed to the formation of ionic aggregates, which act as thermoreversible cross-links\textsuperscript{1} and effectively retard the translational mobility of polymeric chains. The thermoreversible nature of ionic aggregation may address many disadvantages associated with covalently bonded high molecular weight polymers, such as high melt viscosity at the processing conditions. Moreover, the ionic groups can give rise to interactions with dyes and with fillers improving the adhesion of the polymer matrix with the substrate.

The insertion of the ionic groups can be performed along the polymer chain (random ionomers) or only at the end of the chain (telechelic ionomer). Several differences can be expected between the two classes of ionomers. Indeed, telechelic ionomers provide the opportunity for electrostatic interactions without a deleterious effect on the symmetry of the repeating unit. Moreover, the ionic aggregation occurs only at the end of the chain, giving rise to an electrostatic chain extension while random ionomers give rise to a gel-like or cross linked aggregation.

Polyester ionomers could be in principle prepared by adding a mono-functional (for the telechelic) or difunctional (for the random ionomers) sulfonated ester. Random PBT ionomers can be prepared adding dimethyl 5-sulfoisophthalate sodium salt (DMSIP) at the beginning of the polymerization\textsuperscript{2}. On the contrary, PBT telechelic ionomers can not be prepared by melt polymerization adding the sodium salt of 3-sulfobenzoic acid (SBANa) as end-capping agent at the beginning of the polymerization process, since the sulfobenzoic acid salt does not react with the monomers. The main reason of this lower reactivity, lies in the low solubility of sulfobenzoic acid in the reaction medium. We have recently patented a method for preparing PBT telechelic ionomers by pre-reacting the SBANa with the excess BD and then adding DMT. In this communication we report the synthesis of telechelic ionomers and a comparison of the thermo-mechanical properties with that of random ionomers.

Results and discussion

In order to avoid the solubility issues encountered using the sulfobenzoic acid salt, we have pre-reacted butanediol and 3-SBANa in the presence of 175 ppm of titanium tetrabutoxide (TBT) at 230°C until the complete clearing of the reaction mixture (1 hour). The temperature was then decreased to 180°C, DMT was added and a standard PBT polymerization was conducted. The incorporation of the SBANa has been confirmed by NMR analysis of the
polymer dissolved in a trifluoroacetic acid/chloroform solution and precipitated in methanol. The amount of THF formed as by product is higher compared to that for standard PBT but can be reduced adding a buffer agent such as sodium phosphate. The addition of phosphate also increases the polymerization rate.

Random sulfonated PBT with 3% (by mol) ionomer content was synthesized by adding dimethyl 5-sulfoisophthalate sodium salt (DMSIP) at the beginning of the polymerization. In this case, the second stage was stopped just after 30 minutes from the application of full vacuum since the melt viscosity was too high to permit the stirring of the polymer melt. For this reason, only random ionomers with Mw lower than 15000 can be obtain by melt polycondensation.

![Polymerization scheme](image)

**Figure 1: PBT telechelic ionomer polymerization scheme**

<table>
<thead>
<tr>
<th>Run</th>
<th>Ionic content (mol%)</th>
<th>Mw</th>
<th>Cryst time at 200°C (min)</th>
<th>Cryst time at 205°C (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBT control 1</td>
<td>0</td>
<td>87900</td>
<td>1.5</td>
<td>7.4</td>
</tr>
<tr>
<td>PBT control 2</td>
<td>0</td>
<td>43000</td>
<td>1.0</td>
<td>4.4</td>
</tr>
<tr>
<td>1.5% telechel</td>
<td>1.4</td>
<td>56600</td>
<td>1.3</td>
<td>7.1</td>
</tr>
<tr>
<td>3% telechel</td>
<td>2.8</td>
<td>45800</td>
<td>1.5</td>
<td>8.9</td>
</tr>
<tr>
<td>5% telechel</td>
<td>4.8</td>
<td>29700</td>
<td>2.1</td>
<td>12.1</td>
</tr>
<tr>
<td>3% random</td>
<td>3</td>
<td>12300</td>
<td>29.4</td>
<td>&lt;120</td>
</tr>
</tbody>
</table>

There are no significant differences in melting temperature and enthalpy of fusion and crystallization for the telechelic and random ionomers respect to control PBT. On the contrary, the crystallization time (measured as peak time in isothermal conditions) in telechelic polymers increases with the ionomer content even if the molecular weight follows an opposite trend. This means that the electrostatic interactions between the polymer chain ends give rise to an increase in apparent melt viscosity that overcomes the decrease due to the lower molecular weight. The random ionomer presents a consistently slower crystallization rate even if its molecular weight is very low, indicating that the ionic groups along the polymer chains act as cross-link agents giving rise to a gel like aggregate and therefore to a very high melt viscosity while for telechelic ionomers the interactions are of chain-extension type. Ionomers present a slightly lower thermal stability (5-15°C depending on ionic content) compared to PBT, random being less stable respect to telechelics. On the contrary the hydrolytic stability of the random ionomers is considerably lower respect to that of telechelics and PBT. The addition of phosphates both increases the thermal and hydrolytic stability of ionomers. The low hydrolytic stability and the low molecular weight (and therefore
brittleness) are the main problems, thus limiting the potential applications of random ionomers. Telechelic ionomers on the contrary does not have those issues but still presents the beneficial effect of the presence of the ionic groups. DMTA analysis shows a slight increase in Tg and an increase in modulus above Tg by increasing the ionic content.

Acknowledgements
This work was financed by General Electric Company

References
Polyarylates one-pot synthesis using diphenyl carbonate, aromatic diols and
dicarboxylic aromatic acids

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Introduction

The industrial production of polyarylates can be performed by interfacial methods that use water and a water-immiscible solvent such as chloroform or dichloromethane. However, these methods require the use of acyl chlorides that are expensive monomers and the use of large volume of toxic chlorinated solvents. The direct reaction of an aromatic diacid with an aromatic diol is not an efficient method to make polyarylates due to thermodynamic and kinetic issues. The aromatic diol and/or the aromatic diacid should be activated in order to react in the molten state. Two different polymerization routes are reported in the literature\textsuperscript{1} for the melt synthesis of polyarylates: the diacetate route and the diphenyl ester route. The diacetate route consists of the reaction of stoichiometric amounts of an aromatic dicarboxylic acid with the diacetate derivative of an aromatic diol. The diphenyl ester route consists of the reaction of a diphenyl ester of an aromatic dicarboxylic acid with an aromatic diol. This second method is preferred on the basis of the final product properties and cost. The diaryl ester of an aromatic dicarboxylic acid can be synthesized by reaction of a diaryl carbonate and aromatic acids in the presence of acid or basic catalysts.

In this communication we report a novel one-pot method that is a simplification of the diphenate process. In this new method the diaryl ester is generated \textit{in situ} by reaction of the aromatic diacid with a diaryl carbonate in the presence of the aromatic diol.

Results and discussion

We have found by model reactions that both the acid and the diol react with diphenyl carbonate (DPC) leading to the diphenyl ester of the diacid and to the bisphenyl carbonate of the diol. The formation of the diphenyl ester of the diacid is faster compared to the formation of the bisphenyl carbonate of the diol. The activated diacid can undergo transesterification reaction with the diol and therefore, by elimination of phenol, high molecular weight polyarylates can be obtained. The reactions are catalyzed both by Lewis acid and by basic catalysts, the former being consistently more active.

The main issue in using aromatic dicarboxylic acids is connected with their high melting temperature and low solubility in most solvents. Incorporation into polymers depends upon reaching a clearing point during polymerization, in which all the acid dissolves into the molten polymer or oligomer. For this reason a proper temperature profile should be used. Indeed, the temperature of the first part should be high enough to permit the heterogeneous reaction of the diacid with the diaryl carbonate. A slight overpressure can be used in the first step in order to overcome the loss of the aromatic diol and of the diaryl carbonate; the removal of the phenol is a key point in order to achieve high molecular weights. Therefore, the polymerization reactor should be designed in order to efficiently eliminate the phenol and avoiding the loss of reagents by evaporation.

The clearing time depends on the temperature used and on the catalyst type and amount. At 290°C in presence of a titanium based catalyst, clearing times as low as 30 minutes can be achieved. After the clearing the phenol formed must be eliminated under dynamic vacuum in order to build-up the molecular weight. Before applying the vacuum the
temperature should be decreased to 210°C in order to avoid the loss of the diol and of the carbonate not already reacted. In this stage the pressure has to be maintained in the range 50-100 mbar. The temperature was then increased in steps to the final value. The length of the steps and the final temperature (ranging from 260°C to 290°C) depends on the monomers ratio and type and on the catalyst used. A final stage at pressure below 1 mbar is fundamental in order to have final Mw above 50000.

We have initially studied the synthesis of a polyarylate of resorcinol and phthalic acids (a 1/1 mixture of terephthalic and isophthalic acid) using diphenyl carbonate as diaryl carbonate.

\[
\begin{align*}
\text{HO} & \quad \text{COOH} \\
\text{COOH} & \quad \text{COOH}
\end{align*}
\]

A slight excess (5% by mol) of DPC has to be used since part of it is lost in the first part of the reaction. The \(^1\text{H-}\text{NMR}\) analysis shows that the end-groups could be of three types: phenyl ester, carboxylic acid and hydroxy groups. Phenyl carbonate groups are almost not present unless a large excess of DPC is used. The relative amount of the three end-groups can be tailored by using the correct ratio of the monomers. An excess of DPC respect to the resorcinol leads to phenyl ester end-groups, an excess of acid to carboxylic end-groups and an excess of diol to OH end-groups. Also the final molecular weight can be adjusted by using the proper monomers ratio and reaction time of the last step at full vacuum. Indeed, oligomers with OH or COOH end-groups, to be used for the preparation of block copolymers, can be prepared by this method. The \(^1\text{H-}\text{NMR}\), \(^{13}\text{C-}\text{NMR}\) and FTIR analyses show that no side reaction takes place even when the reaction temperature is 290°C. No carbonate moieties along the chain have been detected by FTIR analysis if a DPC excess below 10% is used.

Titanium tetrabutoxide (TBT) proved to be the most efficient catalyst for this reaction. The discoloration of the final product due to the formation of aromatic titanates can be avoided adding a catalyst quencher (e.g. phosphorous acid) at the end of the polymerization process whereas the discoloration due to thermal oxidation can be avoided using an argon purge. Using this procedure, the final polymers are pale yellow. Sodium dihydrogen phosphate can be used as co-catalyst in order to improve the reaction rate and reduce the clearing time. Basic catalysts such as NaOH also catalyze the reaction but clearing time up to 3 hours are needed even at 290°C.

The synthetic route has been successfully applied to the synthesis of other polyarylates. For example polyarylates from phthalic acids, bisphenol A and DPC and from 2,6-naphthalene dicarboxylic acid, resorcinol and DPC have been prepared. Also in these cases no side products have been detected by \(^1\text{H-}\text{NMR}\) and FTIR analysis.

**Acknowledgements**
This work was financed by General Electric Company

**References**
Nonstoichiometric Polymerization of Polyimide by Means of Reaction-induced Crystallization of Oligomers

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As well known, stoichiometric ratio between two reactive groups is of great importance to produce high molecular weight polymer by a step growth type polymerization. We have previously prepared high molecular weight poly(4,4'-oxydiphenylene pyromelliteimide) from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) through the crystallization of oligomers during solution polymerization. The molecular weight increased by solid-state polymerization, even though the end-groups of the precipitated oligomers were not stoichiometric molar ratio. This result implies that the transimidization reaction occurs in the crystals of the oligomers beside the addition of anhydride end-group and amino end-group, and the polymerization by means of the reaction-induced crystallization of oligomers would be unsusceptible to the stoichiometric condition. In this study, the preparation of poly(4,4'-oxydiphenylene pyromelliteimide) under nonstoichiometric condition was examined by using the reaction-induced crystallization of oligomers.

PMDA and Barrel Therm 400 (BT4, Matsumura Oil Co. Ltd, mixture of isomers of dibenzyl toluene) were placed into a cylindrical flask and heated up to 330 °C. PMDA was entirely dissolved. The solution of ODA in BT4 heated up to 330 °C was added into the PMDA solution at 330 °C. Polymerization was carried out at 330 °C. Polymerization concentration was 1.0 %. The solution became turbid immediately and then the precipitated crystals were formed. The crystals were filtrated. Oligomers dissolved in solution also collected and their chemical structures were analyzed by MALDI-TOF MS. Poly(4,4'-oxydiphenylene pyromelliteimide)s were also prepared by the homogeneous solution polymerization of PMDA and ODA, and following thermal imidization according to previous report ¹. Inherent viscosity (η_{inh}) was measured in 97% sulfuric acid at 30 °C and 0.5 g/dL.

The aggregates of plate-like crystals were obtained with quantitative yields. Figure 1 shows influence of stoichiometry on η_{inh}. In the case of homogeneous solution polymerization, the molecular weight was quite sensitive to the imbalance of the stoichiometry. However, in the case of crystallization, the η_{inh} is insensitive toward the imbalance of stoichiometry. The highest η_{inh} of 1.86 dL/g is achieved at the molar ratio of PMDA to ODA in feed (χ) of 0.83, and suprisingly η_{inh} is still 1.34 dL/g even at χ of 0.5. In contrast to this, the drop of η_{inh} is larger at χ > 1.0 than χ < 1.0. However, η_{inh} is 0.87 dL/g at χ of 2.0. The η_{inh} is further increased after 12 hours, especially under

[Figure 1](#) Influece of stoichiometry on inherent viscosity of polyimides prepared by homogeneous solution polymerization (●●) and reaction-induced crystallization of oligomers (→ after 6 h), (→→ after 12 h).
This result indicates that solid-state polymerizations proceed in the products even under nonstoichiometric conditions and their reaction rates would be different at each χ due to the difference on the end groups of oligomers. From MALDI-TOF MS measurement, the end-groups of the oligomers prepared at χ of 0.5 and 2.0 were mainly ODA residue and PMDA residue respectively, and the stoichiometry was not maintained in the precipitated oligomers. Therefore transimidization reactions with eliminating ODA and PMDA occurred in the crystals to increase molecular weight.


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FTIR investigation of the influence of diisocyanate symmetry on the morphology development in model segmented polyurethanes

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Novel segmented polyurethanes with hard segments based on a single diisocyanate molecule with no chain extenders were prepared by the stoichiometric reactions of poly(tetramethylene oxide)glycol ($M_n=1000$ g/mol) (PTMO-1000) and 1,4-phenylene diisocyanate (PPDI), trans-1,4-cyclohexyl diisocyanate (CHDI), bis(4-isocyanatocyclohexyl)methane (HMDI) and bis(4-isocyanatophenyl)methane (MDI). Time dependent microphase separation and morphology development in these polyurethanes were studied at room temperature using transmission FTIR spectroscopy. Solvent cast films on KBr discs were annealed at 100 °C for 15 s and microphase separation due to self organization of urethane hard segments was followed by FTIR spectroscopy, monitoring the change in the relative intensities of free and hydrogen-bonded carbonyl (C=O) peaks. Depending on the structure of the diisocyanate used, while the intensity of free C=O peaks around 1720–1730 cm$^{-1}$ decreased, the intensity of H-bonded C=O peaks around 1670–1690 cm$^{-1}$, which were not present in the original samples, increased with time and reached saturation in periods ranging up to 5 days (Fig. 1). Structure of the diisocyanate had a dramatic effect on the kinetics of the process and the amount of hard segment phase separation. While PPDI and CHDI based polyurethanes showed self-organization and formation of well ordered hard segments, interestingly no change in the carbonyl region or no phase separation was observed for MDI and HMDI based polyurethanes. Quantitative information regarding the relative amounts of non-hydrogen bonded, loosely hydrogen bonded and strongly hydrogen bonded and ordered urethane hard segments were obtained by the deconvolution of C=O region and analysis of the relative absorbances in C=O region.

Figure 1 Time dependent change in the carbonyl region of the FTIR spectra for PPDI+PTMO1000 PU from t=0 (black) to t=8200 min (red)
Mechano-optical properties of two homologous segmented, thermoplastic polyurethanes (TPU) obtained from the stoichiometric reactions of trans-1,4-cyclohexyl diisocyanate (CHDI) and poly(tetramethylene oxide)glycol (PTMO) were investigated. PTMO oligomers used had number average molecular weights $<M_n>$ of 1020 and 2040 g/mol, resulting in TPUs with urethane hard segment contents of 14 and 7.5% by weight respectively. AFM studies showed microphase morphology. Stress-strain measurements demonstrated the formation of very strong, elastomeric materials with ultimate tensile strengths of 23-25 MPa and elongation at break values of about 1000%. 
Luminescent Nd$^{3+}$ doped thermoplastic silicone-urea copolymers

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A simple method for the preparation of rare earth ion-doped polymers, which display luminescence, is reported. For this purpose silicone-urea copolymers were doped with Nd(NO$_3$)$_3$.6H$_2$O. Various structural and physicochemical properties of the resultant materials were investigated. FTIR studies indicated strong interaction of Nd$^{3+}$ ions with urea groups, but no interaction with siloxane backbone, which is expected. Absorption measurements in the visible and near infrared region were performed and the radiative decay rates and branching ratios for the meta-stable $^4F_{3/2}$ level were determined by using Judd-Ofelt theory. The samples were also excited at 800 nm and emission spectra were observed in the near infrared at 905, 1059, and 1331 nm (Fig. 1). In Nd$^{3+}$ doped silicone-urea systems the highest emission cross section at 1059 nm was determined to be 60.7 x10$^{-21}$ cm$^2$. Spectroscopic parameters determined in this study suggest that Nd$^{3+}$ doped silicone-urea copolymers are promising candidates for the development of fiber lasers or amplifiers near 1.06 and 1.3 microns.

Figure 1: Measured luminescence bands of Nd$^{3+}$ doped silicone-urea copolymers between 900 and 1500 nm
Structure-property relationships in segmented, non-chain extended polyureas: Effect of soft segment molecular weight

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Novel, segmented non-chain extended polyureas were synthesized. Soft segments (SS) were based on poly(tetramethylene glycol), PTMO (average molecular weight 1000 or 2000 g/mol) and hard segments (HS) were based on single molecule of a diisocyanate, which was either 1,6-hexamethylene diisocyanate (HDI), 1,4-phenylene diisocyanate (pPDI) or 1,4-trans-cyclohexyl diisocyanate (CHDI). An increase in the SS molecular weight was found to lead to an increased formation of SS crystallites, which increased the low temperature modulus, but adversely influenced the upper and lower service temperatures of the polyureas. Both 1K and 2K PTMO-based polyureas showed a microphase separated morphology, where the HS formed thread-like, crystalline structures that were dispersed in the continuous SS matrix. Upon deformation, the HS were found to break down into distinctly smaller threads, which oriented along the direction of the strain; this effect was found to be partially reversible and time dependent. Both the 1K and 2K polyureas based on HDI HS were found to be thermally stable and potentially melt processible.

Table 1

<table>
<thead>
<tr>
<th>HS contents of the non-chain extended, segmented polyureas investigated</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Amine-terminated PTMO SS molecular weight (g/mol)</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>-------------------------</td>
</tr>
<tr>
<td>1100</td>
</tr>
<tr>
<td>2450</td>
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Highly branched polyurea elastomers through oligomeric $A_2 + B_3$ approach

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Oligomeric $A_2 + B_3$ approach was used for the preparation of highly branched elastomeric polyurea type copolymers. $A_2$ type oligomeric soft segments included PTMO, PEO, PPO and PDMS with average molecular weights between 1000 and 10,000 g/mol. A PPO based $B_3$ oligomer with average branch length of 1000 g/mol was also used. The diisocyanate used was bis(4-isocyanatocyclohexyl)methane (HMDI). Low molecular weight triamines with different structures were used as $B_3$.

In the first part of the research gel points were determined experimentally for reactions where $A_2$ was slowly added onto $B_3$ or vice versa. In the first part of the study, gel points were determined with different solution concentrations where $A_2$ was a difunctional isocyanate and $B_3$ was a trifunctional amine. It was observed that when $B_3$ was added onto $A_2$ gelation took place at lower conversions when compared with the reaction where $A_2$ was added on $B_3$. At a solution concentration of 10% by weight gelation was observed at the stoichiometric ratio $[A_2]/[B_3] = 1.094$ for the addition of $A_2$ over $B_3$. In the case of $B_3$ addition onto $A_2$ gelation was observed at the stoichiometric ratio $[B_3]/[A_2] = 0.569$. No gelation was seen when reactions were carried out at a concentration of 5% solids.

In the second part, highly branched polymers were synthesized by considering the gelation points obtained earlier by using different monomers. Generally, reactions were terminated through the capping of amine end groups with cyclohexyl isocyanate. Materials obtained were characterized by FTIR spectroscopy and mechanical tests. Stress-strain testing indicated that for polymers with similar chemical compositions polymers prepared by the addition of $A_2$ over $B_3$ possessed better mechanical properties than those prepared by $B_3$ over $A_2$ addition. As expected the end capped polymers showed better mechanical strength than their uncapped counterparts. This is mainly due to stronger hydrogen bonding in the capped systems. In some cases a short diamine chain extender was also used during reactions. Increasing the amount of chain extender increased the tensile strength of the polymer, similar to linear materials.

Acknowledgement
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Conjugated Polymer Systems for Optical Sensing and Patterning

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In the past two decades, conjugated polymers have attracted much attention because of their potential applications, such as organic light emitting diodes, organic field effect transistor, organic photovoltaic cell, and chemical sensors [1]. Photopatternable polymers, in addition, have attracted great attention owing to their potential application to opto-electronic devices [2]. In millennium, most people were more concerned about healthcare than any other days. For approach to ultimate applications, biotechnology needs much more developments in analytic tools such as chemical sensors [3]. Most of the chemical sensors exhibit chromo- or fluorogenic response by target analytes. Recently, chemical sensors are reported many examples of chromogenic reagents for anion, or cation detection. However, there are not many examples of highly selective and sensitive for fluoride anion. We, herein, report the use of polymer incorporated azo or diamine group as chromo- or fluorogenic probes for the detection of fluoride anion. These polymers also showed photopatterning on the substrate through deblocking of photo-removable moiety in the polymer backbone. The polymer incorporated benzoxazole, moreover, showed photopatterning on the substrate without any photo-removable moieties.

References


Synthesis and Characterization of a Fulerene Based Copolymer

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Abstract

The first fluorene based copolymer, obtained via ferric chloride oxidative polymerization of 9-alkyl- and 9,9-dialkylfluorenes, reported by Fukuda et al., appears to be a low molecular weight product with some degree of branching and nonconjugated linkages through positions 2 and 7 [1]. These copolymers form poor quality films. It is also difficult to remove the residual metallic impurities, this creating a potential problem for EL devices. Suzuki coupling reaction has also been used in the preparation of well-defined polyfluorene derivatives [2]. A nickel-catalyzed reductive polymerization reaction used by Yamamoto et al. [3] can lead to 2,7-linked polyfluorenes. In light of the success in creating polymers with unique properties, the alternating copolymer approach has been extended to other fluorene monomers. Here we report the preparation of a new statistical copolymer of high molecular weight based on 2,7-dibromo-9-ethylcarpronate-fluorene and 2,7-dibromo-bis(2-ethylhexyl)-fluorene. The chemical modification of the copolymer was performed by saponification in the presence of LiOH:H₂O and yielded an ionic structure.

The copolymers were characterized by GPC, ¹³C-NMR, IR and elemental analysis.

References

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