ABSTRACTS

KL 01

SELF-CONTROLLED SUPRAMOLECULAR AND LIVING RADICAL POLYMERIZATIONS

V. Percec

Department of Chemistry, University of Pennsylvania
Roy & Diana Vagelos Laboratories, Philadelphia, Pennsylvania, 19104-6323, USA
Phone: 215-573-5527 Fax: 215-573-7888 E-mail: Percec@sas.upenn.edu

This lecture will first discuss the transfer of the concepts of quisi-equivalence, self-control and adaptability from the field of structural biology to the field of self-assembly. Subsequently it will demonstrate with recent examples from our laboratory that self-control is responsible for all supramolecular polymerizations and for least selected examples of covalent polymerization including living radical polymerizations. Selected examples of self-controlled supramolecular polymerizations such as the supramolecular polymerization of dendritic dipeptides and living radical polymerizations such as SET-LRP will be discussed in detail.

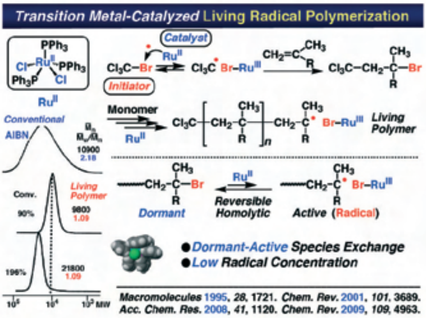
KL 02

TRANSITION METAL-CATALYZED LIVING RADICAL POLYMERIZATION: PRECISION FUNCTIONAL POLYMERS VIA DESIGNED CATALYSTS

M. Sawamoto

Department of Polymer Chemistry, Graduate School of Engineering,
Kyoto University, Katsura, Kyoto 615-8510, Japan
sawamoto@star.polym.kyoto-u.ac.jp

This lecture overviews recent progresses in the precision synthesis of functional polymers by metal-catalyzed living radical polymerization [1] (Fig. 1): (A) Design of functionality-tolerant, versatile, and active catalysts (Fig. 2); (B) Living polymerization of functional monomers in water and alcohol (Fig. 3); (C) Copolymers with addressable multiple functionality (Fig. 4); (D) Functional "meso-polymers" with controlled sequences and ds (Fig. 5).



Macromolecules 1995, 28, 1721. Chem. Rev. 2001, 101, 3689. Acc. Chem. Res. 2008, 41, 1120. Chem. Rev. 2009, 109, 4963.

Fig. 1

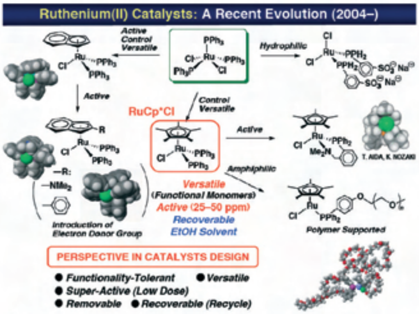


Fig. 2

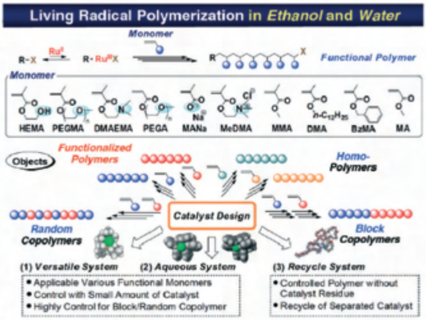


Fig. 3

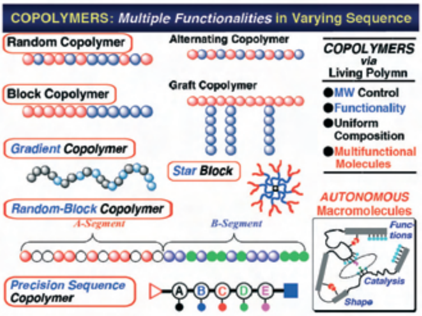
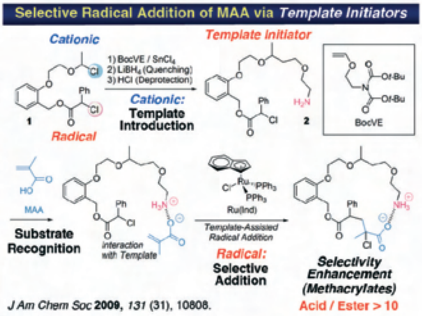


Fig. 4



J Am Chem Soc 2009, 131 (31), 10808.

Fig. 5

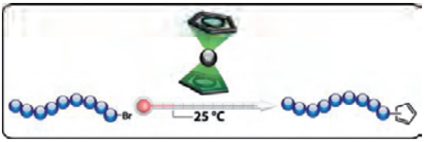
KL 03

HIGH EFFICIENCY APPROACHES TO POLYMER LIGATION AND CHARACTERIZATION

Ch. Barner-Kowollik, A. Inglis, T. Junkers, L. Nebhani, E.H.H. Wong, L. Barner, T. Paulöhrl

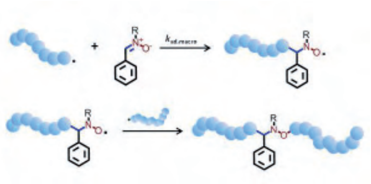
Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie,
Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe
christopher.barner-kowollik@kit.edu

The generation of highly defined macromolecules and their precursor building blocks is a key prerequisite for the generation of functional polymeric materials.[1] The present lecture will highlight recent advances from our group in the synthesis of highly reactive macromolecular building blocks – such as cyclopentadienyl (Cp) functional polymers obtained via nickelocene substitution[2] – and their use in ultra-rapid polymer-polymer ligation chemistries that occur at ambient temperature within a few minutes in the absence of a catalyst.[2] The lecture will further demonstrate how such ligation strategies can be employed to efficiently engineer surface chemistries with a high grafting density, ranging from functional microspheres to stimuli-responsive silicon surfaces.[3] In addition, the facile reversibility of polymer conjugates based on Cp-capped building blocks prepared via hetero Diels-Alder chemistry for materials design will be demonstrated.



Scheme 1: Ambient temperature synthesis of Cp-capped macromolecular building blocks, which are employed in ultra-rapid ambient temperature polymer ligation.

In a second strand, the lecture will showcase how spin traps – most prominently thioketones and nitrones – can be employed as macromolecular design entities with a particular high applicability in modular reaction chemistries.[4] The non-toxic nature of nitrones as well as their facile synthetic access may make them ideal tools for macromolecular design in biological contexts. Throughout the lecture, a strong emphasis will be placed on polymer characterization via hyphenated techniques (i.e. LACCC-SEC and SEC-ESI-MS).



Scheme 2: Spin trap mediated polymerization.

---

[1] Nebhani, L.; Barner-Kowollik, C. *Adv. Mater.* **2009**, *21*, 3442-3468.

[2] (a) Inglis, A. J.; Paulöhrl, T.; Barner-Kowollik, C. *Macromolecules* **2010**, **DOI:** 10.1021/ma902464; (b) Inglis, A. J.; Sinnwell, S.; Stenzel, M. H.; Barner-Kowollik, C. *Angewandte Chemie Int. Ed.* **2009**, *48*, 2411-2414

[3] (a) Nebhani, L.; Gerstel, P.; Atanasova, P.; Bruns, M.; Barner-Kowollik, C. *J. Polym. Sci. – Polym. Chem.* **2009**, *47*, 7090-7095; (b) Nebhani, L.; Schmiedl, D.; Barner, L.; Barner-Kowollik, C. *Adv. Funct. Mat.* **2010**, in press.

[4] Wong, E. H. H.; Stenzel, M. H.; Junkers, T.; Barner-Kowollik, C. *Macromolecules* **2010**, in press.

KL 04

TOPOLOGICAL POLYMER CHEMISTRY: A CYCLIC APPROACH FOR UNUSUAL FUNCTIONS IN POLYMER MATERIALS

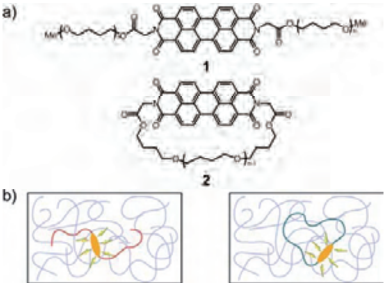
Y. Tezuka

Department of Organic and Polymeric Materials, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo, 152-8552, Japan (ytezuka@o.cc.titech.ac.jp)

A variety of non-linear polymer topologies of precisely controlled geometry has now been realized by the remarkable progress in synthetic techniques including a self-assembly strategy. Nevertheless, the practical synthesis of a class of cyclic and multicyclic polymers has yet been a formidable challenge [1,2].

We have so far developed an *electrostatic self-assembly and covalent fixation* (ESA-CF) technique for a variety of cyclic and multicyclic polymers having functional groups at the designated positions in their unique constructions [1,2]. Moreover, we have shown that a ring-closing metathesis (RCM) is an efficient means to cause polymer cyclization, and has been combined with ATRP technique to prepare not only simple cyclic polymers but also cyclic block copolymers [3]. Furthermore, we have developed a “click” cross-coupling process by making use of cyclic/branched prepolymers having either alkyn and/or azide groups, to construct further complex multicyclic polymer topologies. An effective synthesis of polymer catenanes has also been achieved by the combination of electrostatic/hydrogen-bonding self-assembly and subsequent covalent fixation [4].

Based on these synthetic developments, unprecedented topology effects by cyclic polymer topologies have now been revealed. Those include unique diffusion of cyclic polymers visualized by means of a single-molecule spectroscopy, using a cyclic polymer having a fluorophore unit obtainable by the ESA-CF protocol [5] (Scheme), as well as the formation of thermally stable micelles by cyclic amphiphilic diblock copolymers obtainable by the ATRP-RCM protocol [3].



References

[1] Y. Tezuka, H. Oike, *J. Am. Chem. Soc.*, **123**, 11570 (2001). [2] K. Adachi, Y. Tezuka, *J. Synth. Org. Chem., Jpn.* **67**, 1136 (2009). [3] K. Adachi, S. Honda, S. Hayashi, Y. Tezuka, *Macromolecules*, **41**, 7898 (2008). [4] K. Ishikawa, T. Yamamoto, M. Asakawa, Y. Tezuka, *Macromolecules*, **43**, 168 (2010). [5] S. Habuchi, N. Satoh, T. Yamamoto, Y. Tezuka, M. Vacha, *Angew. Chem., Int. Ed.*, **49**, 1418 (2010)

KL 05

PRACTICAL PRODUCTION OF TAILORED-MADE PRECISION POLYOLEFINS

L.R. Sita

Department of Chemistry and Biochemistry, University of Maryland, College Park,
MD 20742, USA
email: lsita@umd.edu

New paradigms are required that have the potential to dramatically change the range and pace at which specialty polyolefins can be discovered and commercialized. In this regard, we have been pursuing, within a living coordination polymerization system, initial identification of dynamic fast and reversible bimolecular processes that are competitive with chain-growth propagation as a means by which to establish mechanistic control points that can provide external control over the relative rates of these processes in such a fashion that a near continuum of different polyolefin grades between two different limiting stereochemical microstructures, co-polymer compositions or polymer architectures can be generated with a high degree of precision from a single catalyst. When combined with living coordinative chain-transfer polymerization (LCCTP) in which an excess of a main group metal alkyl species is added that can then serve as 'surrogate' chain-growth sites which appear to propagate at the same rate as the active centers, practical (commercial) production of a broad range of specialty 'precision' polyolefin materials can now be brought closer to realization. This talk will focus on the results of our recent efforts made towards achieving this goal.

KL 06

ANIONIC SYNTHESIS OF WELL-DEFINED, CHAIN-END AND IN-CHAIN FUNCTIONALIZED POLYMERS

R.P. Quirk

Institute of Polymer Science and Polymer Engineering, The University of Akron,
Akron, Ohio, USA 44325 (rpquirk@uakron.edu)

One of the unique features of living polymerizations, and alkyllithium-initiated polymerizations in particular, is the ability to prepare chain-end functionalized polymers. After complete monomer consumption, the resulting polymeric organolithiums can react with electrophiles to form ω-chain-end functionalized polymers. Although many such reactions have been investigated, most of these functionalization reactions are not quantitative and each must be optimized. It has been of interest to develop *general anionic functionalization methods* (**GFM**). **GFM** encompass reactions that efficiently introduce a variety of functional groups using the same chemistry for all groups.

One recently developed **GFM** is based on (1) the reaction of polymeric organolithiums with chlorodimethylsilane to form the corresponding ω-silyl hydride-functionalized polymers followed by (2) platinum-catalyzed hydrosilation with substituted alkenes. This **GFM** has also been applied to the synthesis of well-defined, in-chain functionalized polymers by reaction of an excess of polymeric organolithium with dichloromethylsilane followed by platinum-catalyzed hydrosilation with substituted alkenes. Termination with excess methyldichlorosilane followed by reduction produced the corresponding ω,ω-silyldihydride-functionalized polymers. Well-defined ω,ω-difunctionalpolymers have been prepared by subsequent platinum-ctalyzed hydrosilation with substituted alkenes. For synthesis of multiple in-chain-functionalized polymers, anionic polymerization of (4-vinylphenyl)dimethylsilane has been investigated. All hydrosilation reactions utilized Karstedt’s catalyst and alkenes a variety of functional groups, including epoxy, phenol, terpyridine, ether, ester, hydroxyl, amino, amino acid, naphthyl and perfluoroalkyl. The polymeric products were characterized using SEC, ^{13}C and ^{1}H NMR, FTIR, TLC and MALDI-TOF mass spectrometric analyses. The scope, limitations and recent advances for these functionalization reactions will be presented.

KL 07

PHOTOCHEMICAL METHODS FOR THE PREPARATION NANO AND COMPLEX MACROMOLECULAR STRUCTURES

Y. Yagci

Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 34469, Turkey

Photoinitiated polymerization can be conducted via radical, cationic and anionic routes. In this presentation, the major initiation methods for all polymerizations acting at different wavelengths will be discussed. The use of these methods to prepare complex macromolecular architectures including block and graft copolymers, hydrogels and surface modified self assembled monolayers will also be presented. With recent advances in the use of nanomaterials like metals, metal oxides and silicates in coatings, it is now possible to prepare nanocoatings with enhanced physical, chemical and biological properties. This is due, in part, to the difference in surface area per unit of volume at the nanoscale. Nanocoatings are usually prepared by UV irradiation of formulations containing dispersed nanoparticles. However, the homogeneous dispersion of these nanoparticles is a key challenge due to their easy agglomeration arising from their high surface free energy. It is often difficult to obtain well dispersed formulations providing good transmission of light for a complete cure. In this presentation, we report several synthetic methodologies for the preparation of epoxy and (meth)acrylate based nanocoatings containing clay or metal nanoparticles. In the former case, photolysis of intercalated photoinitiator within the layers of montmorillonite clay in the presence of monomers resulted in the *in-situ* formation of exfoliated structures. For the preparation of metal nanocoatings, the formation of silver or gold nanoparticles and crosslinking are accomplished similtaneously by photoinduced electron transfer and polymerization processes. The nanoparticles are homogenously distributed in the network without macroscopic agglomeration. Applicability to both free radical and cationic systems is demonstrated.

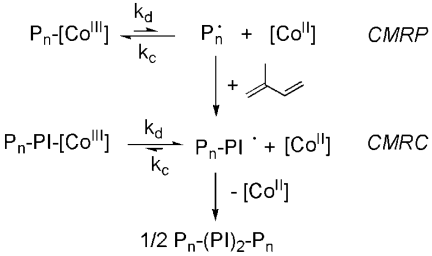
SL 01

DESIGN OF POLYMERS BY COBALT-MEDIATED RADICAL POLYMERIZATION AND COUPLING REACTION

A. Debuigne, M. Hurtgen, Ch. Jérôme, Ch. Detrembleur

Center for Education and Research on Macromolecules (CERM), University of Liege (ULg), Belgium

In the last years, ***Cobalt-Mediated Radical Polymerization*** (CMRP) emerged as a controlled radical polymerization technique of interest.[1,2] This method is based on the temporary deactivation of the radical chains by a cobalt complex, which strongly decreases the probability of bimolecular termination reactions and leads to polymers with predictable molecular weights and precise architectures. Until now, CMRP has proved ability to control the polymerization of monomers with different reactivities such as acrylates, acrylonitrile (AN), N-vinypyrrolidone (NVP) and vinyl acetate (VAc).[1] Recently, we discovered an unusual radical polymer chain coupling reaction, named ***Cobalt-Mediated Radical Coupling*** (CMRC),[3] which is a straightforward approach to the synthesis of symmetrical macromolecules. The latter relies on the addition of 1,3-diene compounds onto polymer precursors preformed by CMRP,[3,4] and thus capped by a cobalt complex. The CMRC mechanism was established on the basis of mass spectrometry and NMR analyses and corroborated by DFT calculations.[5] This coupling process was nearly quantitative when using very different 1,3-diene compounds including functional ones.[5] In all cases, insertion of two diene units was observed in the middle of the coupling product, which is of interest for future use in specific mid-chain functionalization of polymers. Another major interest in CMRC lies in the preparation of highly symmetrical ABA triblock copolymers from tailored diblock precursors.[3,4]



Research supported by the “*National Fund* for *Scientific Research » (FNRS).*

[1] Debuigne, A.; Poli, R.; Jerome, C.; Jerome, R.; Detrembleur, C. *Prog. Polym. Sci.* **2009**, *34*, 211. [2] Hurtgen, M.; Debuigne, A.; Jerome, C.; Detrembleur, C. *Macromolecules* **2010**, 43, 886-894. [3] Debuigne, A.; Jerome, C.; Detrembleur, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 1422. [4] Debuigne, A.; Poli, R.; De Winter, J.; Laurent, P.; Gerbaux, P.; Wathelet, J.-P; Jerome, C.; Detrembleur, C. *Macromolecules*, **2010**, 43(6), 2801–2813. [5] Debuigne, A.; Poli, R.; De Winter, J.; Laurent, P.; Gerbaux, P.; Wathelet, J.-P.; Dubois, P.; Jerome, C.; Detrembleur, C. *Chem. Eur. J.* **2010**, *6*, 1799.

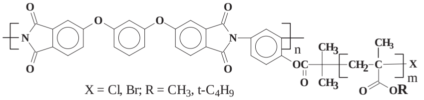
SL 02

SYNTHESIS AND MOLECULAR CHARACTERISTICS OF REGULARLY GRAFTED COPOLYMERS WITH POLYIMIDE BACKBONE AND POLYMETHACRYLIC SIDE CHAINS

A.V. Yakimansky, T.K. Meleshko, D.M. Ilgach, N.N. Bogorad, N.I. Gorshkov,
I.I. Malakhova, V.D. Krasikov, M.A. Simonova, A.P. Filippov

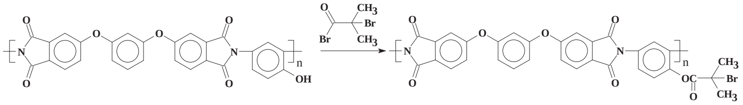
*Institute of Macromolecular Compounds of the Russian Academy of Sciences,
Bolshoi pr. 31, 199004 St. Petersburg, Russia
(yak@hq.macro.ru, http://www.macro.ru)*

Using ATRP of methylmethacrylate and *t*-butyl-methacrylate (TBMA) on polyimide macroinitiators, new polyimide brushes, i.e. regularly grafted copolymers with polyimide backbone and polymethacrylic side chains, are synthesized:



X = Cl, Br; R = CH_3, t-C_4H_9

Synthesis of the macroinitiators was carried out through the reaction of OH-containing polyimides with 2-Br-isobutyroyl bromide:



Acidic hydrolysis of side chains in the copolymers polyimide-*graft*-poly(TBMA) made it possible to obtain novel poyimide brushes with the side chains of polymethacrylic acid.

GPC data show that molecular weight distribution of the polyimide brushes is not broader than that for the original macroinitiator, meaning a rather good control of the ATRP process. According to the results of light scattering, viscosimetry and diffusion studies, polyimide brush macromolecules are characterized by a dense compact structure in solution. Rather high form-factor values (R_g/R_h = 2.5-4.5) are typical of strongly elongated rod-like or cylinder-like particles. The value of R_g/R_h increases with the lengthening of the backbone and with the shortening of the side chains.

D.M. Ilgach is grateful for the financial support from the program U.M.N.I.K. for participants of the Youth Contest in Science and Innovations.

SL 03

SYNTHESIS OF MACROINITIATOR OF POLY(2-METHYL-2-OXAZOLINE) FOR NITROXIDE-MEDIATED RADICAL POLYMERIZATION

G. Volet[a], L. Marx[b], C. Amiel[a]

[a]*Institut de Chimie et des Matériaux Paris-Est (ICMPE) Equipe Systèmes Polymères Complexes, Thiais, France (volet@icmpe.cnrs.fr)*
[b]*Laboratoire des BioMolécules Ecole Normale Supérieure, UMR CNRS-ENS-UPMC 7203, Département de Chimie, 24 rue Lhomond, 75231 Paris cedex 05 France*

Combining different living/controlled polymerizations is a versatile method to prepare well-defined block copolymers. Few reports[1,2] describe the combination of the living cationic ring -opening polymerization (CROP) of 2-methyl-2-oxazoline and of nitroxide mediated radical polymerization (NMRP). This work[3] deals with their stepwise combination, affording block copolymers of various natures.

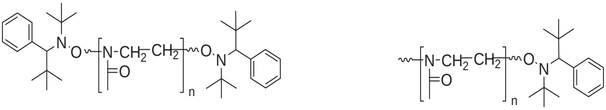


Figure 1: Scheme of polyoxazoline macroalkoxyamines

Well defined polyoxazoline α and α,ω alkoxyamine end-capped (figure 1) with molecular weights of 6.10^3 g/mol were firstly obtained by using bifunctional initiators and / or terminating agents of CROP, that are based on alkoxyamines. Then these POXZ-macroalkoxyamines have been successfully used to initiate NMRP of different monomers: hydrophilic monomer like sodium styrene sulfonate and hydrophobic monomers like styrene and butyl acrylate. The multiblocks copolymers obtained have molecular weight ranging from $3.4.10^4$ to $1.1.10^5$ g/mol with polydispersity indexes from 1.4 to 1.9.

[1] a) Weimer. M. W.; Scherman, O. A.; Sogah, D. Y. *Macromolecules* **1998**, *31*, 8425-8428, b) Puts, R. D.; Sogah, D. Y. *Macromolecules* **1997**, *30*, *7050* -7055.
[2] Ibrahim, S.; Voit, B. *Macromolecular Symposia* **2009**, *275-276*, 59-66.
[3] Volet. G.; Marx, L.; Amiel, C. submitted to *Macromolecules*.

SL 04

“LIVINGNESS” AT NITROXIDE MEDIATED FREE RADICAL POLYMERIZATION

Š. Chmela, J. Kollár, Ľ. Hrčková

Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovak Republic (upolchme@savba.sk)

“Living” free radical polymerization mediated by a stable nitroxide or a substituted alkoxylamine offers simple method for preparation of polymers with low polydispersity which possess remarkable better physical as well as chemical properties. Their can be used as a macro initiators for the synthesis of block copolymers. Till now it has been generally accepted that the extent of “livingness” is high for all conversions. To verify this statement a series of combined regulators has been synthesized, spectrally characterized and used at styrene polymerization. The regulators contained a fluorescence mark beside the stable nitroxide or substituted alkoxylamine. The stable nitroxyl radical represented 2,2,6,6-tetramethylpiperidíne-N-oxyl. Benzothioxanthone, naphthalene as well as substituted 1,8-naphthylimide represented the fluorescence mark. Fluorescence and UV absorption spectroscopy was applied for the quantification of active alkoxyamine-terminated chain ends. Theoretical molar masses were calculated from the obtained concentrations under assumption that all polymer chains are terminated by the fluorescence mark. Comparison of these data with the molar masses from GPC afforded the extent of marked polystyrene chain ends. Application of the regulators bearing the fluorescence mark led to the finding that the extent of “livingness” depended on the conversion. At lower conversion (10 %) roughly 90 % of polymer chain ends contained alkoxylamine while at higher conversion (60 %) this value represented only 50 %. In this case just each second polymer chain is terminated by the alkoxyamine. The extent of „livingness“ of polymerization was decreased. It should result in higher probability of termination and subsequently to the higher polydispersity with increased conversion. Paradoxical is finding that this decreasing of “livingness” does not lead to the natural increase of polydispersity because prepared polystyrenes are characterized by narrow distribution of molar mass for all conversion scale - ca. 1.3. The explanation consists in the extreme rising of viscosity of the system that eliminates the extent of the termination reactions. This was proved by the comparison of kinetics and polystyrenes characteristics prepared by the solvent and block polymerization. Higher polydispersity were reached in the solution polymerization due to the lower viscosity.

Financial support of APVV-0562-07 is gratefully acknowledged.

SL 05

FEATURES CONTROLLED POLYMERIZATION OF VINYL MONOMERS IN THE PRESENCE OF INITIATION SYSTEM AIBN/$FeCl_3$

S. Bulgakova[a], E. Tumakova[a], A. Zhizhikina[b], Yu. Semchikov[b]

[a]Research Institute Chemistry, University of Nizhny Novgorod, pr. Gagarina 23,
bldg. 5, Nizhny Novgorod, 603950 Russia
(sbulg@mail.ru, sbulg@ichem.unn.ru)
[b] University of Nizhny Novgorod, pr. Gagarina 23, Nizhny Novgorod, 603950 Russia

It was found that the polymerization of methyl methacrylate (MMA) in a polar aprotic solvent N,N-dimethylformamide (DMF**)** catalyzed by AIBN/$FeCl_3$ proceeds in controlled fashion on the mechanism of the reverse atom transfer radical polymerization (RATRP) both in the presence of a various structure ligands and in its absence at 70-110 ºC. This implies that DMF acts not only as a solvent in research system but also as a ligand.

The polymerization of *tert*-butyl methacrylate (TBMA), ethoxyethyl methacrylate (EEMA), and styrene (St) in the presence of AIBN/$FeCl_3$/DMF was studied and the mechanism RATRP for these processes was proved by the linear increase of number-average molecular weight with conversion, the first order kinetic in the monomer and a low polydispersity index of polymers (up to 1.3). The relation of kinetic activities with polarity of double bonds of methacrylates was established: than the nucleofilic character of double bond is higher, the rate of polymerization is less. It is shown that the initiation efficiency increases in a number MMA< EEMA< TBMA. The influence of temperature on the molecular weight characteristics of PMMA, PEEMA and PTBMA and also on kinetic regularities of corresponding monomers polymerization was investigated. The apparent activation energy for polymerization of methacrylic monomers was estimated.

The presence of the ω-end chlorine atoms in the chains of PMMA obtained with AIBN/$FeCl_3$/DMF has been manifested by ^1H NMR spectroscopy. Chain extension of styrene and block copolymerization of MMA with PEEMA macroinitiator was performed to confirm the living nature of PSt and PEEMA.

The obtained results showed that the given catalytical system is a more active for ATRP of methacrylates than of styrene. In the latter case some deviations from controllability of process are observed due to a monomer structure and its reactivity.

SL 06

RAFT AND THIOL-ENE CHEMISTRY TOWARD FUNCTIONAL POLYMERS

M.M. Stamenović, P. Espeel, J. Garrevoet, W. Van Camp, F.E. Du Prez

Department of Organic Chemistry, Polymer Chemistry Research Group, Ghent University, Krijgslaan 281 S4bis, 9000 Ghent, Belgium
Filip.DuPrez@UGent.be, www.PCR.UGent.be

Tailor-made macromolecules significantly fulfill high demands in a range of industrial applications, considering necessity to construct nano-materials with precise control over functionality and architecture. Combination of Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization and radical thiol-ene reaction allows for the design of such functional materials. In terms of functional groups, RAFT is the most versatile controlled radical polymerization (CRP) technique, and thiol-ene serves as a robust and rapid post-polymerization modification approach.

Herein, we present two distinct routes toward functional polymers, starting from α and ω RAFT semitelechelics. In the ω approach, aminolysis of trithiocarbonate moiety led to the thiol containing polystyrene (PS) that was functionalized with wide range of low MW compounds, introducing a variety of functional groups in the polymer chain (e.g. hydroxyl, carboxylic). However, attempts to prepare amphiphilic polymer-polymer conjugates of thiol-bearing PS and allyl containing poly(vinyl acetate) (PVAc) largely failed, owing to the side reactions that stop the propagating cycle of the thiol-ene process[1]. Therefore, in the α approach, we utilized a new family of norbornenyl (Nb) based chain transfer agents (CTA) (i.e. tritiocarbonate, dithiobenzoate and xanthate), due to the ring strain promoted reactivity of Nb species toward thiols[2]. Nb based CTAs mediated polymerization of an assortment of monomers, including styrene, acrylates, and vinyl acetate, maintaining high end group fidelity. Corresponding norbornenyl functionalized polymers at the α terminus were modified with a variety of thiol-containing low MW compounds, demonstrating the great potential of thiol-ene chemistry as a mild and straightforward strategy toward well-defined functional polymeric materials.

[1] Koo, S. P. S.; Stamenović, M. M. *et al. J Polym Sci Part A: Polym Chem,* **2010**, 48, 1699-1713.

[2] Hoyle, C. E.; Lee, T. Y.; Roper T. *J Polym Sci Part A: Polym Chem,* **2004**, 42, 5301-5338.

SL 07

THE KINETIC FEATURES OF NITROXIDE-MEDIATED LIVING RADICAL POLYMERIZATION

M.Yu. Zaremski[a], Ch. Xin[a], A.P. Orlova[a], M.I. Shtilman[b], V.B. Golubev[a]

[a]*Moscow State University, Leninskie Gory, Moscow 119992, Russia*
(zaremski@mail.ru)
[b]*D. Mendeleev University of Chemical Technology of Russia, Miusskaya sq. 9,*
Moscow, Russia

Nitroxide-mediated living radical polymerization is one of the main approaches to tailored-made polymers. For the kinetic simulation of this process two main concepts are widely used now. The first one assumes the rate of living polymerization (R) to be identical for the conventional radical polymerization and to correspond to the rate of monomer thermal autopolymerization. The second states that R for living process is determined by the concentration of living chains and the value of constant of quasi-equilibrium. The first model explains the independence of R on the concentration of alkoxyamine initiator. However, it can not explain the first-order kinetic law for living polymerization. On the contrary, the second model can explain the first-order kinetic law for living polymerization, while it does not predict the rate independence on alkoxyamine concentration.

Here we suggest three main factors concept that can explain both above mentioned kinetic phenomena of nitroxide–mediated polymerization. These factors, namely the value of equilibrium constant, the rate of autopolymerization, and the rate of bimolecular self-recombination of macroradicals, determine the "level" of stationary concentration of nitroxide and hence the total rate of polymerization.

The role of each factor is considered for four TEMPO-mediated processes – styrene polymerization in bulk and diluted solution, and 4-vinylpyridine polymerization in bulk and solution. The experimental values are in a good agreement with numeral simulation.

Acknowledgement

This research was supported by the Russian Foundation for Basic Research (project number 08-03-00269-a)

SL 08

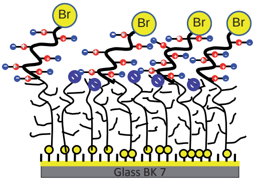
SYNTHESIS OF ULTRA-LOW FOULING SURFACES BY SURFACE INITIATED ATOM TRANSFER RADICAL POLYMERIZATION

C. Rodríguez-Emmenegger[a,b,*], E. Brynda[a], A. Bologna Alles[b]

[a]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
[b]College of Engineering, Universidad de la Republica, Montevideo 11300, Uruguay
(rodriguez@imc.cas.cz)

A major challenge in the field of biomaterials, drug delivery systems and biosensing is the prevention of non-specific protein adsorption. Non-fouling materials are also of interest for separation media, diagnostic, heterogeneous biocatalysis and coating for marine devices. At present very few non-fouling surfaces are effectively able meet the challenges for practical applications. A precise control of biomaterial surface is a crucial step for preparation of functional biomaterials. Growth of polymer brushes is an attractive method for generating robust surfaces with controlled properties and functionalities. Control in the brush grafting density has probed to play a very important role in the design of biosensors based on polymer brushes. Higher grafting density results in more protein resistant films, however, polymer brushes with a lower grafting density allow higher levels of functionalization. Therefore engineering surfaces with combined properties of high density and low density brushes is of great interest. In this work an assessment of the different antifouling surfaces prepared is presented. Ultra-low fouling zwitterionic brushes were synthesized. A new generation of ultra-low fouling surfaces based on poly(hydroxypropyl methacrylamide) brushes was prepared which breaks with the currently accepted design of antifouling surfaces. Block copolymer surfaces with engineered grafting density were prepared.

The use of these surfaces for surface plasmon resonance affinity biosensors, biocompatible nanoparticles and other system of potential biomedical application is shown.



This research was supported by the Academy of Sciences of the Czech Republic under Contract No KAN200670701

SL 09

INVESTIGATION OF ELEMENTARY STEPS OF RAFT POLYMERIZATION USING SPIN TRAP TECHNIQUE

A. Filippov, E. Chernikova, V. Golubev

Chemistry Department, Moscow State University, Lenin Hills, 1/3, 119991 Moscow, Russian Federation (ta-chem@list.ru)

The development of methods of controlled free-radical polymerization provides one with wide opportunity to synthesize well-defined (co)polymers and even block and gradient copolymers, which cannot be synthesized by means of conventional free-radical polymerization.

To conduct the polymerization in conditions of reversible addition-fragmentation chain transfer (RAFT) one should add special compounds – RAFT-agents (commonly, different thioesters, Z-C(=S)-SR) to the reaction mixture. As the result of chain transfer new radical particles – radical intermediates – are formed. Their formation multiplies the number of elementary steps of polymerization dramatically and complicates the mechanism and kinetics of polymerization.

The use of spin trap technique allows to examine kinetics and mechanism of individual elementary steps in model systems and to simplify the investigation of the whole process.

In our work the applicability of spin trap technique for the investigation of photo and thermo initiation processes, reactions of addition of model radicals to RAFT-agents, fragmentation of radical intermediates and their termination reactions is considered. It is proved that, in contrast to computational methods, the spin trap technique provides one with reliable values of rate constants of different elementary steps of RAFT polymerization. Thus, the rate constants of model reactions involving different RAFT agents are determined and the influence of stabilizing and leaving group is discussed.

The suggested method makes it possible to determine constant of chain transfer - the main characteristic of efficiency of RAFT agent.

Higher activity of polymeric RAFT-agents in chain transfer process in comparison with low-molecular compounds is proved and the synthesis of multi-block copolymers is suggested.

This work was supported by Russian Foundation for Basic Research (08-03-00269a)

SL 10

BIODEGRADABLE MICROSPHERES PREPARED FROM POLYSACCHARIDES-*graft*-POLY(*p*-DIOXANONE) COPOLYMERS

F. Lu, Y.-Z. Wang

Center for Degradable and Flame-Retardant Polymeric Materials, National Engineering Laboratory of Eco-Friendly Polymer Materials(SC), College of Chemistry, Sichuan University, Chengdu 610064, China

(yzwang@scu.edu.cn, http://chem.scu.edu.cn/polymer/yzwang/)

A series of novel polysaccharides-*graft*-poly(*p*-dioxanone) copolymer microspheres (Figure 1), which have a big potential in controlled delivery of drugs, are fabricated by solvent evaporation technique using gelatin as surfactant. The desired acetylated starch-*graft*-poly(*p*-dioxanone) (SAn-PPDO) copolymers with different compositions are controllably synthesized and their molecular weights and distribution are characterized by GPC. Effects of molecular architecture of graft polymers and drug payload upon the morphology, size distribution and crystallization properties of drug-free and drug-loaded microspheres are detailed investigated. Results show that by controlling the molecular structure of graft polymer and the drug loading content the controllable drug release behavior can be achieved. This study not only presents a series of novel microspheres generated using polysaccharides and polyester graft copolymer, but also opens a door to further modification of these microspheres and rationally synthesizes controllable and tunable scaffolds from polysaccharides and polyester graft copolymers.

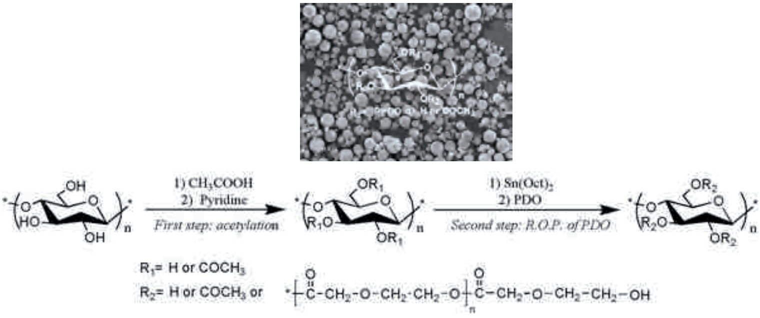


Figure 1. Ring-opening polymerization (ROP) of 1,4-dioxan-2-one (PDO) with an acetylated starch (SA) initiator and a tin 2-ethylhexanoate ($Sn(Oct)_2$) catalyst in bulk and the prepared copolymer microspheres.

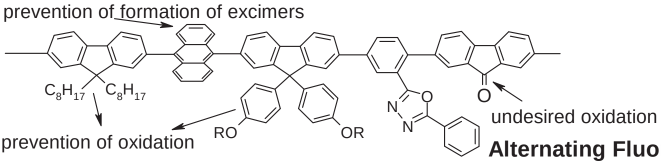
SL 11

TUNING THE STRUCTURE AND PROPERTIES OF CONJUGATED POLYMERS: POLYFLUORENES, POLYTHIOPHENES AND POLYACETYLENES

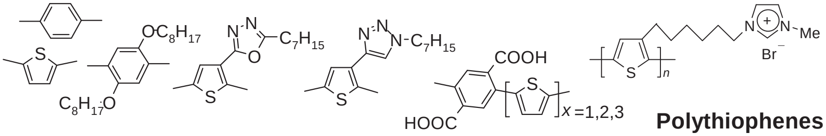
J. Vohlídal, D. Bondarev, R. Sivkova, J. Zedník, J. Sedláček

Charles University, Faculty of Sciences, Department of Physical and Macromolecular Chemistry, Hlavova 2030, 128 40 Praha 2, Czech Republic
(vohlidal@natur.cuni.cz)

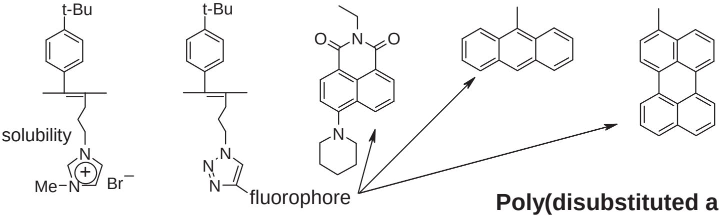
Control of polymerization processes and modification of primary polymers toward new materials with desired properties will be reported. Band-gap position and width (absorption/fluorescence) and polymer solubility and stability have been varied via structures given below. New conjugated polyelectrolytes have been prepared.



Alternating Fluorene Copolymers



Polythiophenes



Poly(disubstituted acetylenes)

References

1. Bondarev D. et al. *J. Polym. Sci. Polym. Chem.* **2009**, *47,* 4532.
2. Bondarev D. et al. *J. Polym. Sci. Polym. Chem.* **2010**, *48,* DOI: 10.1002/pola.24085

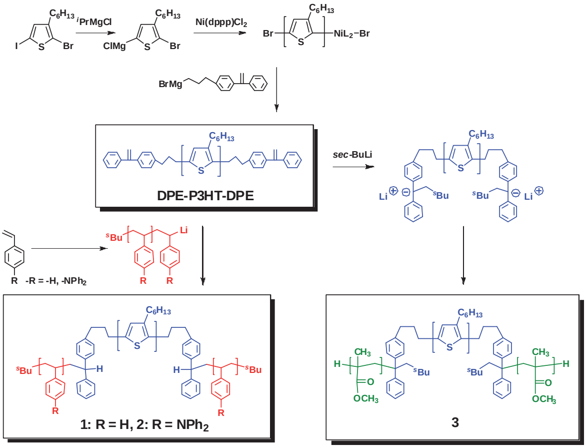
SL 12

NEW BLOCK COPOLYMERS CONTAINING POLY(3-HEXYLTHIOPHENE) SEGMENTS

T. Higashihara, A. Hirao, M. Ueda

Department of Organic and Polymeric Materials, Tokyo Institute of Technology,
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan
(thigashihara@polymer.titech.ac.jp)

A facile synthesis of new coil-rod-coil triblock copolymers containing regioregular poly(3-hexylthiophene) (P3HT) segments has been developed by the combination of quasi-living Grignard metathesis and living anionic polymerization (see Scheme below). The key material is a precursory α,ω-end-functionalized P3HT with 1,1-diphenylethylene moieties (DPE-P3HT-DPE). Two equivalents of living anionic polymers of styrene or 4-vinyltriphenylamine reacted quantitatively with DPE-P3HT-DPE to afford novel coil-rod-coil triblock copolymers, **1** or **2**, respectively. To synthesize **3**, DPE-P3HT-DPE was lithiated with *sec*-BuLi, followed by living anionic polymerization of MMA from the generated 1,1-diphenylalkyl anions. The compositional homogeneity of **1-3** was confirmed by GPC, GPC-RALLS, and NMR spectroscopy. In addition, thermal and optical properties were investigated by DSC and UV-vis spectroscopy, respectively. AFM images of triblock thin films clearly showed vertical lamellar morphology (see Figure 1 for a representative image). Such a neat and periodic nanostructure may possibly be related to low polydispersity (<1.15) of triblocks.



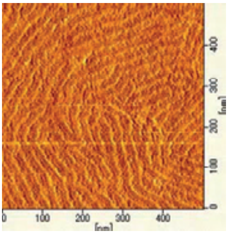


Figure 1. Tapping mode AFM phase image of **2**

SL 13

CONJUGATED LUMINESCENT POLYMERS BEARING CROSS-LINKABLE OXETANE SIDE GROUPS AS VERSATILE MATERIALS FOR ORGANIC OPTOELECTRONICS

J. Morgado[1,2], J. Farinhas[1], A. Charas[1], O. Fenwick[3], F. Cacialli[3], L. Alcácer[1]

[1]Instituto de Telecomunicações, Instituto Superior Técnico, Av. Rovisco Pais, P-1049-001 Lisboa, Portugal
[2]Dep. Eng. Química e Biológica, Instituto Superior Técnico, Av. Rovisco Pais, P-1049-001 Lisboa, Portugal
[3]Department of Physics and Astronomy and London Centre for Nanotechnology, University College London, Gower Street, London WC1E 6BT, UK

Conjugated polymers are at the origin of the new era of organic electronics and optoelectronics, with applications ranging from light-emitting diodes (LEDs), light-emitting field-effect transistors, field-effect transistors (FETs) and photovoltaic devices, to name the most relevant. Besides our ability to tune their properties by molecular engineering, the fact they can be processed from solution is originating new technological platforms for devices fabrication. This property creates new problems such as the need of new patterning techniques and how to deal with sequential polymer layer deposition (as one may destroy the soluble underlying layer).

In the last years, we have been investigating the use of polyfluorenes bearing oxetane side groups, which can undergo acid-catalysed polymerisation, leading to network formation. This ability has been used to fabricate FETs and multi-layer LEDs. More recently we have been addressing the use of phase separation to obtain films with submicron-structured surfaces, which are being explored in photovoltaic devices. As an alternative approach to prepare patterned structures from such materials, scanning near-field optical lithography has also been used.

In this presentation, we will provide an overview of these materials properties and prospects for new developments.

SL 14

TRIPLET EXCITON DYNAMICS AND CHARGE-CARRIER TRAPPING IN TRIPLET-EMITTER CONTAINING CONJUGATED POLYMERS

A. Kadashchuk[a,b], S. Schols[b], P. Heremans[b]

[a] *Institute of Physics, National Academy of Sciences of Ukraine, Prospekt Nauki 46, Kiev-03028, Ukraine, (kadash@iop.kiev.ua)*
[b] *IMEC v.z.w., SOLO-PME, Kapeldreef 75, B-3001 Leuven, Belgium (www.imec.be)*

Internal quantum efficiency of electro-fluorescence OLEDs is limited to be around 25% according to simple spin statistics. In order to overcome this efficiency limit, phosphorescent emitters doped into host material have been used. They are phosphorescent dye molecules incorporating a heavy metal atom with strong spin–orbit coupling and allow for harvesting singlet and triplet excitons. This makes possible an increase of internal quantum efficiency of up to 100%. In the present work [1] the phosphorescent materials consisting of the red triplet-emitting iridium complex $Btp_2Ir(acac)$ doped into poly(2-(6-cyano-6-methyl)-heptyloxy-1,4-phenylene) (CNPPP) and polystyrene (PS) host matrices were characterized by time-resolved photoluminescence techniques. The excitation intensity dependence of the phosphorescence (Ph) emission and the Ph decay kinetics measurements in $Btp_2Ir(acac)$ (1wt.%) doped CNPPP films reveled that the triplet-triplet annihilation inevitably occurs even at a moderate (~ 50 $\mu J/cm^2$ x pulse) excitation intensities due to the annihilation with movable host triplets. It was also found that oxygen has a profound effect on the apparent lifetime of $Btp_2Ir(acac)$ in the doped films at relatively large $Btp_2Ir(acac)$ concentration (~10 wt%) even in inert PS host. The latter evidences on triplet energy migration occurring through the triplet-emitter manifold, that was further supported by the observation of the “spectral diffusion” effect at such doping level. Elimination of the oxygen by the film encapsulation does prevent the $Btp_2Ir(acac)$ triplet quenching. The charge-carrier trapping by a range of triplet emitters doped into different conjugated polymers have been studied by trapping spectroscopy method as thermally stimulated luminescence (TSL). Direct evidence of the hole trapping in studied materials has been obtained and the trap depths were characterized [1]. The obtained hole trap depths appear to be rather close to that estimated from the difference in the host/guest HOMO levels. These results can explain often observed different dopant concentration dependence of the PL and EL in triplet-emitter doped materials, and suggest that the energy transfer dominates the PL of these materials but the charge trapping is responsible for the EL.

[1] A. Kadashchuk, et al., Chem. Phys. **358**, 147 (2009).

SL 15

NOVEL LOW-BAND GAP DONOR-ACCEPTOR COPOLYMERS FOR PHOTOVOLTAICS

V. Cimrová, I. Kmínek, P. Pavlačková, D. Výprachtický

Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

(cimrova@imc.cas.cz, http://www.imc.cas.cz/photonics)

Low-band gap polymers are of interest due to their potential use in organic photovoltaics, where polymers with broad absorption up to longer wavelengths are required to improve harvesting of the terrestrial solar radiation. The most successful strategy how to achieve low-bandgap polymers is copolymerization of an electron-donor and electron-acceptor monomers, where fine tuning of the bandgap is enabled by a choice of building blocks due to the intramolecular charge transfer (ICT) from the donor to the acceptor moiety.

In this contribution, we deal with synthesis and characterization of novel donor-acceptor copolymers containing thienothiadiazole units consisting of 4,6-di(2-thienyl)thieno[3,4-c][1,2,5]thiadiazole and its 3,3''-dialkyl derivatives. The introduction of alkyl chains to the thiophene units increases the molecular weights and solubility of the final copolymers leading to an improved processability of thin films. Effects of side-chain nature and length on photophysical properties were studied and will be discussed. Novel copolymers exhibited long-wavelength absorption in thin films and possess small optical band gap to be in the range 1.0 - 1.4 eV depending on copolymer units and alkyl side-chain nature and length. All copolymers under study exhibited ambipolar redox properties. Spectroelectrochemical study was also performed. Photovoltaic devices with bulk heterojunction made of blends of copolymers and fullerene derivatives were prepared. The power conversion efficiency of the PV devices with various ratios will be discussed in context to morphology.

We acknowledge the support of the Ministry of Education, Youth and Sports of the Czech Republic (grant No.1M06031).

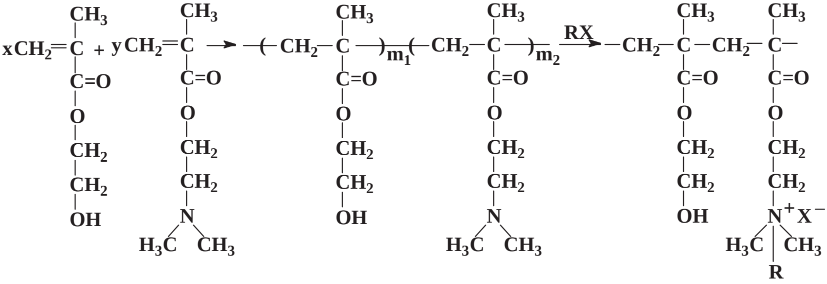
SL 16

FUNCTIONAL COPOLYMERS OF 2-HYDROXYETHYL METHACRYLATE WITH *N, N*-DIMETHYLAMINOETHYL METHACRYLATE

<u>V. Konsulov</u>[a], Tz. Godjevargova[b], Z. Grozeva[a], J. Tacheva[a], P. Saha[c]

[a]*K. Preslavsky University of Shumen, 115 Universitetska St., 9712 Shumen, Bulgaria, e-mail: konsulov@shu-bg.net*
[b]*University "Prof. Dr. Assen Zlatarov", Prof. Yakimov St. 8010 Bourgas, Bulgaria,*
[c]*Tomas Bata University of Zlin, TGM nam.5555, 76001 Zlin, Czech Republic*

In this paper the preparation of functional copolymers of 2-hydroxyethyl methacrylate (HEMA) with N, N-dimethylaminoethyl methacrilate (DMAEMA)-hydrogels, polyzwitterions and quaternary forms is described. The copolymerization of HEMA with DMAEMA has been conducted in solution (ethanol, acetone, benzene, DMF, DMSO and water) at 60°C:



where R is $–C_2H_5$, $–CH_2C_6H_5$, $–CH_2COO^-$, $–(CH_2)_3SO_3^-$; $X^- = Br^-, Cl^-, I^-$.

Experimental results showed that the nature of the solvent influences the copolymerization and the composition of copolymers. The copolymerization of HEMA-DMAEMA was studied by varying the mole fraction of HEMA from 10 to 90 mol.% in the initial mixture, using AIBN as an initiator in ethanol or acetone. The reactivity ratios were determined using computer program by Kelen-Tüdös method as follows: r_1=0.94, r_2=0.85 (in acetone) and r_1=0.82, r_2=0.78 (in ethanol).

pH-Sensitive poly(HEMA-co-DMAEMA) hydrogels were prepared by copolymerization of ternary mixture HEMA-DMAEMA and cross-linking agent ethylene glycol dimethacrylate. Copolymers of carboxybetaines or sulfobetaines, zwitterions and other quaternary forms have been prepared by polymeranalogous reaction in N-alkylation. The quaternary copolymers showed antimicrobial activity against *St.aureus* and *E. coli*.

SL 17

FOAMING OF POLYMERS AND POLYMER COMPOSITES

M. Kozlowski, A. Kozlowska, S. Frackowiak, M. Rudowski

Wroclaw University of Technology, Faculty of Environmental Engineering, Wybrzeze Wyspianskiego 27, Wroclaw, Poland marek.a.kozlowski@pwr.wroc.pl

Cellular plastics represent a group of materials, which have focused an interest of the research groups and industrial consortia, because of their challenging materials engineering demands and practical reasons. The materials are light-weight and exhibit insulating properties, which lies well in line with the materials and energy saving programs according to the sustainable development principle.

Fundamentals for the extrusion foaming of polyolefine and polyolefine composites with wood flour have been presented. The technology of cellular materials manufacturing has to take into consideration the polymer melt viscoelasticity, melt strength in uni-axial deformations, gas-polymer melt thermodynamic equilibria and time factor. Influence of the material and technology parameters on the foam microstructure have been discussed with formulation on the essential criteria on the polymer extrusion foaming.

Examples of polyethylene and polypropylene foaming have been presented. The materials exhibit a deterioration of mechanical properties as compared to bulk polymers; therefore a reinforcement with natural fillers has been performed. The biocomposites have been subjected to foaming by means of the extrusion technology. Comparison of the polymer matrix and wood composite affinity to the cellular structure shaping has been performed.

The end-use properties of the materials have been presented with a primary interest focused on the mechanical strength, application temperature and insulating properties. The properties have been discussed in relation to a microscopic structure of the materials and the parameters which influenced a particular type of morphology generation (Fig. 1).

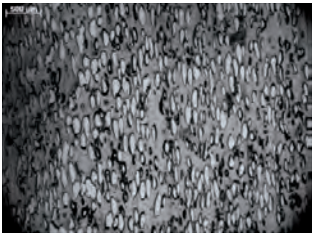


Fig. 1. Microstructure of LDPE foam

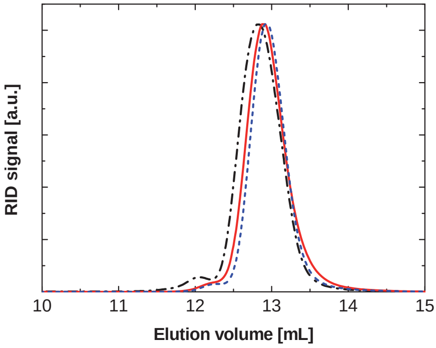
SL 18

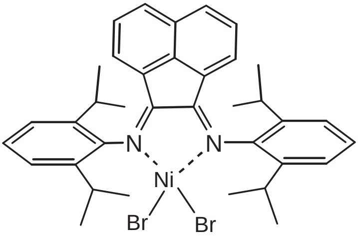
LIVING/CONTROLLED OLEFIN POLYMERIZATIONS INITIATED BY NICKEL DIIMINE COMPLEXES

J. Peleška[a], Z. Hoštálek[b], J. Merna[b]

[a]*Institute of Materials Chemistry, Brno University of Technology, Purkyňova 118,*
612 00 Brno, Czech Republic
[b]*Institute of Chemical Technology Prague, Department of Polymers, Technická 5,*
166 28 Prague 6, Czech Republic
merna@vscht.cz

Living/controlled polymerization of olefins is reported using nickel diimine complexes. The effect of catalyst structure, reaction condition, monomer/initiator ratio and cocatalyst type on extent of transfer and termination reactions was investigated. Even complexes with less bulky substituents were capable of preparation of polyolefins with very narrow molar mass distribution. Several non-methylalumoxane cocatalysts were found to activate nickel complexes that allow controlled olefin polymerization at low Al/Ni ratios. Truly living behaviour was found for some catalytic systems demonstrated by linear dependence of molar mass on monomer conversion and possibility to reinitiate the chain growth by addition of monomer. Due to chain-walking mechanism of nickel catalysts it was simultaneously possible to control branching of polymers beside their molar mass and its distribution.





Complex **1**

Figure 1. SEC traces of poly(hex-1-ene)s obtained by nickel complex **1** activated by methylalumoxane (dash dot), EtAlCl$_2$ (solid) and), Et$_2$AlCl (dash).

SL 19

POLY(10-UNDECENE-1-OL) - SYNTHESIS AND CHARACTERIZATION

M. Johannsen, U. Schulze, D. Jehnichen, L. Häußler, H. Komber, B. Voit

Leibniz-Institut für Polymerforschung Dresden, Hohe Straße 6, D-01069 Dresden, Germany (email to: johannsen@ipfdd.de)

The metallocene-catalyzed synthesis of poly(10-undecene-1-ol)s and the characterization of their chemical structure were published recently[1]. By variation of the polymerization conditions the chain length of the polymer backbone, the tacticity and the type of terminal groups could be controlled.

The main focus of this presentation is on the characterization of the morphology and the thermal behavior of the polymers. DSC curves show distinct endothermic peaks in the isotactic-rich as well as in the atactic poly(10-undecene-1ol)s. Two endotherm transitions were observed for most of the polymers. WAXS investigations show that isotactic-rich and atactic poly(10-undencene-1-ol)s shape frozen smectic structures. We assume that the long side chains supported by the polar groups cause an intermolecular phase separation, which results in an ordered layer structure. The estimated layer distance corresponds to two elongated side chains of the polymer that indicates an orthogonal arrangement. A connection of the side chains by hydrogen bridges is indicated by the relative high melting points of the poly(10-undecene-1-ol)s compared with poly(1-olefin)s of corresponding side chain lengths.

[1] U. Schulze, M. Johannsen, R. Haschick, H. Komber, B. Voit, *Eur. Polym. J.* **2010**, *46*, 578.

SL 20

MECHANICAL AND SURFACE PROPERTIES OF POLYCARBONATE-BASED POLYURETHANE ELASTOMERS

R. Poręba, M. Špírková, A. Strachota

Institute of Macromolecular Chemistry AS CR, v. v. i., Heyrovský Sq. 2, 162 00 Prague 6, Czech Republic

Polyurethane (PU) elastomers (made from macrodiol, diisocyanate and chain extender) consist of soft segment (macrodiol) and hard segment (diisocyanates and chain extender) domains. Novel polyurethane elastomers with superior mechanical properties based on polycarbonate diols, butanediol and hexamethylene diisocyanate were prepared. Some of them contained also layered nanofiller (Bentonite for organic systems) in the concentration bellow 2 wt. %. All samples were prepared as linear polymers, able to be processed by injection molding. All PUs displayed a high rubber modulus in all cases, and remarkable tensile properties. Very high elongation at break, together with high tensile strength lead to very high toughness value, compared to 'classical' (polyether- or polyester- based) PUs. These special properties seem to be as a result of an especially pronounced segmentation of these products, on submicron to nanometer scale. In this contribution, the effect of the kind of the polymeric diol and of macrodiol/butanediol ratio on mechanical properties will be shown. Atomic force microscopy (AFM) was used for surface topography characterization of PU films. This method was also used for the insight into the internal arrangement of PU systems on nanometer/micrometer scale (AFM analysis of broken area of PU sheets).

Acknowledgements: This work is supported by the Grant Agency of the Czech Republic (Czech Science Foundation, project No. P108/10/0195).

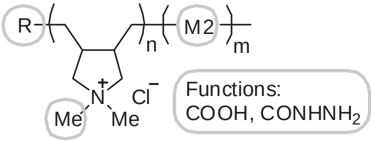
SL 21

FUNCTIONALIZED DERIVATIVES OF POLY(DIALLYLDIMETHYLAMMONIUM CHLORIDE)

P.S. Vlasov[a], O.A. Shishkan[a], N.S. Domnina[a], Z. Sedláková[b], E. Brynda[b]

[a]*Saint-Petersburg State University, 198504, Saint-Petersburg, Universitetskiy pr. 26, Russia (Petr_Vlasov@mail.ru)*
[b]*Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic*

Poly(diallyldimethylammonium chloride) or polyDADMAC is a widely used polymer which is consumed in considerable amount for water purification and paper production. Chemical modification might serve a tool for fitting new applications via rendering additional properties to the polymer. Suitable functional groups, which are essential for modification, do not present in the polymer and therefore must be introduced at polymerization step.



Three main positions of functional groups were considered in this work: (1) chain ends, (2) polymer backbone, (3) pendant substituents. Different groups (COOH and $CONHNH_2$) were selected to prepare functionalized polymers. PolyDADMAC with hydrazide end-groups was prepared by polymerization with functionalized azo-initiator. Carboxylic groups were introduced in polymer backbone by copolymerization of diallyldimethylammonium chloride with maleic acid (MA) or with diallylmethylammonioacetate. Carboxylic functions in poly(DADMAC-co-MA) were transformed into ethoxycarbonyl group via etherification. Copolymerization of diallyldimethylammonium chloride with ethyl diallylmethylammonioacetate chloride gave polyDADMAC derivatives containing COOEt as pendant groups. Treatment with hydrazine allowed conversion of COOEt functions into $CONHNH_2$. This set of functions and positions provided enough space for subsequent chemical modification.

Functionalized polyDADMACs were applied for development of fungicides and additives to paper. Complexes of hydrazide-containing polymers with Cu^{2+} were obtained and were shown to suppress growth of a pathogenic fungus *Fusarium oxysporum*. Functional groups were used to attach 3,5-di-tret-butyl-4-hydroxiphenyl fragments resulting in macromolecular systems with antioxidant activity which will be tested as agents against paper aging.

SL 22

SYNTHESIS OF NOVEL STYRENE/BUTADIENE COPOLYMER RESIN BASED ON ANIONIC POLYMERIZATION

Y. Wang, H. Zhang, H. Ma, Ch. Zhang, Y. Hu, Z. Li, Z. Zhao, Y. Wang, Y. Li

State Key Laboratory of Fine Chemicals, Department of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, No.158, Zhongshan Road, Dalian City, Liaoning, 116012, China
(liyang@dlut.edu.cn)

A novel star comb styrene/butadiene copolymer resin (SC-SBC) with well-defined structure and very high impact strength was synthesized successfully by living anionic polymerization and grafting onto technique. Grafting reaction of the epoxidized liquid star polybutadiene with the active centre of linear poly(styrene/butadiene) lithium yielded star comb styrene/butadiene copolymer resin. Tailor-made star comb architectures were attainable by controlling the epoxidation level and the molecular weight of the side chains used for grafting reaction. The overall shape of the star comb macromolecules could be altered by changing the molecular weight and number of the side chain. The notched Izod impact strength of SC-SBC resin was near to 240 J/m. Following case, based on retarded anionic polymerization (RAP) a series of star high impact polystyrene (S-HIPS) were synthesized by using multifunctional alkyl lithium as initiator and *i*-Bu_3Al (TIBA) as retarder. S-HIPS was composed of star styrene/butadiene copolymer rubber and star polystyrene resin. The influence of the amount of TIBA on the molecular weight of polystyrene and its distribution were discussed. S-HIPS showed very high impact strength and Izod notched impact strength was more than 220 J/m. The relationship between morphology structure and properties of S-HIPS was studied based on the force-time/deflection curve and the analysis of electron microscope (SEM&TEM).

Reference:

[1] Hongxia Zhang, Yang Li, Chunqing Zhang, Zhansheng Li, Xin Li, Yurong Wang, Synthesis of dendrigraft star-comb polybutadienes by anionic polymerization and grafting-onto methodology, Macromolecules, 2009, 42(14): 5073–5079

[2] Hongxia Zhang, Yang Li, Chunqing Zhang, Yanming Hu, Yurong Wang, Hongwei Ma, Wei Li, Synthesis and Characterization of Star-Comb Polybutadiene and Poly(ethylene-co-butene), Chinese Chemical Letters, 2010, 21: 361-364

Acknowledgements: National Science Foundation of China (NSFC)(20674007&20774015&20874008) and National High Technology Research and Development Program of China (2007AA03Z532).

SL 23

AMPHIPHILIC GRAFT COPOLYMERS VIA A COMBINATION OF CONVENTIONAL AND METAL-FREE ANIONIC POLYMERIZATION

J. Zhao[a,b], G. Mountrichas[a], G. Zhang[b], S. Pispas[a]

[a]*Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Ave., 11635 Athens, Greece (pispas@eie.gr, http://www.eie.gr/nhrf/institutes/tpci/index-en.html)*
[b]*Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, Anhui, China*

Amphiphilic graft copolymers with poly(ethylene oxide) being the hydrophilic side chains have gained extensive academic interest both in terms of synthesis and physical properties.[1,2]

In this work we present the synthesis of polystyrene-*block*-poly(*p*-hydroxystyrene-*graft*-ethylene oxide), PS-*b*-(PHOS-*g*-PEO),[3] amphiphilic block-graft copolymers and thermosensitive brush-like copolymers with poly(propylene oxide-*b*-ethylene oxide), PPO-*b*-PEO side chains and a PHOS backbone, (PHOS-g-(PPO-*b*-PEO)).[4] The copolymers were synthesized by a combination of traditional and metal free anionic polymerization. The PEO and PPO-*b*-PEO side chains were synthesized by metal-free anionic ring-opening polymerization of oxirane monomers, using the phosphazene base (*t*-BuP$_4$) and the phenolic hydroxyl groups (PhOH) in the backbones, as the complex multifunctional initiating system. Well defined copolymers of low polydispersity and with variable molecular characteristics were obtained in all cases. The aggregates formed by these copolymers in aqueous media were also studied. The PS-*b*-(PHOS-*g*-PEO) block-graft copolymers form highly swelled aggregates with low aggregation numbers, having nanostructures resembling hyperbranched clusters. For the PHOS-g-(PPO-*b*-PEO) copolymers temperature-induced intramolecular chain contraction/association and intermolecular aggregation could both be observed at different stages of the heating process.

References

1. H-Q. Xie, D. Xie Prog. Polym. Sci. 1999, 24, 275.
2. a) R. Zhang, A. Seki, T. Ishizone, H. Yokoyama Langmuir 2008, 24, 5527. b) A. Oyane, T. Ishizone, M. Uchida, K. Furukawa, T. Ushida, H. Yokoyama Adv. Mater. 2005, 17, 2329.
3. J. Zhao, G.. Mountrichas, G.. Zhang, S. Pispas Macromolecules 2009, 42, 8661.
4. J. Zhao, G.. Mountrichas, G.. Zhang, S. Pispas Macromolecules 2010, 43, 1771.

SL 24

CONTROLLED CATIONIC POLYMERIZATION AT ELEVATED TEMPERATURES USING $B(C_6F_5)_3$ AS CO-INITIATOR

S.V. Kostjuk[a,b], F. Ganachaud[b]

[a]*Research Institute for Physical Chemical Problems of the Belarusian State University, Leningradskaya St., 14, 220030 Minsk, Belarus*
(kostjuks@bsu.by, http://www.fhp.bsu.by/_private/en/labcatalys.htm)
[b] *Institut Charles Gerhardt, UMR5253 CNRS/UM2/ENSCM/UM1, Engineering of Macromolecular Architectures, ENSCM, 8 Rue de l'Ecole Normale, 34296 Montpellier Cedex, France*

This presentation deals with our recent investigations of the $B(C_6F_5)_3$-co-initiated cationic polymerization of different monomers (styrene and its derivatives, cyclopentadiene, isoprene and β-pinene) under mild experimental conditions, that is, room temperature and open air. In contrast to initiating system based on conventional Lewis acids ($TiCl_4$, $AlCl_3$), the high molecular weight polymers (M_n=5,000–50,000 g/mol) can be synthesized in a living fashion under above-mentioned conditions due to the unique ability of $B(C_6F_5)_3$ to generate weakly basic, non-coordinating counteranion. The possibility to control the regiochemistry of monomer insertion during the $B(C_6F_5)_3$-co-initiated polymerization of cyclopentadiene and isoprene will be reported in this presentation. Finally, the mechanism of reaction as well as scope and limitations of the borane-catalyzed cationic polymerization will be discussed.

SL 25

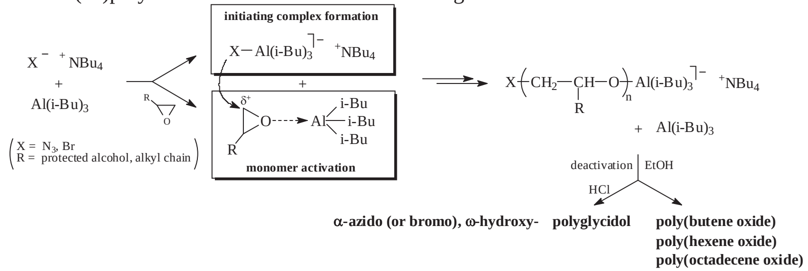
CONTROLLED SYNTHESES OF HYDROPHILIC AND HYDROPHOBIC POLYETHERS BY MONOMER ACTIVATION AND THEIR DIRECT α-AZIDO FUNCTIONALIZATION

S. Carlotti, A.L. Brocas, A. Deffieux, M. Gervais, G. Cendejas

Université de Bordeaux, Laboratoire de Chimie des Polymères Organiques, CNRS, ENSCBP, 16 Av. Pey Berland, 33607 Pessac Cedex, France

Polyethers are widely used for their unique properties of low Tg and high temperature stability. They are mainly synthesized by ring opening polymerization of epoxides or glycidyl ethers. The mechanism can be anionic, cationic or coordinative. However their synthesis is relatively slow and often disturbed by the occurrence of side reactions such as transfer to monomer which prevents the achievement of high molar masses polyethers with a good control of the polymerization. They are especially used as amphiphilic block copolymers with generally a hydrophilic block of poly(ethylene oxide) and a hydrophobic one of poly(propylene oxide). These kinds of copolymers find their applications in surfactant or gelling additives for examples.

Here we present the preparation of hydrophobic polyethers such as Poly(butene oxide), Poly(hexene oxide) and Poly(octadecene oxide) as well as Polyglycidol, a water-soluble polymer, with a great interest mainly for biomedical applications due to their biocompatibility and high hydroxyl functionality. A similar synthetic route was investigated for the preparation of all polymers in order to make amphiphilic copolymers. An ammonium salt was used as initiator in the presence of triisobutylaluminum as co-initiator and activator of the polymerization of butene-, hexene-, and dodecene oxides as well as ethoxy ethyl- and *tert*-butyl glycidyl ether in the aim to synthesize (co)polyethers with linear and controlled high molar masses.



The precise control of chain end functionalization is also essential for the preparation of reactive polymers. As well known, click chemistry can be very efficiently applied to the preparation of linear block copolymers, dendrimers, gels, surface functionalization, as well as to cells and virus modifications in biomolecular engineering. The azide group is so far introduced by mesylation of the hydroxyl terminus of previously formed polymers followed by its subsequent substitution with sodium azide[1,2]. The direct synthesis of α-azido, ω-hydroxy terminated polyglycidols and other polyethers will be also presented. It involves an initiation step of oxiranes using tetrabutylammonium azide in the presence of triisobutylaluminum as activating agent to get a controlled/living anionic polymerization of such monomers[3,4].

References

1. S. Hiki, K. Kataoka, *Bioconjugate Chem.* **2007**, 18, 2191.
2. S. Iyer, A. Anderson, S. Reed, B. Swanson, *Tetrahedron Lett.* **2004**, 45, 4285.
3. M. Gervais, A. Labbe, S. Carlotti, A. Deffieux, *Macromolecules* **2009**, 42, 2395.
4. M. Gervais, A-L. Brocas, G. Cendejas, A. Deffieux, S. Carlotti, *Macromolecules* **2010**, ASAP.

SL 26

A MICROFLUIDIC ‘THIO-CLICK’ APPROACH TOWARDS FUNCTIONAL/CLICKABLE AND DEGRADABLE POLYMER BEADS

R.A. Prasath, M.T. Gokmen, F.E. Du Prez

Department of Organic Chemistry, Polymer Chemistry Research Group, Ghent University, Krijgslaan 281 S4bis, 9000 Ghent, Belgium
Filip.DuPrez@UGent.be, www.PCR.UGent.be

Recently, the radical-mediated thiol-ene and thiol-yne (‘thio-click’) photopolymerisation between thiol groups and π-bonds has attracted significant attention in materials synthesis. We explored both photopolymerisations in a simple microfluidics setup [Fig.1(A)] to produce monodisperse-crosslinked nonporous and porous beads [Fig.1 (B&C)] containing a variety of functional[1]/clickable groups.

On one hand, beads containing amine, carboxyl, hydroxyl, thiol, -ene or -yne groups were prepared by reacting a tetrafunctional thiol with multi- and mono-functional -ene or -yne monomers in the presence of or without a porogen, using a photoinitiator under ambient conditions.

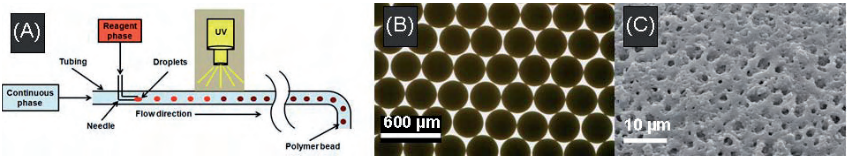


Figure 1. Representation of (A) microfluidic setup; (B) optical image of monodisperse beads and (C) SEM image of porous surface in the beads

On the other hand, degradable polymer beads containing a fluorescent marker (as model drug) were prepared by reacting a tetrafunctional thiol with multifunctional-ene monomers having degradable linkages. The beads were characterized by optical, confocal and scanning electron microscopy, FTIR and Raman spectroscopy, differential scanning calorimetry, and other techniques. This work demonstrates the applicability of both the thiol-ene and thiol-yne ‘click’ reactions in microfluidics as a very attractive and powerful tool for rapid production of novel materials for diverse applications.

(1) Prasath, R.A; Gokmen, M.T., Espeel, P., Du Prez, F.E. *Polym. Chem.*, in press

SL 27

MULTICOMPARTMENT CATERPILLAR MICELLES FROM LINEAR TRIBLOCK TERPOLYMERS

A. Groeschel, S. Tea, A.H.E. Mueller

Department of Macromolecular Chemistry II, University of Bayreuth, Germany (http://www.chemie.uni-bayreuth.de/mcii/)

ABC triblock terpolymers opened up the way towards a wide variety of superstructures due to self-assembly in bulk[1], solvent mixtures, the aid of coordination agents[2] or pure solvent selectivity towards single blocks[3]. Among of those, micelle formation with compartmentalized cores due to simple solvent selectivity has attracted increased attention only recently. Here we want to present a linear triblock terpolymer capable of asymmetric compartmentalization even with blocks found in the lower segregation region.

The Novel linear triblock terpolymer poly(*tert*-butyl methacrylate)-*block*-poly (cinnamoyloxyethyl methacrylate)-*block*-poly(2-dimethylamino ethyl) methacrylate (TCD) was synthesized via sequential anionic polymerization of tBMA, TMS-HEMA and DMAEMA. Aliquots were taken after each monomer was consumed completely and investigated with ^{1}H-NMR and GPC. It was found, that all blocks were initialized quantitatively and no noticeable side reactions took place, resulting in a narrowly distributed terpolymer (PDI < 1.15) with an overall M_n of around 110 kg/mol. In a subsequent post polymerization reaction, P(TMS-HEMA) was deprotected with methanol and esterified with cinnamic acid chloride to form a UV-crosslink-able middleblock. Dialysis of the terpolymer against block selective solvents with increasing polarity (dialysis sequence THF-Methanol-Water) lead to the formation of core phase separated multicompartment micelles with caterpillar like appearance. The prepared superstructures were studied with TEM, cryo-TEM, DLS and AFM. Whereas the caterpillar width was uniform, the length could be steered to a certain extend by varying initial polymer concentration and/or the pH in the last dialysis step. It was also possible to selectively load and fix the PCEMA compartments with e.g. magnetite nano-particles and subsequent UV crosslinking. Crosslinking the micelles will not only help to understand the extend of phase separation, but also open the possibility to lock the structure in order to form particles with non-centrosymmetry

References:

1) Clemens Auschra, Reimund Stadler, *Macromolecules* (1993), **26**, 2171-2174.
2) H. Cui, Z. Chen, S. Zhong, K. L. Wooley, and D. J. Pochan, *Science* (2007), **317**, 647-650.
3) Z. Li, E. Kesselman, M. A. Hillmyer, T. P. Lodge, *Science* (2004), **306**, 98-101.

SL 28

STUDIES ON SPEEK-POLY (AMIDE-IMIDE) POLYMER BLEND MEMBRANES FOR FUEL CELL APPLICATIONS

D. Gupta, V. Choudhary

Centre For Polymer Science and Engineering Indian Institute of Technology, Delhi
Hauz Khas, New Delhi 110016, India
Email: veenach@hotmail.com, Tel. No. 91-011-26591423, Fax. No. 91-011-26591421

This paper describes the preparation of polymer blend membranes using sulfonated poly (ether ether ketone) [SPEEK] as acid component and poly (amide-imide) [PAI] as base component. SPEEK with degree of sulfonation ~ 62 was synthesized in our laboratory by electrophilic substitution reaction of PEEK with conc. H_2SO_4 [98%] at 50 ^{o}C. The purpose of adding PAI was mainly to enhance hydrolytic stability without compromising the proton conductivity.

Required amounts of SPEEK and PAI were dissolved separately in DMAc and the blends were prepared by solution blending technique followed by casting. Several polymer blend membranes were prepared by mixing 5, 10, 15, 20 and 25 % (w/w) of PAI with SPEEK. The blend membranes have been designated as SPT followed by neumerical suffix indicating the amount of PAI. For example blend membranes based on SPEEK having 5 and 10 weight % of PAI have been designated as SPT-5 and SPT-10 respectively. All the membranes were transparent and yellow in color. Yellowish tinge increased with increasing amount of Torlon. No phase separation was seen for blend composition upto 25 % of PAI. The toughness of the film increased with increasing amount of PAI in blend samples.

Thermal characterization was done using Differential Scanning Calorimetery (DSC) and thermogravimetric analyser (TGA). In the DSC traces of SPEEK, SPT-5 and SPT-10, the presence of loosely bound water was evident by presence of endothermic peak at sub zero temeprature whereas no such observation was made in other compositions. TGA studies revealed that 0.5-1.2 % mass loss occurred below 200 ^{o}C and char yield at 800 ^{o}C was in the range of 43-47%. Water uptake studies were performed by immersing the weighed amount of dry membranes in water at 35^{o}C and 80^{o}C for varying interval of time till equilibration is attained. Membrane based on PAI did not show any water uptake even after 24h of immersion at 80 ^{o}C , whereas SPEEK showed water uptake of 42 %. Water uptake decreased significantly upon incorporation of 5 % PAI which decreased further to 4% in case of blend having 15 % PAI. Blend membranes based on samples SPT-20 and SPT-25 did not show any water uptake after immersion at 80 ^{o}C for 24h. Proton conductivity was measured through plane using impedance spectroscopy comprising a two probe method. Before measurement membranes were equilibrated in deionized water at 80 ^{o}C. Proton conductivity of membranes increased with increasing amount of PAI upto 15% followed by a decrease. Samples having 5 and 10% PAI i.e. samples SPT-5 and SPT-10 showed highest proton conductivity and the value was comparable to that of Nafion. These results clearly show that blending of SPEEK with PAI resulted in blend membranes having proton conductivity comparable to Nafion, better hydrolytic stability. higher than SPEEK.

PC 01

TEMPLATE-SYNTHESIZED POLYANILINE WITH POLYSACCHARIDES AS TEMPLATES

S. Bednarz[a], M. Lukasiewicz[b], A. Ptaszek[a], P. Ptaszek[a], I. Raciborski[a], M. Grzesik[a],
A. Bednarz[a]

[a] *Department of Engineering and Machinery for Food Industry, University of Agriculture, ul. Balicka 122 30-149 Krakow, Poland*
(sbednarz@ar.krakow.pl)
[b] *Department of Carbohydrates, University of Agriculture,*
ul. Balicka 122 30-149 Krakow, Poland

We reported synthesis of polyaniline in the presence of polysaccharides gels as soft templates. Polymerization of aniline hydrochloride initiated by ammonium persulfate in the presence of starch, guar gum, xanthan gum, carboxymethyl cellulose or carrageen yields polyaniline dispersed in the polysaccharide matrix. The matrix was removed simply by acidic hydrolysis and resulted polyaniline were characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

PC 02

CONDUCTING POLYANILINE–MONTMORILLONITE COMPOSITES

P. Bober[a], M. Trchová[a], J. Stejskal[a], J. Prokeš[b]

[a]*Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic*
(bober@imc.cas.cz)
[b]*Charles University in Prague, Faculty of Mathematics and Physics, 182 00 Prague 8, Czech Republic*

Polyaniline–montmorillonite (PANI–MMT) composites connect the well-known properties of PANI (high electrical conductivity, environmental stability, ease of preparation from common chemicals, good processibility, and low cost) with properties of clays (an ability to swell and exchange cations) [1–3]. The aim of this work is the chemical synthesis and the characterization of such PANI–MMT nanocomposites. In the first method of synthesis, both aniline and oxidant (ammonium peroxydisulfate) were added to MMT suspension (Fig. 1). In the second, aniline was intercalated into MMT and in the next stop the oxidant was added.

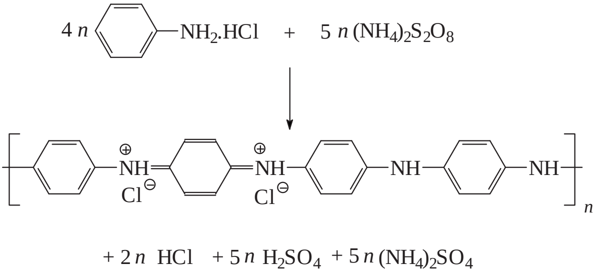


Figure 1. Aniline hydrochloride is oxidized with ammonium peroxydisulfate to polyaniline hydrochloride.

Products were characterized by Fourier-transform infrared and Raman spectroscopy, conductivity measurements, thermogravimetric analysis, and optical and scanning electron microscopies.

1. I. Sapurina, J. Stejskal, *Polym. Int.* 2008, *57*, 1295.
2. G. M. do Nascimento, V. R. L. Constantino, R. Landers, M. L. A. Temperini, *Polymer* 2006, *47*, 6131.
3. S. Yoshimoto, F. Ohashi, Y. Ohnishi, T. Nonami, *Synth. Met.* 2004, *145*, 265.

PC 03

NEW CONJUGATED IONIC POLYMERS WITH POTENTIAL APPLICATIONS IN OPTOELECTRONIC DEVICES – SYNTHESIS AND CHARACTERIZATION

D. Bondarev, J. Zedník, J. Vohlídal

Charles University in Prague, Faculty of Science, Department of Physical and Macromolecular Chemistry, Hlavova 2030, 128 43 Praha 2, Czech Republic (dbondarev@email.cz)

Conjugated polyelectrolytes belong to the class of polymers with potential applications in construction of optoelectronic devices, chemo- and biosensors and nanocomposites. These polymers possess unique properties which arise from a combination of pi-conjugated main-chain and ionic pendant groups. Main-chain conjugation allows expecting active response to optical or electrical stimuli resulting in potential applications in electroluminescence or photovoltaic devices. Attached ionic groups cause the solubility in water-miscible, environmentally friendly solvents and can mediate specific interactions with ionic polymer carrying oppositely charged moieties, metal nanoparticles or metal oxide surfaces such as titanium dioxide structures which are widely used in construction of photovoltaic devices.

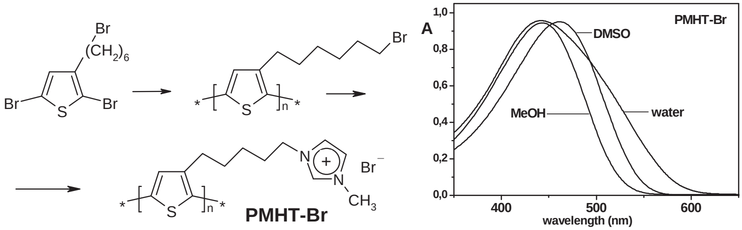


Fig 1: An example of synthesis and absorption spectra of cationic polymer

In current contribution we report the synthesis and characterization of cationic and anionic polymers based on thiophene main-chain units. Characterization by means of SEC chromatography, NMR, FTIR, absorption and photoluminescence spectroscopy was performed and properties of polymers are compared from point of view of chemical composition and variances in the microstructure.

PC 04

EFFECTS OF STRUCTURE AND COMPOSITION OF THE POLYMER MATRIX ON THE MORPHOLOGY AND ELECTRO-OPTICAL PROPERTIES OF LIQUID CRYSTAL POLYMER COMPOSITES

S. Bulgakova, M. Johns, I. Kazantzeva

Research Institute of Chemistry N.I. Lobachevsky State University of Nizhny Novgorod, Pr. Gagarina 23, bldg.5, Nizhny Novgorod 603950, Russia (sbulg@ichem.unn.ru)

The morphology and electro-optical properties of composites based on 2-ethyl hexyl acrylate (EHA) with acrylic acid (AA) amphiphilic copolymer and liquid crystal (LC) E7 (Merck) prepared of photopolymerization-induced phase separation were studied. It was found that the submicron sizes LC drops are formed in given system and their value depends on composition of initial monomer mixture. It was shown that the hyperbranched copolymer structure formed at introduction in photocurable composition of molecular weight regulators of copolymer such as the chain transfer agent dodecyl mercaptane (DDM) and cross-linker ethylene glycol dimethacrylate (EGDMA) and an increase of LC concentration results in decrease of the sizes of LC drops. The directly proportional dependence between the sizes of LC drops and electro-optical properties of polymer-dispersed liquid crystal (PDLC) films was revealed.

For the first time the highly orientated domain structure in nematic LC composite arising after the application of an external electric field (Fig. 1), and the attributes of its origin in the initial films on a basis of EHA-AA copolymer (Fig. 2) have been found by the scanning electron microscopy. The "translucence" effect of PDLC films appeared in increase of the films transmittance in the off -state after the first field switching was investigated. This effect depends on increase of the LC droplet size and partial "freezing" of orientation of the drops director in a direction of a field and it weakens at introduction of modifiers in curable composition in the following number: potassium acetate, EGDMA/DDM, potassium acetate/ EGDMA/DDM. The PDLC films having the threshold about 2Vμm^{-1}, on-time (τ_{on}= 0.7 ms) and off-time (τ_{off} = 1.4 – 4.6 ms) have been developed.

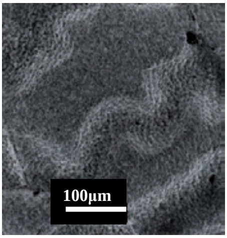


Fig. 1. SEM image of the polymer phase in the initial PDLC film

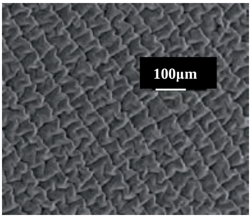


Fig. 2. SEM image of the polymer phase in the PDLC film after the application of an external electric field

PC 05

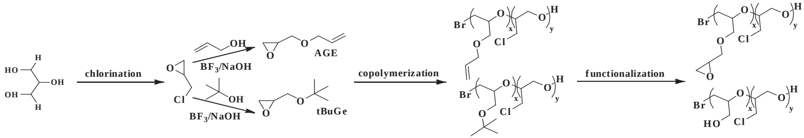
BIO-BASED FUNCTIONAL POLYETHERS: APPLICATION TO POLYURETHANES AND EPOXY RESINS MATERIALS

A.L. Brocas, A. Deffieux, G. Cendejas, S. Carlotti

Université de Bordeaux, Laboratoire de Chimie des Polymères Organiques, CNRS, ENSCBP, 16 Av. Pey Berland, 33607 Pessac Cedex, France

Polyurethanes and epoxy resins materials are widely used in various areas like building, coating, automobile or aeronautic industries. Because of the increasing energy demand, the decrease of petroleum products and new regulations, new routes for the synthesis of bio-based polymers and materials derived thereof have to be developed. Renewable resources, in particular wood derivatives and seed oils, can be used as raw materials owing to their significant availability. Extracted from vegetal oils, glycerol allows several epoxidized monomers to be prepared, as epichlorohydrin (ECH) or glycidol. Starting from these monomers, some glycidyl ethers like allyl glycidyl ether (AGE)[1] or tert butyl glycidyl ether (tBuGE) can be prepared.

The copolymerizations between ECH and AGE or ECH and tBuGE were carried out by monomer activation[2,3] anionic polymerization in a few hours. The process required an organic initiator (tetraoctylammonium bromide) and an activator (triisobuylaluminium).The activator was used in slight excess (~2) compared to the initiator. The polymerization was controlled and the size exclusion chromatography showed a narrow molar mass distribution. Copolymers with various molar mass were then functionalized by several reactive groups. Double bond side chains were used to introduce epoxide groups thanks to meta-chloroperbenzoic acid. tBuGE is a protected form of polyglycidol and the deprotection of hydroxyl groups was carried out by acidic treatment in few hours at 60°C. The different steps for the preparation of functionalized copolymers are shown on the next figure:



The occurrence of the different functionalizations was checked by ^{1}H and ^{13}C NMR analysis which showed the total disappearance of the characteristic peaks of double bounds and tert butyl group present in these copolymers. These polymers are the precursors for the preparation of epoxy resins (poly(allyl glycidyl ether-co-epichlorohydrin)) and polyurethanes (poly(glycidol-co-epichlorohydrin)).

The polymers having pendant epoxy groups were mixed with amines with functionality higher than 2 to form a cross-linked epoxy network. The crosslinking reaction was followed by DSC analysis which showed an increase of the glass transition temperature (Tg) after reaction. The influence of the number of epoxy groups on the Tg was investigated in order to obtain materials with different propertie.

Polyols were used with diisocyanates to form cross-linked polyurethanes. The reaction was performed at 70°C in a few hours with di-butyltindilaurate as catalyst. Materials became insoluble in organic solvent and FT-IR was used to characterize the formation to polyurethanes thanks to the appearance of the characteristic band at 1720cm-1(C=O).

1 Xie H., Guo J., Yu G., Zu J., Journal of applied polymer science, 80, 2446-2454, **2001**
2 Billouard C., Carlotti S., Desbois P., Deffieux A. *Macromolecules ,37(11)*, 4038, **2004**
3 Carlotti S. and al, Macromolecules, 41, 7058-7062, **2008**

PC 06

THE THEORETICAL DESCRIPTION OF SUPRAMOLECULAR STRUCTURES FORMED BY POLY(VINYLDIAMINOTRIAZINE) AND NUCLEIC ACID BASES

J. Czernek

Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovsky Sq. 2, 162 06
Prague 6, Czech Republic (czernek@imc.cas.cz, voice: +420-296809290)

Komiyama et al. described that poly(2-vinyl-4,6-diamino-1,3,5-triazine) (PVDAT) could efficiently recognize nucleic acid bases and their derivatives. The different recognition in water **[1]** and methanol **[2]** was attributed to changes in the microenvironment around DAT residues, which disfavors the formation of hydrogen bonds and promotes stacking interactions in the case of water, while the opposite trend holds in methanol solutions. In the absence of any direct structural information, molecular modeling can be usefully applied to analyze the factors contributing to the stabilization of the complexes formed between PVDAT and nucleobases or related compounds. Thus, the system was approximated by the DAT trimer and three guest molecules, and using the RI-BP-D/TZVPP quantum chemical method (see ref. **[3]**), its energy-minima were established for a number of starting structures, which covered various mutual orientations of the guests. The resulting geometries could be roughly divided into two groups, *i.e.*, one maximizing the number of hydrogen bonds between DAT residues and the guests, and the other featuring a “hydrophobic pocket” in the mid part of the DAT trimer occupied by one of the guests and stabilized mostly by stacking. Representative structures were used to estimate their RI-MP2 interaction energies ΔE extrapolated to the complete basis set limit by applying the variational supermolecular approach together with the cc-pVDZ and cc-pVTZ basis sets **[3]**. Interestingly, the stabilization of the hydrogen-bonded and stacked fragments was found to be similar for the most stable structures (*i.e.*, the two corresponding ΔE values lied within several kJ/mol from each other). This finding could be instrumental for an interpretation of the experiments **[1]**, **[2]**.

References:

[1] Asanuma, H.; Ban, T.; Gotoh, S.; Hishiya, T.; Komiyama, M. *Macromolecules* **1998**, *31*, 371–377.

[2] Asanuma, H.; Hishiya, T.; Ban, T.; Gotoh, S.; Komiyama, M. *J. Chem. Soc., Perkin Trans. 2* **1998** 1915–1918.

[3] Jurečka, P.; Černý, J.; Hobza, P.; Salahub, D. R. *J. Comput. Chem.* **2007**, *28*, 555–569.

PC 07

PHOTOCURED THYMOL-BASED COATINGS FOR BIOACTIVE FOOD PACKAGING

M. Degli Esposti[a], M. Toselli[b], F. Pilati[a], M. Bondi[c], R. Iseppi[c]

[a]*Department of Materials and Environmental Engineering, University of Modena and Reggio Emilia, via Vignolese 905/A, 41100 Modena, Italy*
(micaela.degliesposti@unimore.it)
[b]*Department of Applied Chemistry and Material Science, University of Bologna, via Terracini 28, 40131 Bologna, Italy*
[c]*Department of Biomedical Sciences, University of Modena and Reggio Emilia, via Campi 287, 41100 Modena, Italy*

Incorporation of antibacterial agents in coatings applied to food-packaging is an open approach to prepare active antibacterial packaging able to prevent the surface growth of bacteria and fungi and therefore the risk of food borne illness. In recent years there has been an increasing interest in the development of new types of effective and non toxic antimicrobial compounds which would not be considered as chemicals, but as natural ingredients, by the consumers. Among them, thymol, one of the most active antimicrobial constituents of essential oils, can be easily derived from plants (thyme and oregano) and it has been accepted by FDA and has received a positive opinion by Europe.

In this context, the preparation of thymol-doped antibacterial coatings based on a photo-crosslinkable diacrylic resin has been investigated. The antibacterial activity of thymol-doped coatings has been evaluated against Gram-positive (*Listeria monocytogenes* and *Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) bacteria. This activity is expected to depend on the thymol concentration in the coating and to its ability to move to the surface and to be released in the surrounding medium. For this purpose, release tests have been performed with the aim to give a quantitative description of the migration of thymol from the photocured diacrylic resin containing increasing amount of thymol into various media (air, water, ethanol, methanol, ethyl acetate and *n*-hexane) under different conditions.

PC 08

FAST THERMORESPONSIVE POLY(*N*-ISOPROPYLACRYLAMIDE) BASED HYDROGEL NANOCOMPOSITES WITH IMPROVED MECHANICAL PROPERTIES FOR POTENTIAL USE IN MECHANICAL ACTUATORS

K. Depa, A. Strachota, M. Šlouf

Department of Polymer Networks and Mechanical Properties, Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovský sq. 2, 162 00 Prague 6, Czech Republic
(depa@imc.cas.cz, strachota@imc.cas.cz)

Stimuli-responsive hydrogels are subject of great interest due to their unique properties and a rich field of applications. Poly(N-isopropylacrylamide) is one of the most popular thermoresponsive hydrogels. It is highly swollen at temperatures below the so-called lower critical solution temperature and shrinks at higher ones. The use of poly-NIPA hydrogels as mechanical actuators (applying force to, or moving mechanical parts in response to stimulus), on which our contribution focuses, is an attractive potential application of their volume thermo-responsivity.

In the presented contribution, we modified our previously developed nanocomposite silica-filled poly-NIPA hydrogels with very high response rates to temperature, in order to optimize them for the potential application as mechanical actuators. The aim was to obtain materials with notably higher moduli, which would be able react with strong force to external stimuli, while keeping the fast responsivity and the original volume ratio of the swollen and deswollen state. This main goal was achieved by synthesizing new highly porous gels with thicker pore walls as well as by preparation of nanocomposites with several types of nanofillers such like silica, titanium dioxide nanoparticles and hectorite clay. The amount of nanofiller in the new products was optimized. The mechanical properties, the morphology, the kinetics of the volume- and force- response to temperature and to pH will be discussed.

Acknowledgement: the authors thank the Grant Agency of the Czech Republic, Grant Nr. 106/09/1101, and the Charles University in Prague, Faculty of Science, for financial support of this work

PC 09

THE CARBONIZATION OF A CONDUCTING POLYMER, POLYANILINE, TO NITROGEN-CONTAINING ANALOGUES

M. Exnerová, Z. Rozlívková, M. Trchová, J. Stejskal

Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovsky Sq. 2, 162 06
Prague 6, Czech Republic
(exnerova@imc.cas.cz)

Polyaniline (PANI) was prepared by the oxidative polymerization of aniline. The product was carbonized in inert atmosphere at temperature up to 800 °C and for various times. The mass of the product decreased to 40–50 wt.% at temperatures above 600 °C. The progress of carbonization was followed by FTIR and Raman spectroscopies, and the carbonization at 650 °C for 1 h has been found to be optimal for complete conversion of PANI to a carbon analogue. The product retains the original globular structure of PANI [1,2] (Figure). The conductivity was low, $<10^{-10}$ S cm^{-1}, for the carbonizations below 600 °C, and increased to 10^{-4} S cm^{-1} after treatment at 800 °C. The content of nitrogen, ~10 wt.%, has not been virtually affected by the carbonization [1,2]. The presence of nitrogen in the carbonized product increases the hydrophilicity of this material. The novel form of carbon-like material can be used, *e.g.*, as a support of noble metals in catalysis.

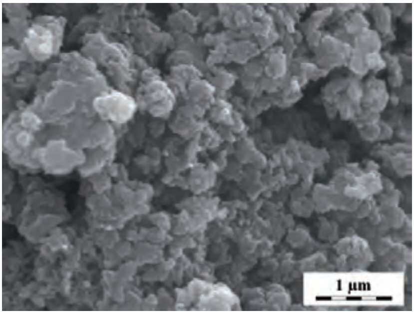


Figure. Granular morphology of PANI powder.

[1] Trchová M., Matějka, P., Brodinová J., Kalendová A., Prokeš J., Stejskal J., *Polym. Degrad. Stab.* **2006**, *91*, 114.
[2] Trchová M., Konyushenko E.N., Stejskal J., Kovářová J., Ćirić-Marjanović G., *Polym. Degrad. Stab.* **2009**, *94*, 929.

PC 10

PEO-SILICA HYBRIDS ENTRAPPING pH SENSITIVE DYES: MOLECULAR DYNAMICS AND OPTICAL RESPONSE

P. Fabbri[a], F. Pilati[a], L. Rovati[b], J. Mijovic[c]

[a]*Department of Materials and Environmental Engineering, University of Modena and Reggio Emilia, via Vignolese 905/a, 41125 Modena (Italy)*
paola.fabbri@unimore.it
[b]*Department of Information Engineering, University of Modena and Reggio Emilia, via Vignolese 905/a, 41125 Modena (Italy)*
[c]*Othmer-Jacobs Department of Chemical and Biological Engineering, Polytechnic Insitute of New York University, Six Metrotech Center, Brooklyn, 11201 New York (USA)*

Polymer-silica hybrid nanocomposites prepared by sol-gel process based on triethoxisilane-terminated poly(ethylene oxide) (PEO) chains and tetraethoxysilane as silica precursor, doped with organic pH sensitive dyes, have been prepared and their suitability for use as sensors coupled with plastic optic fibers has been evaluated. Sensors were prepared by immobilizing a drop of the hybrid materials onto the tip of a multi-mode poly(methyl methacrylate) optic fiber. The performance of the optical sensor in terms of sensitivity and response time was tested by dipping the sensor into solutions having different pH levels, ranging from 4 to 9. Optical response times were found as short as one second[1]. Since there is a paucity of information about how molecular motions affect the intensity and kinetics of the optical response of sol-gel hybrids entrapping pH sensitive dyes, a study was performed on the molecular dynamics of the PEO chains within the hybrid by broadband dielectric relaxation spectroscopy (DRS) over a wide range of frequency and temperature[2]. The very fast kinetic of the hybrid's optical response was supported on the molecular level by DRS, showing that PEO chains maintain their fast dynamics even when covalently bonded to silica domains, which decrease the self-association interactions and promote motions of polymer chain segments.

---

[1] L. Rovati, P. Fabbri and F. Pilati, Development of a low-cost pH sensor based on plastic optical fibers, (2009) IEEE Intrumentation and Measurement Technology Conference, I2MTC 2009, pp. 1662-166

[2] J. Mijovic, Y. Han, M. Sun, S. Pejanovic, Interplay of Segmental and Normal Mode Dynamics in Polymer Networks Undergoing Chemical Cross-Linking. Epoxy/Amine-Terminated Linear and Star PPO Formulations, Macromolecules 36 (2003) 4589-4602

PC 11

THE ESARA PROCESS: COMBINING NITROXIDE-MEDIATED AND RAFT CONTROLLED RADICAL POLYMERIZATION TECHNIQUES

A. Favier,[a,b,*] B. Luneau,[a] J. Vinas,[a] N. Laïssaoui,[a] D. Gigmes,[a] D. Bertin[a]

[a] UMR 6264 CNRS-Universités Aix-Marseille I, II et III, Laboratoire Chimie Provence, Equipe Chimie Radicalaire et Polymères de Spécialité, Avenue Escadrille Normandie-Niemen, 13397 Marseille, France
[b] UMR 5223 CNRS, Ingénierie des Matériaux Polymères, Université de Lyon - INSA de Lyon, 69621 Villeurbanne, France. USR3010 CNRS-ENS Lyon, Laboratoire Joliot-Curie, ENS-Lyon, 46, allée d'Italie, 69364 Lyon, France. E-mail : arnaud.favier@ens-lyon.fr

We developed a radical process abbreviated ESARA[1] for "Exchange of substituent between (macro)Alkoxyamines and (macro)RAFT Agents" allowing to combine two controlled radical polymerization (CRP) techniques, nitroxide-mediated polymerization (NMP)[2] and reversible addition-fragmentation chain transfer polymerization (RAFT)[3].

Proof of concept was first obtained with low molecular weight compounds in selected experimental conditions, opening the way for the synthesis of original control agents. Then, the process was successfully implemented at the macromolecular level. Polystyryl (PS) macroalkoxyamines were converted to the corresponding PS macro-RAFT agents using thiocarbonylthio compounds. In addition, PS macroRAFT agents were converted back to PS macroalkoxyamine after reaction with an alkoxyamine (Figure 1).

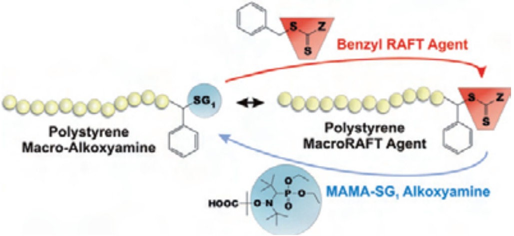


Figure 1: Conversion of PS macroalkoxyamines onto PS macroRAFT agents and vice versa

The bridge created between the two CRP techniques offers an access to a large number of well-defined polymer architectures such as block copolymers that would be difficult to obtain by only one technique.

1. Favier, A.; Luneau, B.; Vinas, J.; Laîssaoui, N.; Gigmes, D.; Bertin, D. *Macromolecules* **2009**, *42*, 5953.
2. Solomon, D. H.; Rizzardo, E.; Cacioli, P. *US 4,581,429*, **1986**.
   Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661.
3. Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *WO 98/01478*, E.I. Dupont de Nemours, **1998**.
   Corpart, P.; Charmot, D.; Biadatti, T.; Zard, S. Z.; Michelet, D. *WO 98/58974*, Rhodia, **1998**.
   Favier, A.; Charreyre, M.-T. *Macromol. Rapid Commun.* **2006**, *27*, 653.

PC 12

HYBRID MACROMOLECULAR ANTIOXIDANTS: SYNTHESIS, PROPERTIES AND APPLICATION IN MEDICINE

N. Domnina[a], S. Filippov[b], R. Khrustaleva[c], O. Sergeeva[a], E. Komarova[a], A. Lezov[d]

[a]Chemical Faculty, St. Petersburg State University, University Av. 26, 198504, Saint-Petersburg, Russia
[b]Institute of Macromolecular Chemistry AS CR,v.v.i., Heyrovský sq. 2, 162 06 Prague 6, Czech Republic
[c]Almazov Research Institute of Cardiology, St. Petersburg, 194156, Russia
[d]V.A. Fock Institute of Physics, St. Petersburg State University, Uljanovskaja ul.1, 198504, St. Petersburg, Russia

At the present time, the capability of antioxidant application for the correction of a variety of pathologies arising at the distortion of physiologic lipid peroxidation was verified both experimentally and theoretically. Now, the chemistry of phenol antioxidants reached its apex and simple variation of molecular elements does not gain a significant change of antioxidant effectiveness.

Thereby it is very perspective to synthesize hybrid macromolecular antioxidants combining in structure valuable macromolecular and antioxidant properties. New approaches have been developed for the chemical modification of such polymers[1]. Synthesized hybrid antioxidants can be varied in terms of molecular mass, the content of antioxidant and the nature of antioxidant-polymer covalent bond. For this purpose hydrophilic bio- and synthetic polymers were used together with some derivatives of sterically hindered phenols. Hydrophilic-hydrophobic balance which is sensitive to the presence of antioxidant attached to a polymer backbone allows controlling solubility in a variety of solvents. One of the ways to exploit the unique properties of the synthesized compounds is their utilization in blood plasma replacement solutions that demands deeper understanding of hybrid antioxidants behavior in aqueous systems. By means of DLS, TEM and fluorescence spectroscopy methods, the molecular properties of the hybrid antioxidants were investigated. It was established that in water single macromolecules coexist with aggregates those concentration, however, is negligible in comparison with single molecules.

On the basis of the hybrid macromolecular antioxidants new types of blood plasma replacement solutions are developed (Patent № 2273483, 2005)

The tests on laboratory animals proved that the designed hybrid macromolecular antioxidants were acting as a blood plasma substituent and as an antioxidant. The increasing of the survivorship rate by two orders of magnitude at conditions of acute hemorrhage was observed.

1. D. Arefjev , N. Domnina, E. Komarova , A. Bilibin , *E. Polymer J.*, **1999**, 35, 279-284

PC 13

QUANTIFICATION IN MALDI-TOF MS OF MODIFIED POLYMERS

V. Kolesov[a,b], Z. Walterová[a], J. Horský[a]

[a] *Department of Supramolecular Polymer Systems, Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovského sq. 2, 162 06 Prague 6, Czech Republic (horsky@imc.cas.cz)*

[b] *Participant of UNESCO/IUPAC Postgraduate Course in Polymer Science 2009-2010*

Resolution of MALDI-TOF mass spectrometry (MS) in the reflectron mode is so high that molecular weight of individual species can be determined and thus the polymer modification, e.g., at the end groups, can be verified. On the other hand, the relation between the signal intensity and the content of the compound in the sample is rather weak due to poor reproducibility and compositional and molecular-weight discrimination. It was suggested[1] that quantification can be done adding an internal standard. This would require a pure quantified compound to be available too. With polymers, only relative quantification, i.e., the ratios of component concentrations, is usually sought and any component available in a pure form can be used as an internal standard. The precursor polymer can serve as such for modified polymers.

Poly(ethylene glycol) methyl ether (MPEG) and poly(ethylene glycol) (PEG) with corresponding molecular weight distributions (PEG: M_w=1953, M_n=1950; MPEG: M_w=1953, M_n=1950) were used as a model of modified polymer and its precursor and MALDI-TOF mass spectra of their mixtures were obtained under the same conditions. Although the reproducibility of overall intensities of MPEG and PEG ($\sum I_{\mathrm{MPEG}}$ and $\sum I_{\mathrm{PEG}}$) was poor (relative standard deviation, RSD, 20-30%) the ratio $\sum I_{\mathrm{MPEG}}/\sum I_{\mathrm{PEG}}$ was significantly less scattered (RSD ~5%), indicating strong correlation between signals of components and substantiating the internal-standard concept. On the other hand, not only $\sum MI_{\mathrm{MPEG}}/\sum MI_{\mathrm{PEG}}$ differed generally from $c_{\mathrm{MPEG}}/c_{\mathrm{PEG}}$ even for averaged values but $\sum MI_{\mathrm{MPEG}}/\sum MI_{\mathrm{PEG}}$ was not proportional to $c_{\mathrm{MPEG}}/c_{\mathrm{PEG}}$, as $\sum MI_{\mathrm{MPEG}}$ was affected by c_{PEG} and *vice versa*.

Consequently, correction of MALDI-TOF MS quantification based on the proportionality assumption is not justified and in fact, may increase the error. A series of mass spectra of the sample with increasing amount of the precursor polymer added has to be measured in order to get a reliable estimate of the precursor content in the sample. The overall content of the modified polymer can be then estimated as long as there is no other component in the sample. To quantify various modifications (e.g., telechelic vs. semitelechelic one) is not possible.

[1] H. Chen, M. He J Am Soc Mass Spectrom 2005, 16, 100–106

PC 14

PHOTO AND THERMAL CROSS-LINKING REACTION AND NEGATIVE TYPE MICROPATTERN FORMATION OF POLYMERIC PHOTOBASE GENERATOR CONTAINING PHTHALIMIDO CARBAMATE GROUPS

K.H. Chae, H.I. Cho

Department of Applied Chemistry, Chonnam National University
300 Yongbong-dong, Buk-gu, Gwangju 500-757, Republic of Korea

Photobase generators (PBGs) are a group of compounds which produce amine upon irradiation. They are increasingly used in the development of new technologies such as photolithography, photo-imaging, and photoinduced cross-linking, etc. Previously, we have shown that phthalimido carbamates (PCs) are a group of PBGs, and a polymer containing PC groups can be applied as a bicolor fluorescent imaging material [1]. Since PCs are known as a thermal precursor for isocyanates, the combination of photochemical and thermal reactions of PC groups can constitute a highly sensitive system for photo-crosslinking reaction. Here, we report on the photo and thermal cross-linking reaction and negative type micropattern formation of a polymeric photobase generator containing PC groups, and the reaction mechanism for the cross-linking reaction was investigated using a model compound.

Reference

[1] K. H. Chae and Y. H. Kim, *Adv. Func. Mater.*, **2007**, *17*, 3470-3476.

PC 15

TOWARDS UNDERSTANDING OF TEMPERATURE DEPENDENT CHARGE TRANSPORT IN POLYMER FIELD-EFFECT TRANSISTORS

I.I. Fishchuk[a], A.K. Kadashchuk[a,b], H. Sitter[c], N.S. Sariciftci[c]

[a] *Institute of Physics, National Academy of Sciences of Ukraine, Prospekt Nauki 46, Kiev-03028, Ukraine, (kadash@iop.kiev.ua).*
[b] *IMEC, Kapeldreef 75, B-3001, Heverlee-Leuven, Belgium*
[c] *Johannes Kepler University of Linz, A-4040 Linz, Austria*

Temperature activated charge carrier transport in conjugated polymer films at large carrier concentrations, especially relevant in polymer-based field-effect transistors (FETs), has been thoroughly considered using a recently developed analytical model [1] assuming a Gaussian density-of-states (DOS) distribution and Miller-Abrahams jump rates. Here I present an overview of our theoretical description of the FET charge mobility in organic disordered materials [1,2]. In particular, we demonstrate that the apparent Meyer-Neldel compensation rule (MNR) is recovered regarding the temperature dependences of the charge carrier mobility upon varying the carrier concentration, but not regarding varying the width of the DOS [2]. We show that establishment of the MNR is a characteristic signature of hopping transport in a random system with variable carrier concentration. The polaron formation does not need necessarily be involved to rationalize this phenomenon. We show that this phenomenon is entirely due to the evolution of the occupational DOS profile upon increasing carrier concentration and this mechanism is specific to materials with Gaussian-shaped DOS. The suggested model provides compact analytical relations which can be readily used for the evaluation of important material parameters from experimentally accessible data on temperature dependence of the mobility in organic electronic devices. The presented model has been applied to describe experimental results on temperature dependent charge mobility measured in different conjugated polymers, as poly-thiophene and poly-phenylene-vinylene derivatives [2].

[1] I. I. Fishchuk, V. I. Arkhipov, A. Kadashchuk, P. Heremans, and H. Bässler, *Phys. Rev. B,* 76, 045210 (2007).
[2] I. I. Fishchuk, A. K. Kadashchuk, at al. *Phys. Rev. B.,* 81, 045202 (2010).

PC 16

BIOCOMPATIBLE POLY(2-OXAZOLINES) FOR BIOMEDICAL APPLICATION

J. Kronek[a], J. Lustoň[a], Z. Kroneková[a], N. Petrenčíková[a], E. Paulovičová[b],
L. Paulovičová[b], P. Farkaš[b], J. Korcová[b]

[a] *Polymer Institute, Centre of Excellence, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovak Republic, upokron@savba.sk*
[b]*Institute of Chemistry, Centre of Excellence, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, SlovakRepublic, upokron@savba.sk*

2-Oxazolines represent promising compounds for the preparation of well-defined polymers[1]. Polymers prepared from 2-alkyl-2-oxazolines with a shorter alkyl substituent are water-soluble materials. They exhibit thermosensitive properties and are used in drug and gene delivery, membrane technology or (bio)catalysis[2]. In spite of this fact, less attention has been given to the study of undesirable response of the living organisms to the treatment of this kind of polymers.

In this work, we focused on the preparation of new copolymers based on 2-oxazolines containing aromatic amino groups. Copolymers containing a free amino group were prepared by the cationic copolymerization of 2-ethyl-2-oxazoline and 2-(4-aminophenyl)-2-oxazoline. The spectral analysis of free amino groups in the resulting polymers confirmed high cooncentration of free amino groups in the macromolecule.

Cytotoxicity tests confirmed high cell viability of fibroblasts and macrophages in the presence of the copolymer containing 10 mol. % of aromatic building units (**AEOX10**). Based on in vitro immunological assays, we can conclude that the copolymer **AEOX10,** even in the concentration of 5 mg/mL, does not exert any immunosuppressive or toxic behaviour.

The prepared copolymers were used for the immobilization of proteins and polysaccharides. The novel conjugates consisting of detoxified lipopolysaccharide of Vibrio cholerae O135, 2-oxazoline copolymer and BSA (as immunogenic protein), have been prepared.

This work was supported by Project no. 2/0157/09 from the Slovak Scientific Grant Agency and Project no. 003206 from the Slovak Research and Development Agency.

REFERENCES

1. Aoi K., Okada M., *Prog. Polym. Sci.* **21,**151 (1996).
2. Adams N., Schubert U.S., *Adv. Drug Deliv. Rev.* **59**, 1504 (2007).

PC 17

EPOXY-SILICA NANOSTRUCTURED POLYMERS

M. Kubiszyn, J. Pleštil, L. Matějka

Institute of Macromolecular Chemistry AS CR, v.v.i., Department of Polymer Networks and Mechanical Properties, Heyrovsky Sq. 2,
Prague 6, 162 06, Czech Republic

We have synthesized and characterized a series of epoxy-silica hybrids with silica nanostructures in situ generated within the epoxy network. Both rubbery and glassy epoxy-amine systems have been used as an organic matrix of the organic-inorganic (O-I) nanocomposites. Silica domains were formed by hydrolytic polycondensation (sol-gel process) of alkoxysilane derivatives – tetraethoxysilane (TEOS), (3-glycidyl- oxypropyl)trimethoxysilane (GTMS) and (3-glycidyloxypropyl)methyldimethoxysilane (GMDES). We have determined structure and morphology of the prepared nanocomposites, as well as their mechanical properties. Control of the nanocomposite structure, reinforcement of the epoxy matrix and determination of the structure-properties relationships were the aim of the study.

Structure and morphology of the nanostructured O-I polymers depend to a great extent on an interphase interaction. We have controlled the interaction between phases in the epoxy-silica hybrids by adjustment of the structure of both the epoxy network and silica domains. Reaction conditions, catalysis and polymerization procedure (1 step or 2 step) during the sol-gel process determine the formed silica structure, i.e. the size and compactness of silica clusters, content of silanol groups, etc. Structure of the epoxy networks was modified by using different amine curing agents including aromatic or cycloaliphatic diamines as well as oligomeric diamines (Jeffamines) with PPO or PPO/PEO chains of various lengths.

Strong H-bond interphase interaction results in the system homogenization and an efficient reinforcement of the epoxy matrices. This is the case of the epoxy networks based on Jeffamines modified by the sol-gel process under acid catalysis promoting formation of silica nanostructures with a high content of SiOH. The nanocomposite modulus was further increased by incorporating the PPO based monoamines as dangling chains to enhance an interaction with the silica nanostructures. Coupling agents, such as GTMS and GMDES, were also used to modify the interphase interaction. The effect of both the physical (H-bond) and covalent interactions between phases as well as their combination were determined.

Acknowledgment

The authors acknowledge financial support of the Grant Agency of the Academy of Sciences of the Czech Republic (IAA 400500701).

PC 18

POLYFUNCTIONALITY COPOLYMERS OF CHITOSAN WITH ACRYLAMIDE AS FLOCCULANTS, COAGULANTS AND SORBENTS

A. Mochalova[a], I. Bodrikov[b], L. Smirnova[a], P. Tatarinov[b]

[a]Nizhny Novgorod State University. NI Lobachevsky, 603950 Nizhny Novgorod, Gagarin Av. 23, Russia, (unn@unn.ru, http://www.unn.ru)
[b]Nizhny Novgorod State Technical University. RE Alekseeva

At the present time the development of highly effective reagents for the purification of waste in the remains problematic. More than half of wastewater entering the water give the four major industries: pulp and paper petroleum refining organic synthesis industry and ferrous metallurgy. Wastewater enterprises in these sectors represent the dispersion of negatively charged particles and their removal are carried out either with coagulants or flocculants of cationic type. Variety of cationic flocculants used for these purposes is limited synthetic (co) polymers based on amines, vinylpyridines, polietilenaminov. Cleaning the coagulation is mainly with the use of inorganic chemicals. Constantly growing demands on the quality of wastewater treatment create demand for new high-performance materials broad-spectrum, combining multiple functions of floculant-sorbent, sorbent-coagulant, coagulant-floculant. Actual problem of obtaining such materials can be solved by creating hybrid products that combine the useful properties of materials of synthetic and natural origin. The aim of work was the synthesis of graft and block copolymers of chitosan with acrylamide and study of their coagulating and floculative ability to different wastewater. Graft copolymers of chitosan with acrylamide with high efficiency and the degree of grafting were obtained. Developed a new low-temperature method of synthesis of block copolymers. The structure of block copolymers was investigated. It is shown that block and graft copolymers based on chitosan possess polyfunctional properties in water purification. Compositions based on chitosan are able to serve concurrently as coagulant, floculant and adsorbent. Coagulating ability of the compositions based on it is 100 times more aluminum compounds. The degree of extraction of impurities from waste water reaches 90%. This work was supported by grant RFBR № 08-03-97051-r_povolzhe_a

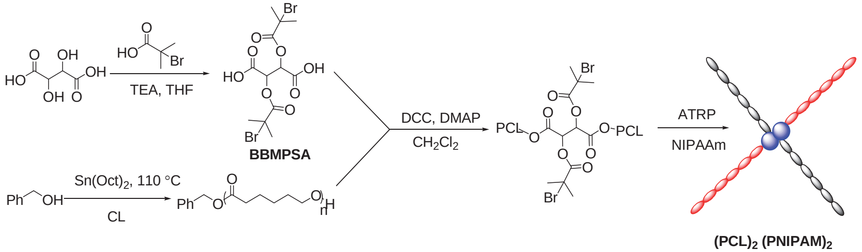
PC 19

CONTROLLED SYNTHESIS OF THERMO-RESPONSIVE AMPHIPHILIC A_2B_2 MIKTOARM STAR BLOCK COPOLYMER BY COMBINATION OF ATRP AND RING OPENING POLYMERIZATION

M.R. Nabid, S.J. Tabatabaei Rezaei, M. Abedi

Department of Chemistry, Shahid Beheshti University, G.C., P.O. Box 19396-4716
Tehran, Iran
(E-mail: m-nabid@sbu.ac.ir)

The Thermo-responsive amphiphilic A_2B_2 miktoarm star block copolymer, poly(ε-caprolactone)$_2$-poly(N-isopropylacrylamide)$_2$ [(PCL)$_2$(PNIPAM)$_2$], with controlled molecular weight and well-defined structure was successfully synthesized via combination of atom transfer radical polymerization and ring-opening polymerization (ROP) methods. Bifunctional macroinitiator (PCL)$_2$-Br$_2$ was synthesized by condensation reaction in two steps. First, 2,3-bis(2-bromo-2-methylpropanoyloxy) succinic acid (BBMPSA) was prepared by treatment of tartaric acid with α-bromoisobutyryl bromide in the presence of triethylamine as a catalyst. Second, the bifunctional macroinitiator (PCL)$_2$-Br$_2$ was obtained by condensation reaction of PCL-OH (it was synthesized by the ring-opening polymerization of ε-caprolactone in the presence of stannous (II) 2-ethylhexanoate and benzyl alcohol) and BBMPSA by using N, N'-Dicyclohexyl carbodiimide (DCC) as the efficient condensation agent. Finally, the A_2B_2 miktoarm star block copolymer (PCL)$_2$ (PNIPAM)$_2$ was prepared by ATRP polymerization of N-isopropylacrylamide using (PCL)$_2$-Br$_2$ obtained as the macro-ATRP agent. The miktoarm star block copolymer was characterized by GPC, ^{1}H-NMR, and FT-IR spectra.



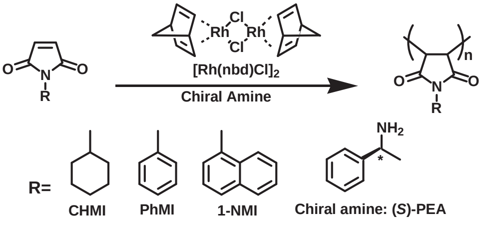
PC 20

ASYMMETRIC POLYMERIZATION OF *N*-SUBSTITUTED MALEIMIDE WITH RHODIUM CATALYST-CHIRAL AMINE COMPLEX

T. Oishi, M. Azechi, N. Toyota, K. Yamabuki, K. Onimura

Department of Applied Chemistry, Graduate School of Science and Engineering,
Yamaguchi University, 2-16-1 Tokiwadai, Ube, Yamaguchi 755-8611 Japan
(oishi@yamaguchi-u.ac.jp, http://web.cc.yamaguchi-u.ac.jp/~oishi/)

N-Substituted maleimides (RMI) are attractive monomers because their asymmetric anionic polymerizations can easily provide optically active polymers. The authors have systematically investigated on polymerizations of RMI with various *N*-substituents and chiroptical properties of the polymers. In this study, asymmetric polymerizations of RMI (substituent (R)=phenyl (PhMI), cyclohexyl (CHMI) and 1-naphthyl (1-NMI)) were performed with $[Rh(nbd)Cl]_2$ – chiral amine complex, as shown in Scheme 1. No polymerizations of RMI only with rhodium catalyst proceeded in THF, toluene, acetone and DMF, but proceeded in DMSO to give the corresponding polymers (*M*n=7300 – 19800). Varying the molar ratios of rhodium catalyst and chiral amine (*S*)-PEA, the polymerizations of RMI were carried in DMSO at 30 deg C for 24 hrs to obtain the poly(RMI) having +5.5 to -36.5 deg (in chloroform) of specific optical rotation and 1000 to 5700 of *M*n. When the ratio of rhodium catalyst and chiral amine (*S*)-PEA was 0.025, poly(PhMI) exhibited the highest negative specific rotation (-36.5 deg) in the poly(RMI). The poly(CHMI) and poly(PhMI) included about 36 to 32% of *threo*-diisotactic structures calculated by ^{13}C NMR spectra. In the presence of (*S*)-PEA the polymerization proceeded even in DMF to give the polymer with -15.5 to -17.8 deg of specific rotation and 1200 - 3500 of *M*n in 10.1 – 17.2 % yield. According to the NMR, GPC, optical rotation, and circular dichroism (CD) measurements, an asymmetric induction was caused on the polymer main chain by the polymerization using chiral amines.



Scheme 1. Asymmetric Polymerization of RMI.

PC 21

EPOXY RESINS WITH NANOSTRUCTURED REINFORCEMENTS – INORGANIC AS WELL AS ORGANIC

M. Perchacz[a], A. Strachota[a], L. Starovoytova[a], B. Mossety-Leszczak[b]

[a]*Department of polymer networks and mechanical properties, Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic*

[b]*Rzeszow University of Technology, Faculty of Chemistry, ul. Powstańców Warszawy 6, PL 35-959 Rzeszów, Poland*

(perchacz@imc.cas.cz, strachota@imc.cas.cz, mossety@prz.rzeszow.pl)

Two groups of epoxy resins with nanostructured reinforcement were prepared. As first, elastic epoxy resins based on poly(oxypropylene)-α,ω-diamine (Jeffamine "D2000") and diglycidylether of bisphenol A ("DGEBA") were synthesized. As nano-reinforcement, we incorporated the n-butyl stannoxane clusters of the formula $[(C_4H_9Sn)_{12}O_{14}(OH)_6]^{2+}$ $[^-O_3S\text{-}X]_2$, where X were ionic bonded end groups: 4-amino-phenyl in "Sn4" clusters, 3-cyclohexylamino-prop-1-yl in "Sn2", and 4-toluyl in "Sn0". The nanocomposites with "Sn2" and "Sn4" show a considerable reinforcement due to reversible aggregation of network-bonded nanofiller molecules (physical crosslinking), while the non-reactive "Sn0" – which was incorporated as inert particles - did not reinforce the matrix. Of especial interest is the ability of the stannoxanes to chemically stabilize the networks against oxidation. This occurs obviously via radical crosslinking reactions between stannoxane and matrix, as was proven by our experiments. The focus in this contribution was to find the minimum stannoxane amount necessary for efficient anti-oxidative stabilization. "Sn2" seems to be the most efficient among the stannoxanes studied.

A second group of nanostructured epoxies was prepared using a purely organic filler. The aim was to obtain strong physical networks similar to thermosets, but melting and processable at higher temperatures and also to demonstrate analogy between inorganic and organic aggregating nano-reinforcements. The epoxy resins were based on 1,2,7,8-diepoxyoctane and N,N'-dimethylhexanediamine into which aromatic mesogenic molecules were incorporated, based either on biphenyl or on oligomeric aromatic polyester. A strong physical crosslinking via aggregation of the mesogen units was observed, as well as a distinct shifting of the melting region to higher temperatures.

Acknowledgement: the authors thank the Grant Agency of the Czech Republic, Grant Nr. 106/09/1101, and the UNESCO/IUPAC Postgraduate Course in Polymer Science 2009/10, for financial support of this work.

PC 22

NMP-DESIGN AND CHARACTERISATION OF COMB-SHAPED COPOLYMERS

L. Petton, F.E. Du Prez

Polymer Chemistry Research Group (PCR), Department of Organic Chemistry,
Ghent University, Krijgslaan 281 S4-bis, B-9000 Ghent, Belgium
website: www.pcr.ugent.be, email: Lionel.Petton@UGent.be

Amphiphilic copolymers are an important class of polymers that exhibit very specific properties such as self assembly or phase behaviour. Stringent reaction conditions associated with ionic polymerisation used to be necessary in order to obtain those copolymers. However, polymer chemists now have an increasing access to macromolecular engineering ‘tools’[1], which allows for the synthesis of complex structures under mild conditions.

More specifically, the use of nitroxide mediated polymerisation[2] (NMP) in combination with the ‘grafting through’ method allows for the synthesis of controlled graft copolymers. The key advantage of NMP is the possibility to polymerise a wide range of monomers up to relatively high molecular weights (>100,000 g/mol).

The nitroxide copolymerisation of styrene with poly(ethylene oxide) (PEO) macromonomers bearing α-methylstyrene functions was carried out in solution with TEMPO or SG1[3] as nitroxide. The polymerisations were performed between 120°C and 135°C using azobisisobutyronitrile (AIBN) as initiator. The kinetics as a function of the reaction conditions was studied. The structures were then characterised by NMR, GPC and DSC. The thermal stability of the copolymers was studied by TGA. Diffusion NMR[4] (DOSY) was used to confirm the incorporation of the macromonomer into the comb-shaped copolymers.

---

[1] Matyjaszewski, K. *Prog. Polym. Sci.* **2005**, *30*, 858

[2] Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661

[3] Benoit, D.; Grimaldi, S.; Finet, J.-P.; Tordo, P.; Fontanille, M.; Gnanou, Y. *ACS Symp. Ser.* **1998**, *685*, 225

[4] McCord, E. F.; Dai, H.; Vega, A. J.; Lozada, E. U.; Vargeson, J. *Polym. Prepr.* **2003**, *44*, 291

PC 23

SYNTHESIS AND CHARACTERIZATION OF LINEAR POLYURETHANES WITH MESOGENS IN SIDE CHAINS

L. Poláková, Z. Sedláková, P. Látalová

Department of Controlled Macromolecular Synthesis, Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic (polakova@imc.cas.cz)

Organic compounds from the azobenzene-family are of great interest of our laboratory due to their possibility to create one or more liquid-crystalline (LC) states (called mesophases) in the dependence on temperature. The formation of mesophases in azobenzene-moieties is tightly connected with the ability of azobenzene to undergo the process of *cis-trans* isomerization that can be also easily induced by UV-irradiation. This feature make such materials to be promising in photonic, ferroelectric and antiferroelectric applications and in non-linear optics.

Azobenzene can be also introduced to main or side chains of a suitable polymer compound; such resulting polymer structure usually shows LC properties. The presence of the covalently bound polymer chains often leads to promising improvement of the 3D stability and mechanical properties of the origin low-molecular mesogens.

To synthesize a novel type of LC polymers, we have at first prepared polyurethanes by the polyaddition reactions of the commercially available telechelic poly(butadiene)diol (declared M_n ~ 2 600 Da, M_w/M_n ~ 1.10, functionality of terminal hydroxyl groups $f_{OH-} = 2.0$) on 1,6-hexamethylenediisocyanate with varying molar ratio of the NCO/OH groups in the feed. The obtained polymers were characterized by size-exclusion chromatography (SEC) with conventional dual RI/UV detection and with tripple RI/RALLS/DV detection, FTIR and ^{1}H NMR spectroscopies.

Prepared linear polyurethanes were subsequently modified with low-molecular LC precursors containing azobenzene mesogenic units. The synthesized azobenzene mesogens equipped with various alkoxy- substituents in *para*-position of the aromatics were grafted under radical addition reaction conditions onto double bonds of the diol incorporated in the linear polyurethane chains. The extent of the addition reactions was evaluated by SEC, elemental analysis and ^{1}H NMR spectroscopy. Thermal behavior of the low-molecular LC units and the comb-like polyurethanes with the respect to a mesophase formation was checked by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM).

PC 24

ROOM TEMPERATURE SYNTHESIS OF BOEHMITE AND CRYSTALLIZATION OF NANOPARTICLES: EFFECT OF CONCENTRATION AND ULTRASOUND

L. Rajabi [a] , A. A. Derakhshan [b], Sh. Ghorabi [a]

[a] *Department of Chemical Engineering, College of Engineering, University of Razi, Kermanshah-67149, Iran*

[b] *College of Chemistry, University of Razi, Kermanshah-67149, Iran*

In the present work, boehmite naoparticles with the size of 15-30 nm have been synthesized on addition of NaOH to the solution of $Al(NO3)3.9H2O$ as the source of aluminum. FTIR, SEM and TEM have been employed for characterization of samples. Bayerite formed by mixing the starting materials at room temperature which was immediately transformed to boehmite at that temperature. Crystallization of boehmite nanoparticles was achieved by imposing hydrothermal conditions. The size of boehmite particles obtained was strongly dependent on the concentration of Al-containing solution and also the OH/Al ratio. Among the various synthesis conditions employed, the best reaction route at room temperature was obtained. Agglomerates of the size 900 µm formed in some of the synthesis methods, the size of which was decreased to about 50 µm on concentration variations. Agglomeration mechanism and effect of ultrasonic mixing on the particle size has been discussed.

Keywords: Bayerite, boehmite naoparticles, hydrothermal conditions, Crystallization, Concentration, Ultrasound.

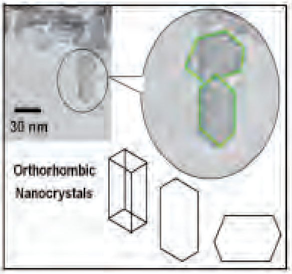


Figure: TEM image of the boehmite synthesized

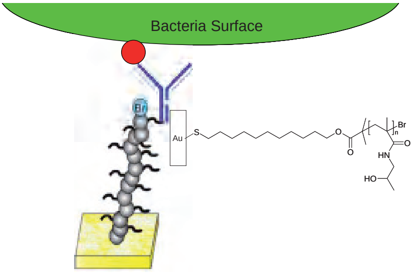
PC 25

THE APPLICATION OF POLYMER BRUSHES PREPARED BY ATOM TRANSFER RADICAL POLYMERIZATION FOR FABRICATION OF BIOSENSORS DETECTING FOOD BORNE PATHOGENS

C. Rodríguez-Emmenegger[a,b], O. Avramenko[a], E. Brynda[a], A. Bologna Alles[b]

[a]*Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic*
[b]*College of Engineering, Universidad de la Republica, Montevideo 11300, Uruguay*
(rodriguez@imc.cas.cz)

Methods for the detection of food borne pathogens in beverages and food samples are highly desired to provide early information to prevent dangerous infections. Surface plasmon resonance (SPR) biosensors offer a potential tool for detecting the contamination in real time. However, their performance is usually hampered by fouling from biological samples. Herein we present the preparation of functionalizable polymer brushes grafted from SPR sensor surface that are able to resist the fouling from milk and powdered infant formulas. Polymer brushes of methoxy and hydroxy capped olygoethyleneglycol methacryalate and 2-hydroxyethyl methacrylate (HEMA) were synthesized by well controlled surface initiated atom transfer radical polymerization. Grazing angle specular reflectance FTIR, elipsometry and contact angle were used to study the chemical composition, thickness and wettability of the polymer layers. Their fouling resistant ability in relation to their thickness was assessed by SPR. Poly(HEMA) brushes were functionalized using disuccinimidyl carbonate and dimethyl aminopyridine to covalently attach antibodies anti-*Cronobacter ssp.* SPR sensor with the above sensing layers was capable of detecting the bacteria in PBS, milk and powdered infant formula. Currently, *Cronobacter ssp* is linked with life-threating infections in neonates with case fatality rates of 50-80%.[1]



1. B. Healy, S. Cooney, S. O'Brien, C. Iversen, P. Whyte, J. Nally, J. J. Callanan and S. Fanning, *Foodborne Pathogens and Disease*, 2010, **7**, 339-350.

This research was supported by the Academy of Sciences of the Czech Republic under Contract No KAN200670701

PC 26

EVOLUTION OF THE MOLECULAR STRUCTURE OF POLYANILINE BASE DURING CARBONIZATION IN INERT ATMOSPHERE

Z. Rozlívková, M. Exnerová, M. Trchová, J. Stejskal

Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovsky Sq. 2, 162 06
Prague 6, Czech Republic
(rozlivkova@imc.cas.cz)

The carbonization of polyaniline (PANI) in inert atmosphere yields nitrogen-containing carbons. Carbonization of PANI is a simple way to prepare materials with new chemical and physical properties, which may serve in sensors, corrosion protection, catalysis, fuel cells, electrodes, or in electronics components, *etc.*

The globular morphology of PANI remained preserved even after the carbonization of PANI in air [1]. The samples had about the constant content of nitrogen, ~14 wt.%, irrespective of the processing temperature up to 800 °C, which was assigned to the formation of phenazine-like crosslinks [1] (Fig. 1). In order to increase the yield, the same approach has been used for the preparation of nitrogen-containing carbon nanotubes by the exposure of PANI nanotubes at elevated temperature up to 830 °C in a nitrogen atmosphere [2]. In the present study, PANI base has been exposed to various temperatures between 100 °C and 800 °C for various times in nitrogen atmosphere. The evolution of the molecular structure has been studied by FTIR and Raman spectroscopies. The final conversion to graphitic material has been detected.

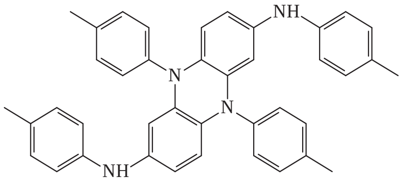


Figure 1. The chemical structure of carbonized PANI [1].

1. Trchová M., Matějka, P., Brodinová J., Kalendová A., Prokeš J., Stejskal J., *Polym. Degrad. Stab.* 2006, *91*, 114.
2. Trchová M., Konyushenko E.N., Stejskal J., Kovářová J., Ćirić-Marjanović G., *Polym. Degrad. Stab.* 2009, *94*, 929.

PC 27

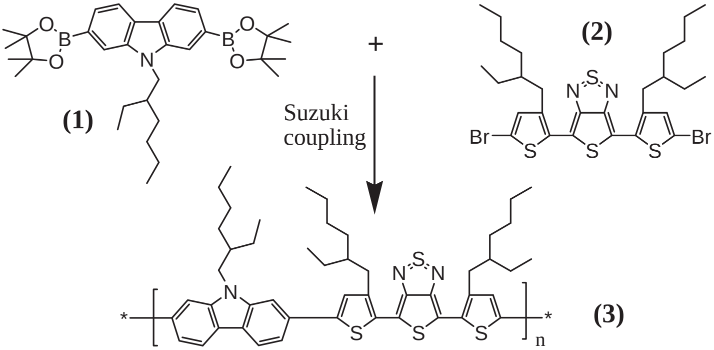
SYNTHESIS OF CONJUGATED CARBAZOLE-THIENOTHIADIAZOLE COPOLYMER FOR ORGANIC SOLAR CELLS

D. Výprachtický, V. Cimrová, I. Kmínek, P. Pavlačková

Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovský Sq. 2, 162 06
Prague 6, Czech Republic
(vyprach@imc.cas.cz, cimrova@imc.cas.cz)

Polymer solar cells are a promising alternative for harvesting energy directly from sunlight using photovoltaic technology and are considered to be an important way for solution of global energy needs using renewable sources.

The Suzuki coupling reaction was utilized for the preparation of poly{4,6-bis[3`-(2-ethylhexyl)thien-2`-yl]thieno[3,4-c][1,2,5]thiadiazole-5`,5`-diyl-*alt*-9-(2-ethyl-hexyl)carbazole-2,7-diyl} **(3)**, which is intended as a donor-acceptor conjugated polymer material for organic photovoltaics.



The syntheses of both monomers, i.e. the electron-deficient 4,6-bis[5-bromo-3-(2-ethylhexyl)thien-2-yl]thieno[3,4-c][1,2,5]thiadiazole **(2)** and the electron-rich 9-(2-ethylhexyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole **(1)** will be reported and discussed. The polymer synthesis via Suzuki C-C coupling will be reported and discussed as well.

Acknowledgement
We acknowledge the support of the Ministry of Education, Youth and Sports of the Czech Republic (grant No.1M06031).

PC 28

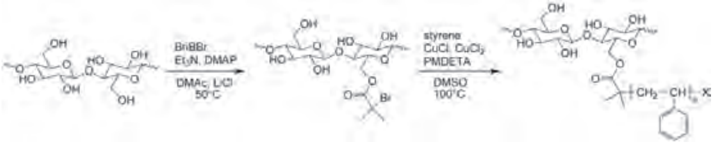
GRAFT COPOLYMERS OF CELLULOSE WITH CONTROLLED ARCHITECTURE PREPARED IN HOMOGENEOUS PHASE

V. Raus, P. Látalová, A. Šturcová, J. Dybal, J. Kříž, J. Svobodová and P. Vlček

Department of Controlled Syntheses of Macromolecules, Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic (raus@imc.cas.cz)

Grafting of cellulose by synthetic polymers represents a facile way for introduction of new properties, enhancing the range of potential application of this natural polymer. In this regard, homogeneous modifications are convenient, as they generally lead to more uniform distribution of grafts along the cellulose backbone.

Microcrystalline cellulose AVICEL PH-101 was dissolved in the N,N-dimethylacetamide/LiCl (DMAc/LiCl) solvent system. Various methods of cellulose activation, a process facilitating dissolution in DMAc/LiCl, were evaluated in terms of their influence on the efficiency and reproducibility of subsequent modification step. In this step, some of the hydroxyl groups of cellulose were acylated by 2-bromoisobutyryl bromide to yield polyfunctional macroinitiators for atom transfer radical polymerization (ATRP). Stoichiometric control of the degree of substitution was employed in order to pre-determine the grafting density of resulting cellulose copolymers. It was shown that cellulose activation methods play an important role in this esterification reaction. New modification of the solvent-exchange protocol based on the use of 1,4-dioxane as activation agent was introduced and proven to be efficient, non-destructive, and experimentally convenient method.



Scheme 1. Preparation of an ATRP macroinitiator by esterification of cellulose, and its subsequent grafting with styrene.

Prepared cellulose esters were used for initiation of polymerization of styrene and methyl methacrylate, affording series of cellulose copolymers having variable architecture and composition of the grafts.

Homogeneous reaction conditions, stoichiometric control in the preparation of macroinitiators, and ATRP grafting jointly allowed for an extensive control of copolymers architecture, i.e. density of grafting and molecular parameters of the grafts.

PC 29

SYNTHESIS OF POLY[POLY(ETHYLENE OXIDE) METHACRYLATE]-POLY(ISOBUTYLENE) BLOCK COPOLYMERS

Á. Szabó[a,b], B. Iván[a,b]

[a]Department of Polymer Chemistry and Material Science, Institute of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences, Pusztaszeri u. 59-67., H-1025 Budapest, Hungary
(szabo.akos@chemres.hu, http://www.chemres.hu/aki.polychem)
[b]Institute of Chemistry, Eötvös Loránd University, Pázmány Péter sétány 1/A., H-1117 Budapest, Hungary

In our work novel amphiphilic BAB-type block copolymers composed of hydrophobic polyisobutylene and hydrophilic poly(poly(ethylene oxide) methacrylate) segments (P(PEOMA)-*b*-PIB-*b*-P(PEOMA), Figure 1) were synthesized via combining of different quasiliving polymerization techniques.

First, 2-bromoisobutyrate telechelic polyisobutylenes were prepared using quasiliving carbocationic polymerization and subsequent chain end modification reactions.

Second, quasiliving atom transfer radical polymerizations of poly(ethylene oxide) methacrylate macromonomers were performed using the polyisobutylene macroinitiator. The reaction conditions were optimized to reach high conversion and initiator efficiency.

Finally, CBABC-type pentablock terpolymers were synthesized via quasiliving atom transfer radical polymerization of methyl methacrylate using the triblock copolymer as macroinitiator. The obtained polymer proved to be appropriate for film preparation. The resulting polymer films have good mechanical properties.

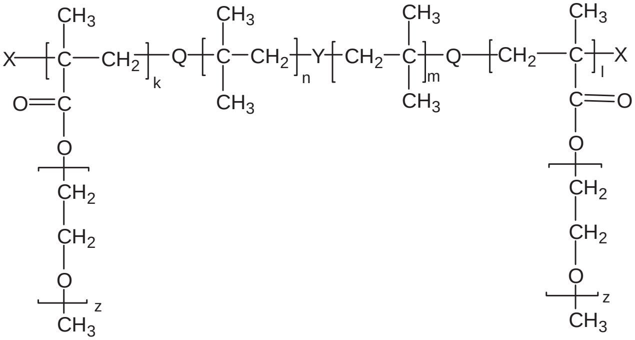


Figure 1: The structure of the P(PEOMA)-*b*-PIB-*b*-P(PEOMA) triblock copolymer

PC 30

SYNTHESIS OF WELL-DEFINED POLY-ε-CAPROLACTONE, POLY-D,L-LACTIDE AND THEIR COPOLYMERS USING TITANIUM COMPLEXES OF DIALKANOLAMINE LIGANDS

Yu.A. Piskun[a], I.V. Vasilenko[a], S.V. Kostjuk[a], K.V. Zaitsev[b]

[a] *Research Institute for Physical Chemical Problems of the Belarusian State University, 14 Leningradskaya St., 220030 Minsk, Belarus*
(vasilenkoi@bsu.by)
[b] *Chemistry Department, Moscow State University, B-234 Leninskie Gory, 119899 Moscow, Russia*

Polymers possessed biodegradable and biocompatible properties are widely used in medicine and pharmacology. The new possibilities in the regulation of degradation rate, hydrophilic-hydrophobic properties are appeared due to the synthesis of well-defined (co)polyesters by living ring-opening polymerization, which can be used as macroinitiators in the polymerization of cyclic, polar and other monomers.

Different titanium (IV) complexes with one and two dialkanolamine ligands were tested in the ring-opening polymerization of ε-caprolactone in a bulk at temperatures 40–130°C. For all polymerizations, the liner increase of molecular weight of synthesized polymers with conversion as well as a first kinetic order in monomer dependence of reaction rate were observed. The ^{1}H NMR analysis and MALDI-TOF-MS of the polymers were used to determine chain end functionality. It was found that $\mathrm{MeN[(CH_2CMe_2O)(CHMeCHPhO)]Ti(O\textit{i}Pr)_2}$ complex allowed to synthesize poly-ε-caprolactone exclusively with OH-group at the α-end and *i*PrOCO-group at the ω-end. On the contrary, two populations corresponded to α-hydroxyl-ω(carboxylic acid) poly-ε-caprolactone chains and α,ω-dihydroxyl-poly-ε-caprolactone chains were obtained in the presence of $\mathrm{[MeN(CH_2CH_2O)(CHPhCHPhO)]_2Ti}$. Taking into account these results, the former complex was investigated as catalyst for the polymerization of D,L-lactide and its copolymerization with ε-caprolactone. It was shown that these processes also proceeded in a living fashion affording well-defined high molecular weight (co)polymers. Finally, the possible polymerization mechanism of esters in the presence of titanium (IV) complexes of dialkanolamine ligands will be presented.

PC 31

CONJUGATED COPOLYMERS BASED ON THIOPHENE UNITS CARRYING OXADIAZOLE AND TRIAZOLE PENDANT GROUPS

D. Bondarev, J. Zedník, J. Vohlídal

Charles University in Prague, Faculty of Science, Department of Physical and Macromolecular Chemistry, Hlavova 2030, 128 43 Praha 2, Czech Republic (dbondarev@email.cz)

Properties of conjugated polymers can be tuned by various methods, of which the copolymerization of two or more comonomers seems to be the promising one. A conjugated polymer with potential applications in a construction of polymer light-emitting diodes (PLED) should be chemically and morphologically stable, exhibit light emission in a selected wavelength region, high photoluminescence quantum efficiency as well as good ability to accept and transport injected charge carriers. These properties are mostly affected by the chemical composition of the polymer and by the morphology of the polymer in the thin layer.

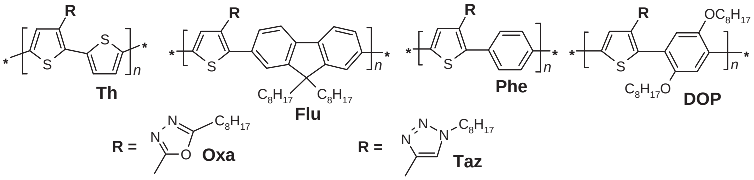


Figure 1: Structures of studied copolymers

In this contribution we report synthesis, characterization and photoluminescence properties of alternating copolymers based on Oxa- and Taz-substituted thiophene units and various arylene co-units (Th, Flu, DOP and Phe). The Oxa and Taz groups were chosen, as they are known as the hole-blocking/electron-transporting moieties which can improve charge-injection and charge-transport properties of the copolymers compared to homopolymers and copolymers of alkyl-substituted thiophenes.

PC 32

CURE BEHAVIOR OF EPOXY/ TiO_2 NANOCOMPOSITES

L. Rajabi[a], N. Rezai[b], S. Kaihani[b] , A.R. Kurdian[a]

[a]*Department of Chemical Engineering, College of Engineering,*
University of Razi, Kermanshah-67149, Iran
[b]*College of Chemistry, University of Razi, Kermanshah-67149, Iran*

The objective of this research work was to study the curing kinetics of epoxy/TiO_2 nano composites. Effect of TiO_2 nano particles on the curing kinetics of epoxy/amine resin systems has been investigated dynamically at four heating rates using TG/DTA. Genetic algorithm was successfully used to calculate the fractional extent of conversion.

The initial curing temperature and the peak exothermic temperature at four heating rates (5, 10, 15 and 20 °C/min) have not been affected considerably due to the presence and varying the amount of nano TiO_2 particles, indicating that the presence of nano TiO_2 particles neither retarded nor accelerated the cure reaction of epoxy/amine system. The ΔH values obtained, indicated the lowering of the extent of cure as a result of addition of lower amounts of TiO_2 nano particles. On superposing the S-shaped fractional conversion curves, almost equal deviation of the curves was observed from the reference curve (α at the heating rate of 20°C/min) for all the systems, suggesting the kinetic control mechanism throughout the cure reactions. The presence of nano TiO_2 particles in various amounts did not seem to have caused any considerable barrier effect on the curing process of the resin systems studied.

Keywords: Titanium dioxide nano particles; Epoxy nanocomposites; Cure kinetics

PC 33

BLOCK-GRADIENT COPOLYMERS OF STYRENE AND ACRYLIC ACID SYNTHESIZED BY NITROXIDE-MEDIATED RADICAL POLYMERIZATION

O. Borisova[a,b], L. Billon[a], M. Zaremski[b], O. Borisov[a], A. Lapp[c], B. Grassl[a]

[a]UPPA, Laboratoire de Physico-Chimie des Polymères, Pau, France
[b]Department of Polymer Science, Moscow State University, Leninskie Gory, Moscow 119191, Russia (BorisovaOlya@yandex.ru)
[c]Laboratoire Leon Brillouin/LLB CNRS/CEA Saclay, France

The ability to prepare copolymers with different architecture is one of the main advantages of controlled radical polymerization. In our work new type of copolymer structure was suggested for the preparation of “living” micelles.

Amphiphilic block-gradient copolymers consisting of hydrophilic block of polyacrylic acid and hydrophilic-hydrophobic block of gradient copolymer of acrylic acid and styrene were synthesized by nitroxide-mediated polymerization. At the first stage we polymerized acrylic acid in the presence of SG1 as a control agent and the alkoxyamine (MAMA) as an initiator. At the second stage we used two techniques to obtain different gradient profiles: semi-batch method with different rate of addition of styrene and addition of styrene in one step (batch method). The growth of molecular weight during polymerization proves controlled character of process.

All copolymers were characterized by ^{1}H NMR, size-exclusion chromatography (SEC). The structure of gradient copolymers was carried out by atomic force microscopy (AFM).

The rate constant of decomposition of "dormant" adducts: polyacrylic acid-SG1, polystyrene-SG1 and copolymer-SG1, - was determined by means of ESR.

The self-assembly of these block-gradient copolymers in water at different pH was studied by DLS and SANS. In contrast to block copolymers with the same composition which form “frozen” micelles, such copolymers can form “living” micelles with a core of gradient PS-PAA part and a corona of PAA.

This research was supported by Conseil régional d’Aquitaine and the Russian Foundation for Basic Research (project number 08-03-00269-a).

PC 34

GROWTH OF ANTIFOULING POLYMER BRUSHES AT ANY SUBSTRATE

C. Rodríguez-Emmenegger[a,b], O. Kylián[c], M. Houska[a], E. Brynda[a], J. Kousal[c], A. Bologna Alles[b], H. Biederman[c]

[a]*Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovsky Sq.2, Prague 6, Czech Republic*
[b]*College of Engineering, Universidad de la Republica, Uruguay,*
[c]*Charles University in Prague, Faculty of Mathematics and Physics Czech Republic.*
(rodriguez@imc.cas.cz)

When a synthetic surface contacts complex biological fluids, non-specific deposition of protein rapidly occurs, that can impair the surface properties and performance. Particularly blood plasma poses a great challenge for materials in contact with it. Thus, antifouling surfaces are of great interest for the development of biomaterials, and bioanalytical devices. Currently, only surfaces based on polyethyleneglycol and zwitterionic poly(carboxybetaine) brushes are able to resist the fouling from blood plasma effectively. Up to now, most techniques for preparation of those surfaces rely on grafting polymer brushes from self assembled monolayers of ω-mercaptoundecyl bromoisobutyrate grafted on metals, particularly gold, surfaces. As an alternative, polymer brushes were prepared using DOPAmine units linked to metals and metal oxides [1-2] surfaces via complexation reactions of cathecols groups. [3] Herein we present a new route for the preparation of antifouling polymer layers on any substrate. The technique consists in the deposition of amino-rich adhesion layers by magnetron sputtering of Nylon, the covalent attachment of initiators via amino groups on the surface, and the well controlled surface initiated atom transfer radical polymerization of antifouling polymer brushes. In this work, polymer brushes of hydroxyl and methoxy capped oligoethyleneglycol methacrylate and carboxybetaine acrylamide were grafted from a 15 nm thick adhesion layer functionalized with bromoisobutyrate initiator. FTIR grazing angle specular reflectance, X-rays photoelectron spectroscopy, spectroscopic ellipsometry, and contact angle were used to characterize the chemical composition, thickness and wettability of the films. Control of the thickness of the brush in the nanometric scale was achieved. The fouling resistant ability of the surfaces contacted protein solutions of human serum albumin, fibrinogen, lysozyme, and undiluted human blood plasma was assessed using surface plasmon resonance spectroscopy. Zero fouling from single protein solution was achieved and more than 90% of the fouling from blood plasma was diminished.

1. X. Fan, L. Lin, J. L. Dalsin and P. B. Messersmith, *Journal of the American Chemical Society*, 2005, **127**, 15843-15847.
2. C. Gao, G. Li, H. Xue, W. Yang, F. Zhang and S. Jiang, *Biomaterials*, 2010, **31**, 1486-1492.
3. J. H. Waite, N. H. Andersen, S. Jewhurst and C. Sun, *The Journal of Adhesion*, 2005, **81**, 297-317.

This research was supported by the Academy of Sciences of the Czech Republic under Contract No KAN200670701 and by

PC 35

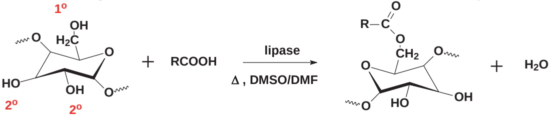
NEW ROUTE FOR BIOPOLYMER FUNCTIONALISATION. LIPASE BIOCATALYSIS IN FATTY ACID STARCH ESTERS PREPARATION

M. Lukasiewicz, S. Bednarz

Department of Food Technology; Agricultural University in Krakow
ul. Balicka 122; PL-30-149 Krakow, Poland; e-mail: rrlukasi@cyf-kr.edu.pl

Enzymatic transformation are going to play a significant role in both organic synthesis and industrial practice. Lipases are one of the examples. It is known that lipase may be employed as effective catalyst for esterification, transesterification or ester hydrolysis in organic solvents. On the other hand polysaccharides may be treated as rather water soluble polyalcohols. The esterification of starch by means of biocatalysis may allow obtaining the product with higher degree of substitution that looks very promising as an eco-friendly and biodegradable.

Presented works focuses on some detailed studies on (maize) starch esterification using carboxylic acids with different aliphatic chains carried out at different temperatures, using different solvents and substrate: enzymes ratio.



R = $-CH_3$, $-C_{10}H_{21}$, $-C_{17}H_{35}$

Obtained esters were analysed according to the degree of substitution, degradation of polymer chains and changes in topography of modified starch granules. Obtained results shows that investigated method may be used for obtaining high substituted starches; however the DS strongly depends on the aliphatic chain of the acid.

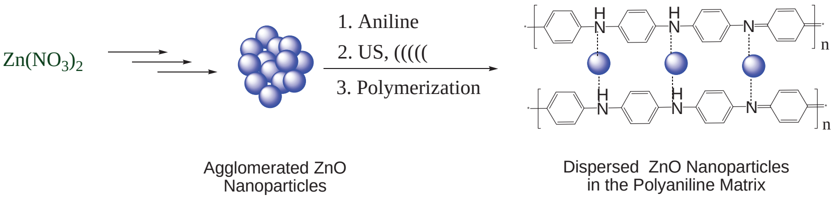
PC 36

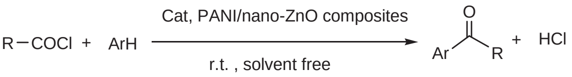
SYNTHESIS OF CONDUCTING POLYMER SUPPORTED ZINC OXIDE (ZnO) NANOPARTICLES IN AQUEOUS MEDIUM AND CATALYTIC ACTIVITY TOWARDS FRIEDEL–CRAFTS ACYLATION REACTION

M.R. Nabid, S.J. Tabatabaei Rezaei, S.Z. Hosseini

Department of Chemistry, Shahid Beheshti University, G.C., P.O. Box 19396-4716
Tehran, Iran
(E-mail: m-nabid@sbu.ac.ir)

We report here the synthesis of zinc oxide (ZnO) nanoparticles incorporated polyaniline (PANI) matrix in aqueous medium and its catalytic performance towards Friedel–Crafts acylation reactions. The acylation reactions showed that polyaniline/nano-ZnO composites was a very active catalyst and able to activate the reactant at relatively low temperature such as 298 K. Such outstanding catalytic performance should be attributed to the dispersion of ZnO in the polyaniline matrix and presence of active sites from ZnO nanoparticles. The obtained nanocatalyst was characterized by FT-IR, TGA, SEM, BET, XRD and particle size analyzer techniques. The catalyst was found to be reusable for five cycles without appreciable loss in activity.





PC 37

THERMAL AND RELAXATION BEHAVIOUR OF NANOSTRUCTURED ORGANIC-INORGANIC HYBRID MATERIALS

H. Valentová[a], Z. Sedláková[b], J. Pleštil[b], M. Neubert[a], J. Nedbal[a]

[a]*Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, CZ-182 00 Praha 8, Czech Republic*
[b]*Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic*

Polymer nanocomposites have recently attracted enormous interest not only in the field of basic research but mainly in applications using advanced technologies because they promise substantial improvement of physical properties at very low filler loadings. Very interesting class of polymer materials represent polymer/clay nanocomposites (organic-inorganic hybrids) with well defined morphology and structure controlled at the nanometric scale.

We have investigated the relaxation properties of the polymer/organically modified montmorillonite (MMT) latexes prepared via in-situ emulsion radical copolymerization. The final structure of prepared aqueous polymer dispersions were characterized by dynamic light scattering and by WAXS, SAXS, and transmission electron microscopy (TEM) [Z. Sedláková et al: Polymer Bull. Vol.63, 365-384, (2009)].

Physical properties of the prepared nanocomposites were studied by DSC, dynamic mechanical and dielectric spectroscopy in a broad temperature and frequency region. It turned out that the structure and amount of clay had practically no effect on T_g in both, polystyrene/Nanocor and polybutadiene/Nanocor systems. Simple mechanical and dielectric (with three various relaxation regions) behaviour for all measured systems was found. The position of the main transition region is practically independent on composition and corresponds to the T_g determined by DSC. All measured relaxations are only slightly affected by the amount of clay and its structure. The dynamic mechanical measurements have shown the increasing value of rubbery plateau modulus with increasing clay content – three times higher modulus in comparison to the neat latexes at 160°C. This confirms that an increase in content of inorganic exfoliated particles in polymer matrix acted as physical crosslinker.

Acknowledgements: Financial support of Ministry of Education, Youths and Sports of the Czech Republic (grants MSM 0021620835, ME09058) and of Ministry of Industry and Trade of the Czech Republic (Project FR-TI1/537) is gratefully acknowledged.

PC 38

SYNTHESIS OF STYRENE–ALKYLACRYLATES GRADIENT COPOLYMER USING TEMPO-MEDIATED POLYMERIZATION

D.I. Kalugin, M.Yu. Zaremskiy, V.B. Golubev, E.S. Garina, C.Yu. Erdyakov,
T.E. Grokhovskaya

Lomonosov Moscow State University, Chemical Faculty,
Polymers Department, Moscow, Russia
shotoden@gmail.com

To obtain gradient copolymers TEMPO-mediated copolymerization of styrene with acrylic monomers (tert-butylacrylate and methylacrylate) was performed. The influence of reaction mixture composition and concentration of accelerating additive (cumene hydroperoxide) on polymerization process, molecular-weight characteristics and copolymer composition was investigated. As the result an optimal conditions for obtaining gradient copolymers were found. Gradient structure of the copolymers obtained was confirmed with GPC and HNMR methods. Gradient copolymers obtained have been characterized with GPC, NMR, DSC and AFM. These copolymers possess very interesting properties different from those with similar structure – homogenous and non-homogenous random copolymers. It is the first example of gradient nitroxide-mediated styrene-tert-butylacrylate synthesis.

PC 39

SYNTHESIS OF BIOPOLYMERES CONTAINING α-AMINOACIDS

G. Tabak, D. Kada

Laboratory of Macromolecular Chemistry and Thioorganic ,Faculty of Chemistry
University of sciences and Technology Houari Boumediene USTHB
BP 32 El Alia Bab Ezzouar Algiers Algeria
tabakghe@yahoo.fr

New polyamides containing αaminoacids were synthetized by polycondensation. The aim of this design was to obtain biodegradable polymers. Most of them contain amide linkage as key site for biodegradation. L alanine, phenylalanine, glycine, leucine and valine were chosen as αaminoacids. In this work we describe the synthesis and characterization of a set of polyamides prepared from αaminoacids and 6 aminohexanoicacid with yields going from 31 to 62%. These water soluble polymers present a polyelectrolyte effect at concentration lower than 0,3g/dL and an intrinsic viscosity varying from 0,19 to 1 dL/g.

Semi aromatic polyamides were also obtained with good yields by polycondensation of 1,6 hexamethylene diamine and a bis amidoacid prepared by reaction of Terephtalic diacid (1éq) and the various αaminoacids (2 eq).

Their inherent viscosity vary from 0,35 to 0,60 dL/g. These polyamides were soluble in polar solvants and hence had better processability then the first set of polyamides.

The resulting polyamides were characterized by viscosity measurements, FTIR spectroscopy, UVspectroscopy , RMN^{1}H, RMN ^{13}C.

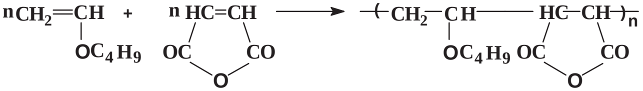
PC 40

SYNTHESIS OF ALTERNATING COPOLYMERS OF THE VINYL BUTHYL ETHER, CONTAINING STABLE NITROXIDE RADICALS

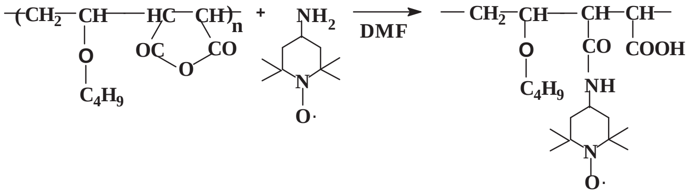
V. Konsulov[a], A. Lyapova[a], G. Petrov[a], P. Saha[b]

[a]*K. Preslavsky University of Shumen, 115 Universitetska St., 9712 Shumen, Bulgaria*
[b]*Tomas Bata University of Zlin, TGM nam.5555, 76001 Zlin, Czech Republic*

The alternating copolymers poly(vinylbuthylether-alt-maleic anhydride) were prepared by the complex-radical copolymerization of vinylbuthyl ether (VE) with maleic anhydride (MA) at the presence 2,2'-azobisisobutironitrile as an initiator in solvent (benzene, toluene, 1,4-dioxane or tetrahydrofurane) at 60-65°C:



The experiment shows that charge-transfer complex (CTC) was formed in VE→MA system. The equilibrium contstant for the donor-acceptor complexformation were determined ^{1}H NMR in dioxane K=0.125 l/mol. The monomer reactivity ratios r_1 and r_2 approximately to zero. The polymeranalogous reaction of the alternating copolymer poly(VE-alt-MA) with 4-amino-2,2,6,6-tetramethylpyperidine (A-TEMP) and 4-amino-2,2,6,6-tetramethylpyperidine-1-oxyl (A-TEMPO), also 2-, 3- or 4-amino-pyridine were investigated. New functional copolymer, containing carboxylic, adhesive alkyl group and stable TEMPO-radicals were synthesized:



The structure of the resulting functional copolymers was proved by FT-IR and EPR spectroscopy. The typical triplet signals in the EPR-spectra, also bands about 1198-1230 cm^{-1} FT-IR spectra is a proof for stable piperidil-oxide radicals in the macromolecules.

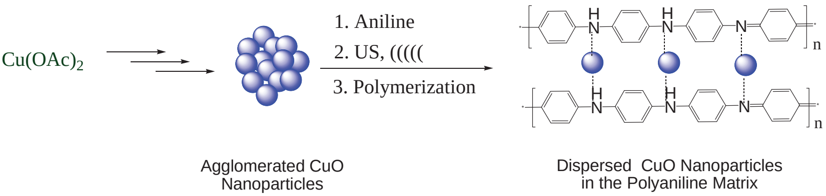
PC 41

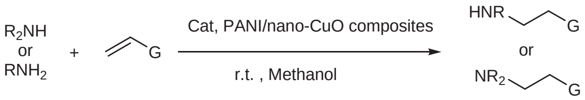
SYNTHESIS OF POLYANILINE SUPPORTED COPPER OXIDE (CuO) NANOPARTICLES AND CATALYTIC ACTIVITY TOWARDS AZA- MICHAEL REACTION

M.R. Nabid, S. J. Tabatabaei Rezaei, M. Abedi, N. Mousavi Rad

Department of Chemistry, Shahid Beheshti University, G. C. 1983963113, Tehran, Ira
(E-mail: m-nabid@sbu.ac.ir)

The synthesis of copper oxide (CuO) nanoparticles incorporated polyaniline (PANI) matrix in water and its catalytic performance towards aza-Michael reactions is reported. The aza-Michael reactions showed that polyaniline/nano-CuO composites was a very active catalyst and able to activate the reactant at room temperature. In polyaniline/nano-CuO catalyst, the fixed position of the metal on the polymer matrix may contribute to greater isolation of catalytically active sites and therefore can increase the catalytic activity. Aromatic amines do not participate effectively in the reaction. The obtained nanocatalyst was characterized by FT-IR, TGA, SEM, TEM, BET, XRD and particle size analyzer techniques. The catalyst was found to be reusable for three cycles without remarkable loss in activity.





G = electron with-drawing group

PC 42

POLY[(SULFAMATE/CARBOXYLATE)ISOPRENE-*b*-2-VINYL PYRIDINE] BLOCK POLYAMPHOLYTES: SYNTHESIS AND SOLUTION SELF-ASSEMBLY

Ch. Mantzaridis, S. Pispas

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vass. Constantinou Av., 11635 Athens, Greece
(pispas@eie.gr, http://www.eie.gr/nhrf/institutes/tpci/index-en.html)

Polyampholytes are a family of polymers that bear opposite charges within their chains. The field of polyampholytes research has drawn considerable attention,[1-4] due to their behavioral similarities with biological macromolecules (e.g. proteins).

In this work we report on the synthesis and the solution self-assembly of novel diblock polyampholytes based on poly(2-vinylpyridine), P2VP, and poly(sulfamate-carboxylate-isoprene), SCPI. The precursor copolymers for the polyampholytes, are PI-b-P2VP diblock copolymers, which were prepared by living anionic polymerization high vacuum techniques, by sequential addition of monomers. After the polymerization a two step functionalization reaction was utilized in order to produce the polyampholytes, involving the reaction of the PI block with chlorosulfonylisocyanate, followed by alkaline hydrolysis.

The behavior of the resulting polyampholytes was investigated in aqueous solutions at varying pH. Results from static, dynamic and electrophoretic light scattering, as well as fluorescence spectroscopy and AFM, indicate that at lower pH values, where P2VP is protonated, complexes are formed in the solution of the polyampholytes, due to electrostatic attraction between the oppositely charged blocks. As the solution pH shifts to higher values, these complexes seem to disassociate and the polymeric chains adopt a core-shell micellar structure with a P2VP uncharged (hydrophobic) core and a CSI-PI charged corona. The nanostructures were found to be reversible to changes in pH.

References

1.J. Bohrish et all, Adv. Polym. Sci. 2004, 165, 1.
2.A. V. Dobrynin, R. H. Colby, M. Rubinstein, J. Polym. Sci. Part B 2004, 42, 3513.
3.A. Ciferri, S. Kudaibergenov, Macromol Rapid. Commun. 2007, 28, 1953.
4.A. Ciferri, S. Kudaibergenov, Macromol Rapid. Commun. 2007, 28, 1969.

PC 43

BIODEGRADABLE MATERIALS BASED ON GRAFT AND BLOCK COPOLYMERS OF CHITOSAN AND SYNTHETIC POLYMERS: SYNTHESIS, PROPERTIES AND MECHANISM OF DEGRADATION

L. Smirnova, A. Mochalova, V. Smirnov

Nizhny Novgorod State University. NI Lobachevsky, 603950 Nizhny Novgorod,
Gagarin Av. 23, Russia
(unn@unn.ru,http://www.unn.ru)

Nowadays the elaboration of new biodegradable polymeric materials with adjusted operating characteristics and regulated time of degradation is of vital importance. One way to solve this problem it is to create mix compositions based on natural and synthetic polymers, another way is synthesis of new hybrid (co)polymers and a wide scale of vinyl monomers. The aim of this research is to study microbe resistance (fungi resistance) of 14 new polymer compositions (grafted polymers and blockcopolymers, and mixtures of homopolymers) based on polysaccharides (chitozan, cellulase, starch) and synthetic polymers (polymethacrylate (PMA), polyacrylonitrile (PAN), polyacrylamide, polyvinylchloride (PVC), polyvinyl alcohol (PVA) in relation to 11 species of micromycetes. Were the most active fungi destructors.

It has been proved that microbiological resistance of hybrid compositions do not depend on bioresistance of their polymer components. As opposite to individual polymers- PVC, ethylmethylcellulose, chitozan, starch, oxyethylcellulose-all received composition based on PVC with inclusion of natural biodegradated components turned out to be bad substratum for fungi. Compositions based on grafted polymers and blockcopolymers of chitozan with methacrylates, mixtures PVA and starch in relation to most test cultures are found easily bioutilisated. The destruction mechanism of hybrid polymers has been studied by the example of grafted polymers and block-copolymers of chitozan with PMA. We also studied changes in the physico-mechanical properties of materials and, most importantly, lower molecular weight fragments of chains of synthetic polymers. Thus, changing the structure and properties of copolymers it is posible can be obtained biodegradable polymer materials. This work was supported by project AVTSP № 2.1.2/1056.

PC 44

PREPARATION AND PROPERTIES OF HYBRID ORGANIC-INORGANIC POLY- TiO_2 BASED COMPOSITES

E.V. Salomatina[a], A.P. Aleksandrov[b], A. Afanasiev[b], N.M. Bityurin[b], T.A. Gracheva[a], A.V. Markin[a], A.E. Mochalova[a], L.A. Smirnova[a]

[a]Lobachevsky State University of Nizhny Novgorod, National Research University, University of Nizhny Novgorod, 23 Pr. Gagarina, 603950, Nizhny Novgorod, Russia (semchikov@ichem.unn.ru)
[b]Institute of Applied Physics RAS, 46 Ulianov str., 603950 Nizhny Novgorod, Russia

In recent decades, research to develop new polymer composites containing nanoparticles metals or their oxides, as well as nanostructured hybrid organic-inorganic composites has been in rapid progress. Interest to these objects is very strong because of by the transition from micro- to nanoparticles a qualitative change in many physical and chemical properties have taken place. Often this materials show complex of unique properties such as structural, catalytic and biological.

Among the hybrid organic-inorganic polymer composites particular interest represent the copolymers poly-TiO_2. Gels of poly-TiO_2 have demonstrated unique optical properties. By the UV light excitation observed reversible conversion $Ti^{4+} \leftrightarrow Ti^{3+}$ which accompanied by darkening - the enlightenment of samples. However the instability and absence of shape of this gels determine the need in synthesis of solid samples which can withstand mechanical handling. In this regard the synthesis of hybrid copolymers contained poly-TiO2 component which stabilized by polymeric matrix organic nature are promising.

In this work, two-stage method of synthesis samples has been used: at first - hydrolytic polycondensation $Ti(OPr^i)_4$ in organic monomer - hydroxyethyl methacrylate, and then by low-temperature radial polymerization of the latter. The optically transparent hybrid organic-inorganic copolymers has been obtained. The exchange reactions between the components of the reaction system have been proved. The existence of an ordered structure in the hybrid samples has been established by small-angle X-ray. This copolymers retain unique optical properties of gels of poly-TiO_2. The dependence of the optical and physical-mechanical properties of composites on the ratio of organic and inorganic components has been educed. Hybrid copolymers possess photochromic properties. The speed of transition depends on the composition of components. Laser UV irradiation of hybrid sample through the mask causes formation of diffraction grating with period 10 micron. Nanodispersion gold in hybrid copolymer with controlled size nanoparticles have been obtained. Properties of this composites have been stadied.

This work was supported by grant RFBR № 08-02-97031-r_povolzhe_a.

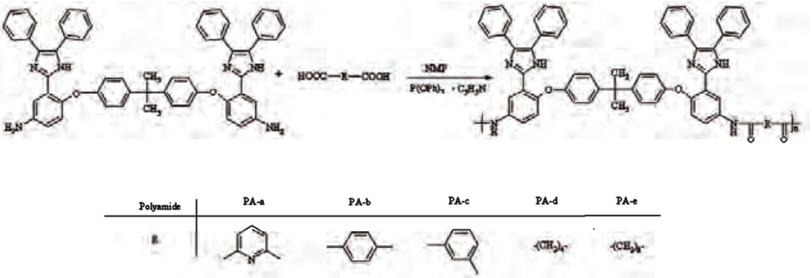
PC 45

SYNTHESIS AND IDENTIFICATION OF ORGANOSOLUBLE AND THERMALLY STABLE POLYAMIDES AND POLYIMIDES BEARING A TRIARYL IMIDAZOLE PENDENT: PHOTOPHYSICAL, CHEMILUMINESCENT AND ELECTROCHEMICAL CHARACTERIZATION WITH A MODIFIED CARBON NANOTUBE ELECTRODE

M. Ghaemy, S.M. Amini Nasab

Faculty of Chemistry, University of Mazandaran, Babolsar, Iran
E-mail address: ghaemy@umz.ac.ir

A novel monomer containing a triaryl imidazole pendent group was successfully synthesized by nucleophilic substitution of bisphenol A with 2-(2-chloro-5-nitrophenyl)-4, 5-diphenyl-1H-imidazole. A series of new polyamides (PAs) and polyimides (PIs) with inherent viscosities in the ranges of 0.95-1.2 dL/g and 0.45-0.75 dL/g was prepared by direct polycondensation of the diamine with various dicarboxylic acids and tetracarboxylic dianhydrides, respectively. All the resulting polymers were amorphous and readily soluble in many organic solvents such as NMP, DMSO, DMAc, DMF, m-cresol, and pyridine, and gave tough and flexible films by solution casting. The PAs and PIs exhibited glass-transition temperatures in the ranges of 189-252 °C and 245-254 °C, and 10% weight loss temperatures in excess of 400 °C and 500 °C, respectively, with up to 65% char yield at 600 °C in air. These polymers showed fluorescence emission in dilute solutions, with quantum yields in the range of 10-25%. The chemiluminescent activity and electrochemical oxidation of these polymers were also investigated.



Scheme 1. Synthesis of PAs.

PC 46

FUNCTIONALIZATION OF NATURAL FIBERS USING GRAFT-POLYMERIZATION TECHNIQUE

M. Chobit, V. Tokarev, S. Voronov

Lviv Polytechnic National University, Institute of Chemistry and Chemical Technologies, 12 S. Bandery Str., Lviv, 79013, Ukraine
chobit@polynet.lviv.ua

Natural cellulose-containing materials such as natural fibers, wood flour have attracted increasing attention because of their advantages as compared with other kinds of fillers: low abrasivity and cost, and especially biodegradability.

Properties of polymer composites are determined first of all by their structure and properties of interfacial layers. The design of polymer layers on phase boundary plays the significant role at obtaining polymer mixtures and filled thermoplastics. The problem of their obtaining is caused by thermodynamic incompatibility of the most polymers. The localization of compatibilizers on the phase boundary is one of the main methods of polymer compatibility increasing. From this point of view the activation of the surface of cellulose-containing materials and the formation of grafted layers of polymer macromolecules on this surface is the prospective method to obtain polymer composites with enhanced physico-mechanical properties.

We have carried out the modification of cellulose samples with peroxide oligomer containing anhydride groups. Such the method of cellulose-containing material modification is characterized by process accessibility as well as by the possibility to control the content of peroxide groups in the sample. Oligoperoxide grafting to the surface of filler allows to initiate diverse radical process: polymerization, grafting, cross-linking.

On the second stage we have performed the initiation of graft-polymerization from the surface of peroxidized cellulose. This method of functionalization allows to control chemical and physico-chemical properties of cellulose fiber surface as well as physico-mechanical properties of filled composites. The graft-polymerization of different unsaturated monomers (acrylonitrile, styrene, butyl methacrylate etc.) has been carried out in water and organic media. Polymerization kinetics has been studied using gas-liquid chromatography and dilatometric method. The presence of grafted polymer layers on cellulose surface has been proved by IR-spectroscopy, elemental analysis of modified cellulose as well as by thermo-mechanical studies of polymerization filled composites.

PC 47

PROCESS FOR PREPARATION OF CONDUCTING POLYANILINE WITH LOW MOLECULAR WEIGHT USED IN FABRICATION OF MEMBRANE ANTI-INFLAMMATORY

R. Abdelkader, A. Harrane, M. Belbachir

Université d'Oran Es-Senia, Département de Chimie, Faculté des Sciences,
BP 1524 El M'nouar 31000 Oran, Alegeria

In order to prepare conducting polyaniline composite and nanocomposite soluble in various organics solvents before and after doping , and we based on these experimentally resultants finding , the present invention relate to a new process for preparing conducting polyaniline with low molecular weight in non acid medium .

The present study provide process for preparing polyaniline or another polymer conductors such as (polypirole , polythiophene) or substituted polyaniline (o-anisidine , o-methoxy-aniline , o-toluidine …….) , wich comprises dissolving oxidizing agent (solid) slowly in mixture of catalyst and monomer (Mag-H , aniline) after 30 mn at ranging temperature (0ºc to 4º) and during 10 mn , after this time we added drop by drop 15 ml to 20 ml of water , the reaction mixture was stirred for 1h 30 mn at the optimal conditions . At the end of polymerization, we obtained the emeraldine salt /clay (PANI-ES / Mag-H). Whereas, the Mag-H it's separate by filtration because it's insoluble in the solvents in which the polymer is soluble. Eventually, the result it's black solution (polymer-solvent) , after evaporation result a black powder it's (PANI-ES) , washed several times with water and methanol , where dried at 60ºc for 48 h for characterization .The polyaniline base (PANI-EB) was obtained by deal treatment of polyaniline salt (PANI-ES) with an solution of dilute NaOH (0, 5 M) .

In a more specific aspect of the present study, the polymer is formed in non acid medium. Another embodiment, the polymer is formed by layered catalyst MMT (Mag-H).

Another embodiment the polymer is formed by oxidizing agent powder (solid) contained alkali metal salt.

In another specific aspect, the polymer is formed by intervention of deferent's reactors and water in three steps;

(a) between MMT and monomer

(b) between mixture of (MMT-monomer) and oxidizing agent

(c) between second mixture (MMT-monomer-oxidant) and water

AUTHOR INDEX

Abdelkader R. PC 47
Abedi M. PC 41, PC 19
Afanasiev A. PC 44
Alcácer L. SL 13
Aleksandrov A.P. PC 44
Amiel C. SL 03
Amini Nasab S.M. PC 45
Avramenko O. PC 25
Azechi M. PC 20

Barner-Kowollik Ch. KL 03
Barner L. KL 03
Bednarz A. PC 01
Bednarz S. PC 01, PC 35
Belbachir M. PC 47
Bertin D. PC 11
Biederman H. PC 34
Billon L. PC 33
Bityurin N.M. PC 44
Bober P. PC 02
Bodrikov I. PC 18
Bogorad N.N. SL 02
Bologna Alles A. PC 34, SL 08, PC 25
Bondarev D. PC 03, PC 31, SL 11
Bondi M. PC 07
Borisov O. PC 33
Borisova O. PC 33
Brocas A.L. SL 25, PC 05
Brynda E. PC 34, SL 08, PC 25, SL 21
Bulgakova S. PC 04, SL 05

Cacialli F. SL 13
Carlotti S. PC 05, SL 25
Cendejas G. PC 05, SL 25
Chae K.H. PC 14
Charas A. SL 13
Chernikova E. SL 09
Chmela Š. SL 04
Cho H.I. PC 14
Chobit M. PC 46
Cimrová V. SL 15, PC 27
Czernek J. PC 06

Debuigne A. SL 01
Deffieux A. PC 05, SL 25
Degli Esposti M. PC 07
Depa K. PC 08
Derakhshan A.A. PC 24
Detrembleur Ch. SL 01
Domnina N.S. SL 21, PC 12
Du Prez F.E. PC 22, SL 26, SL 06
Dybal J. PC 28

Erdyakov C.Yu. PC 38
Espeel P. SL 06
Exnerová M. PC 09, PC 26

Fabbri P. PC 10
Farinhas J. SL 13
Farkaš P. PC 16
Favier A. PC 11
Fenwick O. SL 13
Filippov A. SL 09
Filippov A.P. SL 02
Filippov S. PC 12
Fishchuk I.I. PC 15
Frackowiak S. SL 17

Ganachaud F. SL 24
Garina E.S. PC 38
Garrevoet J. SL 06

Gervais M. SL 25
Ghaemy M. PC 45
Ghorabi S. PC 24
Gigmes D. PC 11
Godjevargova Tz. SL 16
Gokmen M.T. SL 26
Golubev V.B. SL 07, SL 09, PC 38
Gorshkov N.I. SL 02
Gracheva T.A. PC 44
Grassl B. PC 33
Groeschel A. SL 27
Grokhovskaya T.E. PC 38
Grozeva Z. SL 16
Grzesik M. PC 01
Gupta D. SL 28

Harrane A. PC 47
Häussler L. SL 19
Heremans P. SL 14
Higashihara T. SL 12
Hirao A. SL 12
Horský J. PC 13
Hosseini S.Z. PC 36
Hoštálek Z. SL 18
Houska M. PC 34
Hrčková Ľ. SL 04
Hu Y. SL 22
Hurtgen M. SL 01

Ilgach D.M. SL 02
Inglis A. KL 03
Iseppi R. PC 07
Iván B. PC 29

Jehnichen D. SL 19
Jérôme Ch. SL 01
Johannsen M. SL 19
Johns M. PC 04
Junkers T. KL 03

Kada D. PC 39
Kadashchuk A. SL 14, PC 15
Kaihani S. PC 32
Kalugin D.I. PC 38
Kazantzeva I. PC 04
Khrustaleva R. PC 12
Kmínek I. SL 15, PC 27
Kolesov V. PC 13
Kollár J. SL 04
Komarova E. PC 12
Komber H. SL 19
Konsulov V. SL 16, PC 40
Korcová J. PC 16
Kostjuk S.V. SL 24, PC 30
Kousal J. PC 34
Kozlowska A. SL 17
Kozlowski M. SL 17
Krasikov V.D. SL 02
Kříž J. PC 28
Kronek J. PC 16
Kroneková Z. PC 16
Kubiszyn M. PC 17
Kurdian A.R. PC 32
Kurushina L. PC 48
Kylián O. PC 34

Laïssaoui N. PC 11
Látalová P. PC 23, PC 28
Lezov A. PC 12
Li Y. SL 22
Li Z. SL 22
Lukasiewicz M. PC 01, PC 35
Luneau B. PC 11
Lustoň J. PC 16

Lyapova A. PC 40
Ma H. SL 22
Malakhova I.I. SL 02
Mantzaridis Ch. PC 42
Markin A.V. PC 44, PC 48
Marx L. SL 03
Matějka L. PC 17
Meleshko T.K. SL 02
Merna J. SL 18
Mijovic J. PC 10
Mochalova A. PC 18, PC 43, PC 44
Morgado J. SL 13
Mossety-Leszczak B. PC 21
Mountrichas G. SL 23
Mousavi Rad N. PC 41
Mueller A.H.E. SL 27

Nabid M.R. PC 41, PC 36, PC 19
Nebhani L. KL 03
Nedbal J. PC 37
Neubert M. PC 37

Oishi T. PC 20
Onimura K. PC 20
Orlova A.P. SL 07

Paulöhrl T. KL 03
Paulovičová E. PC 16
Paulovičová L. PC 16
Pavlačková P. SL 15, PC 27
Peleška J. SL 18
Percec V. KL 01
Perchacz M. PC 21
Petrenčíková N. PC 16
Petrov G. PC 40
Petton L. PC 22
Pilati F. PC 07, PC 10
Piskun Yu.A. PC 30
Pispas S. SL 23, PC 42
Pleštil J. PC 17, PC 37
Polákova L. PC 23
Poręba R. SL 20
Prasath R.A. SL 26
Prokeš J. PC 02
Ptaszek A. PC 01
Ptaszek P. PC 01

Quirk R.P. KL 06

Raciborski I. PC 01
Rajabi L. PC 32, PC 24
Raus V. PC 28
Rezai N. PC 32
Rodríguez-Emmenegger C. PC 34, SL 08, PC 25
Rovati L. PC 10
Rozlívková Z. PC 09, PC 26
Rudowski M. SL 17

Saha P. SL 16, PC 40
Salomatina E.V. PC 44
Sariciftci N.S. PC 15
Sawamoto M. KL 02
Schols S. SL 14
Schulze U. SL 19
Sedláček J. SL 11
Sedláková Z. SL 21, PC 23, PC 37,
Semchikov Yu. SL 05, PC 48
Sergeeva O. PC 12
Shishkan O.A. SL 21
Shtilman M.I. SL 07
Simonova M.A. SL 02
Sita L.R. KL 05
Sitter H. PC 15
Sivkova R. SL 11
Šlouf M. PC 08
Smirnov V. PC 43

Smirnova L.A. PC 18, PC 43, PC 44
Špírková M. SL 20
Stamenović M.M. SL 06
Starovoytova L. PC 21
Stejskal J. PC 02, PC 09, PC 26
Strachota A. PC 08, PC 21, SL 20
Šturcová A. PC 28
Svobodová J. PC 28
Szabó Á. PC 29

Tabak G. PC 39
Tabatabaei Rezaei S.J. PC 41, PC 36, PC 19
Tacheva J. SL 16
Tatarinov P. PC 18
Tea S. SL 27
Tezuka Y. KL 04
Tokarev V. PC 46
Toselli M. PC 07
Toyota N. PC 20
Trchová M. PC 02, PC 09, PC 26
Tumakova E. SL 05

Ueda M. SL 12

Valentová H. PC 37
Van Camp W. SL 06
Vasilenko I.V. PC 30
Vinas J. PC 11
Vlasov P.S. SL 21
Vlček P. PC 28
Vohlídal J. PC 03, PC 31, SL 11
Voit B. SL 19
Volet G. SL 03
Voronov S. PC 46
Výprachtický D. SL 15, PC 27

Walterová Z. PC 13
Wang Y. SL 22
Wang Y.-Z. SL 10
Wong E.H.H. KL 03
Xin Ch. SL 07

Yagci Y. KL 07
Yakimanskiy A.V. SL 02
Yamabuki K. PC 20

Zaitsev K.V. PC 30
Zaitsev S. PC 48
Zaremskiy M. PC 33
Zaremskiy M.Yu. PC 38, SL 07
Zedník J. PC 03, PC 31, SL 11
Zhang Ch. SL 22
Zhang G. SL 23
Zhang H. SL 22
Zhao J. SL 23
Zhao Z. SL 22
Zhizhikina A. SL 05