جامعة الملك عبدالله
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King Abdullah University of
Science and Technology

FROM SYNTHESIS TO PROPERTIES AND APPLICATIONS

KAUST Polymer Conference

November 9–13, 2013
Level 0 auditorium, between Ibn Sina and Ibn Al-Haytham (buildings 2 and 3)

Organizers:
Prof. Nikos Hadjichristidis, Dean Yves Gnanou,
and Vice President for Research Jean M.J. Fréchet
With the support of the office of Competitive Research Funds (OCRF) and the KAUST Catalysis Center (KCC)

KAUST Polymer Conference
From Synthesis to Properties and Applications
9 to 13 November 2013

Saturday - November 9th 2013

Upon Arrival	Registration – check-in KAUST Inn 1, KAUST campus	
17:30 – 21:00	Dinner at Island Recreation Center for external speakers	

Sunday - November 10th

7:30 – 8:30	*Light breakfast buffet – Auditorium 0215, Between building 2 and 3*	
8:30 – 9:00	*Welcome Remarks:* Jean-Lou Chameau, KAUST, President; Ihab N. Odeh, SABIC, Global Director of Advanced Materials	
	Chairman: Nikos Hadjichristidis	
9:00 – 9:45	**Opening Lecture**	
	Krzysztof Matyjaszewski	*ATRP: From mechanism and synthesis to materials and applications*
9:45 – 10:15	Yves Gnanou	*Examples of green polymer chemistry*
10:15 – 10:45	**Coffee Break**	
10:45 – 11:25	Christopher K. Ober	*Next generation high resolution photoresists: Making patterns on the size scale of molecules*
11:25 – 12:05	Geoffrey W. Coates	*New polymers from old monomers: Advances enabled through catalyst design, discovery and applications*
12:05 – 13:30	Lunch – KAUST Diner	
	Chairman: Frank Bates	
13:30 – 14:00	Jean M.J. Fréchet	*Starting a 21st century science and technology university: The KAUST model*
14:00 – 14:40	Roland G. Larson	*Long-chain branching characterized by advanced chromatographic and rheological methods*
14:40 – 15:20	Ihab N. Odeh	*SABIC: The Success Story of Innovation*
15:20 – 15:50	**Coffee Break**	
15:50 – 16:30	Dave Haddleton	*Living radical polymer synthesis in aqueous media*
16:30 – 17:10	Dave Lohse	*Discovering useful polyolefin materials based on polymer physics principles*
17:30 – 21:00	Welcome Reception at Island Recreation Center	

Monday - November 11th

7:30 – 8:15	*Light breakfast buffet – Auditorium 0215, Between building 2 and 3*	
	Chairman: Mitsuo Sawamoto	
8:20 – 9:00	Virgil Percec	*A materials genome approach to complex systems and synthetic methods*
9:00 – 9:40	Martin Möller	*From hierarchical self-organisation towards polymer systems with functional and active properties*

9:40 – 10:20	Axel Müller	*Self-organized multicompartment nanostructures from triblock terpolymers*
10:20 – 10:50	**Coffee Break**	
10:50 – 11:30	E.W. (Bert) Meijer	*Supramolecular polymers in action: a modular approach to functionality*
11:30 – 12:10	Jimmy Mays	*Synthesis and characterization of asymmetric H-shaped polybutadienes*
12:10 – 13:30	Lunch – KAUST Diner	

Chairman: Martin Möller

13:30 – 14:10	Frank Bates	*Multiblock polymers: Panacea or Pandora's Box?*
14:10 – 14:50	Dimitris Vlassopoulos	*Rheology of entangled branched polymers with varying number and size of branches*
14:50 – 15:30	Redouane Borsali	*Sugar-based block copolymer thin films for opto- and bio-electronic devices*
15:30 – 16:00	**Coffee Break**	
16:00 – 16:30	Jean-Marie Basset	*The metathesis of alkanes and related reactions with olefins via surface organometallic chemistry*
16:30 – 17:00	Ingo Pinnau	*Polymers of intrinsic microporosity for membrane-based gas separations*
17:00 – 17:30	Luigi Cavallo	*Concepts for the stereoselective polymerization of polar monomers*
19:00 – 21:00	Dinner in Jeddah for invited speakers, Hainan restaurant, Corniche Road	

Tuesday - November 12th

8:30 – 13:00	Boat Trip for registered persons only
14:15 – 16:00	Core Labs and KAUST Museum Tour
16:30 – 18:30	Poster Section in the Library
19:00 – 21:00	Dinner – Harbor Recreation Center – Patio of the restaurant

Wednesday - November 13th

7:45 – 8:30	*Light breakfast buffet – Auditorium 0215, Between building 2 and 3*

Chairman: Dave Haddleton

8:30 – 9:00	Klaus-Viktor Peinemann	*Multicomponent polymeric membranes: from multilayer to self-assembled structures*
9:00 – 9:30	Suzanna Nunes	*Pore formation in block copolymer membranes*
9:30 – 10:00	Pierre M. Beaujuge	*Molecular design and ordering effects in π-functional polymers for efficient solar cells*
10:00 – 10:30	**Coffee Break**	
10:30 – 11:00	Niveen Khachab	*Stimuli Responsive Polymeric Capsules for Controlled Release and Imaging Applications*
11:00 – 11:30	Valentin Rodionov	*Catalysis with soluble polymers: Towards enzyme-like materials*
11:30 – 12:00	Nikos Hadjichristidis	*Well-defined polyethylenes and polyethylene-based block copolymers by anionic polymerization and polyhomologation*

12:00 – 13:30	Lunch – Working buffet in the Foyer of the Auditorium	
Chairman: Yves Gnanou		
13:30 – 14:10	Olli Ikkala	*From static self-assemblies, hierarchies and biomimetic materials to dynamic self-assemblies*
14:10-14:55	**Closing Lecture**	
	Mitsuo Sawamoto	*Metal-catalyzed living radical polymerization: From catalysts to functional polymers*
14:55 – 15:30	Yves Gnanou	*Closing Remarks*
16:00 – 17:00	KCC Tour	
18:30 – 21:00	Closing reception at Al-Marsa, Yacht Club	

Speaker Abstracts

Speaker	Title
Krzysztof Matyjaszewski	ATRP: From mechanism and synthesis to materials and applications
Yves Gnanou	Examples of green polymer chemistry
Christopher Kemper Ober	Next generation high resolution photoresists: Making patterns on the size scale of molecules
Geoffrey Coates	New polymers from old monomers: Advances enabled through catalyst design, discovery and applications
Jean M.J. Fréchet	Starting a 21st century science and technology university: The KAUST model
Ronald Larson	Long-chain branching characterized by advanced chromatographic and rheological methods
Atieh Abu Raqabah	SABIC: The Success Story of Innovation
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David Lohse	Discovering useful polyolefin materials based on polymer physics principles
Virgil Percec	A materials genome approach to complex systems and synthetic methods
Martin Möller	From hierarchical self-organisation towards polymer systems with functional and active properties
Axel Mueller	Self-organized multicompartment nanostructures from triblock terpolymers
E.W. (Bert) Meijer	Supramolecular polymers in action: a modular approach to functionality
Jimmy W. Mays	Synthesis and Characterization of Asymmetric H-Shaped Polybutadienes
Frank Bates	Multiblock Polymers: Panacea or Pandora’s Box?
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Redouane Borsali	Sugar-based block copolymer thin films for opto- and bio-electronic devices
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Klaus-Viktor Peinemann	Multicomponent Polymeric Membranes: from Multilayer to Self-assembled Structures
Suzanna Nunes	Pore formation in block copolymer membranes
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Olli Ikkala	From static self-assemblies, hierarchies and biomimetic materials to dynamic self-assemblies
Mitsuo Sawamoto	Metal-catalyzed living radical polymerization: From catalysts to functional polymers

ATRP: FROM MECHANISM AND SYNTHESIS TO MATERIALS AND APPLICATIONS

Krzysztof Matyjaszewski

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Abstract

Copper-based ATRP (atom transfer radical polymerization) catalytic systems with polydentate nitrogen-based ligands is among most efficient controlled/living radical polymerization systems.[1] Recently, by applying new initiating/catalytic systems, Cu level in ATRP was reduced to a few ppm[2]. Various reducing agents include zerovalent metals, sulfites, sugars, phenols, amines, or even amine containing monomers and ligands, radical initiators as well as electrical current and light. Similar control can be achieved with ppm of Fe-based catalysts.[3]

Control over ATRP requires its precise the mechanistic understanding. ATRP proceeds by inner sphere electron transfer process with Cu^{I}/L species as activators of alkyl halides and $X-Cu^{II}/L$ species as deactivators of growing radicals.[4]

ATRP of acrylates, methacrylates, styrenes, acrylamides, acrylonitrile and other vinyl monomers provides polymers with molecular in a large range and with designed dispersities.[5] Water can serve as solvent for many water soluble polymers and also as dispersed medium for microemulsion, miniemulsion, dispersion and suspension polymerization.[6] Block, graft, star, hyperbranched, gradient and periodic copolymers, molecular brushes and various hybrid materials as well as bioconjugates have been prepared and some new applications of ATRP polymers will be presented.

References

[1] (a) Matyjaszewski, K. Macromolecules 2012, 45, 4015-4039; (b) Matyjaszewski, K.; Spanswick, J. In: Matyjaszewski K and Möller M (eds.) Polymer Science: A Comprehensive Reference 2012, Vol. 3, 377-428; Amsterdam: Elsevier BV.

[2] (a) Tsarevsky, N. V.; Matyjaszewski, K. Chemical Reviews 2007, 107, 2270-2299; (b) Matyjaszewski, K.; Jakubowski, W.; Min, K.; Tang, W.; Huang, J.; Braunecker, W. A.; Tsarevsky, N. V. PNAS 2006, 103, 15309-15314.

[3] Wang, Y.; Zhang, Y.; Parker, B.; Matyjaszewski, K. Macromolecules 2011, 44, 4022-4025.

[4] (a) Zhong, M.; Wang, Y.; Krys, P.; Konkolewicz, D.; Matyjaszewski, K. Macromolecules 2013, 46, 3816-3827; (b) Peng, C.-H.; Zhong, M.; Wang, Y.; Kwak, Y.; Zhang, Y.; Zhu, W.; Tonge, M.; Buback, J.; Park, S.; Krys, P.; Konkolewicz, D.; Gennaro, A.; Matyjaszewski, K. Macromolecules 2013, 46, 3803-3815; (c) Wang, Y.; Zhong, M.; Zhu, W.; Peng, C.-H.; Zhang, Y.; Konkolewicz, D.; Bortolamei, N.; Isse, A. A.; Gennaro, A.; Matyjaszewski, K. Macromolecules 2013, 46, 3793-3802.

[5] Matyjaszewski, K.; Tsarevsky, N. V. Nature Chemistry 2009, 1, 276-288.

[6] (a) Simakova, A.; Averick, S. E.; Konkolewicz, D.; Matyjaszewski, K. Macromolecules 2012, 45, 6371-6379; (b) Konkolewicz, D.; Magenau, A. J. D.; Averick, S. E.; Simakova, A.; He, H.; Matyjaszewski, K. Macromolecules 2012, 45, 4461-4468.

EXAMPLES OF GREEN POLYMER CHEMISTRY

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Abstract

In an effort to advance green polymer chemistry, several groups, including ours, have pioneered the use of organocatalysts for the synthesis of miscellaneous polymers. Among environmentally friendly organic catalysts, *N*-heterocyclic carbenes (NHC) have been indeed shown to be one of the most active and versatile species that can rival metal-based catalysts and bring about a number of polymerizations: for instance, we have demonstrated that polymerizations as different as the ring-opening polymerization of heterocycles[1,2], the group transfer polymerizations of (meth)acrylates[4a,4b] and several step-growth processes[5] could be carried out under controlled conditions in the presence of these NHCs[8].

Yet, the very fact that NHCs are hardly recyclable is an issue. One way to make carbenic catalysts recyclable is to prepare polymer-supported carbenes or "polycarbenes" that could be isolated by mere filtration and recycled upon use. Poly(*N*-heterocyclic carbene)s[6], denoted poly(NHC)s, were thus readily obtained in two steps: first by free-radical polymerization of 1-vinyl-3-alkylimidazolium-type monomers, affording poly(1-vinyl-3-alkylimidazolium bis(trifluoromethanesulfonyl)imide) precursors, and second by deprotonation of the formed polymeric ionic liquids with a strong base. The resulting poly(NHC)s were then used to catalyze transesterification and benzoin condensation reactions under homogeneous conditions. But the manipulation of these poly(NHC)s turned complicated owing to their air and moisture sensitivity, which limited the number of possible catalytic cycles when used in the above mentioned condensation reactions.

One strategy was thus to "protect" the poly(NHC)s synthesized from air and moisture by reacting them with carbon dioxide (CO_2), the poly(NHC-CO_2) adducts formed being found air-stable and thermolabile. Upon heating, the zwitterionic poly(NHC-CO_2) adducts indeed released CO_2 and afforded free poly(NHC)s: through such protection-deprotection steps, polycarbenes retained excellent yields in the two organocatalyzed reactions mentioned above, even after several recycling[6].

Another strategy was to get access to air stable imidazol(in)ium hydrogen carbonates by anion metathesis of imidazol(in)ium chlorides. In solution, these compounds, (NHC(H))(HCO_3), were found to be in equilibrium with their corresponding imidazol(in)ium carboxylates, which are merely *N*-heterocyclic carbene (NHC)-CO_2 adducts. The latter actually behave as masked NHCs, or precatalysts that could be successfully used in two selected organocatalyzed reactions: namely, the benzoin condensation reaction and the ring-opening polymerization of d,l-lactide[7,8].

References

[1] Raynaud, J.; Absalon, C.; Gnanou, Y.; Taton, D. *J. Am. Chem. Soc.,* **2009**, *131*, 3201
[2] Raynaud, J.; Nzahou Ottou, W.; Gnanou, Y.; Taton, D. *Chem. Commun.* **2010**, 3203
[3] Raynaud, J.; Absalon, C.; Gnanou, Y.; Taton, D. *Macromolecules,* **2010**, *43*, 2814
[4] (a) Raynaud, J.; Ciolino, A.; Baceiredo, A.; Destarac, M.; Bonnette, F.; Kato, T.; Gnanou, Y.; Taton, D. Angew. Chem. Int. Ed., 2008, 47, 5390
(b) Raynaud, J.; Gnanou, Y.; Taton, D. Macromolecules, 2009, 42, 5996
[5] Pinaud, J.; Vijayakrishna, K.; Taton, D.; Gnanou, Y. Macromolecules, 2009, 42, 4932
[6] Pinaud, J. ;Vignolle, J. ; Gnanou, Y. ; Taton, D. Macromolecules, 2011, 44, 1900
[7] Fevre, M. ; Pinaud, J. ; Leteneur, A. ; Gnanou Y.; Vignolle, J. ; Taton, D. ; Miqueu, K. ; Sotiropoulos, J.M. J. Am. Chem. Soc. 2012, 134, 6776
[8] Fevre, M. ; Pinaud, J. ; Gnanou, Y. ; Vignolle, J. ; Taton, D. Chem. Soc. Rev. 2013,42(5), 2142.

NEXT GENERATION HIGH RESOLUTION PHOTORESISTS: MAKING PATTERNS ON THE SIZE SCALE OF MOLECULES

Christine Ouyang, Souvik Chakrabarty, Marie Krysak, M. Elizabeth Welch, Li Li, Emmanuel Giannelis, Christopher K. Ober

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Abstract

One of the great challenges given by advances in microelectronics is the ongoing need to reduce the critical dimensions of semiconductor devices. To make this possible, photolithography has evolved dramatically to the point that it now produces patterns on the length scale of the macromolecules used in photoresists. The result is a host of new approaches to the patterning of polymer systems and the need for precise characterization of their processing and properties. Block copolymers offer a means to resolve this impasse by removing part of the polymer chain to make small patterns, but like any other resist system they have distinct limitations. We have been investigating several block copolymers that have in common a functional, polar block and a readily scissionable block due to their potential for patterning by both bottom-up self-assembly and top-down lithography. A polar block such as poly(4-hydroxystyrene) is capable of exploiting all the photoresist chemistry of advanced photoresists. We have recently shown we can control the self-assembly process by solvent vapor annealing, and by choice of solvent [1]. In addition to self-assembly, approaches using molecular glass and nanoparticle photoresists will also be described [2]. The systems have the advantage that they may be used to produce arbitrarily shaped patterns in contrast to self-assembled materials and show prospects of sub-20 nm structure formation. New tools for thermal processing such as laser spike annealing enable thermal excursions above 500 °C in microsecond time regions and will be discussed [3].

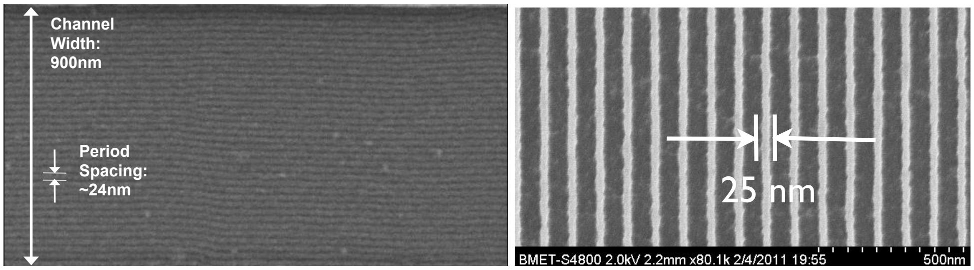

Fig. 1: Small scale features made by (left) self-assembly of block copolymers and (right) direct patterning of nanoparticle photoresists.

References

[1] Bosworth, J.K.; Sha, J.; Black, C.T.; Ober, C.K. ACS Nano, 3(7), (2009) 1761.
[2] Trikeriotis, M.; Krysak, M.; Chung, Y.S.; Ouyang, C.; Cardineau, B.; Brainard, R.; Ober, C.K.; Giannelis E.P.; Cho, K. Journal of Photopolymer Science and Technology, 25(5), (2012) 583.
[3] Jung, B.; Sha, J.; Paredes, F.; Chandhok, M.; Younkin, T.; Wiesner, U.; Ober, C.K.; Thompson, M., ACS Nano, 6(7), (2012) 5830-5836.

NEW POLYMERS FROM OLD MONOMERS: ADVANCES ENABLED THROUGH CATALYST DESIGN, DISCOVERY, AND APPLICATION

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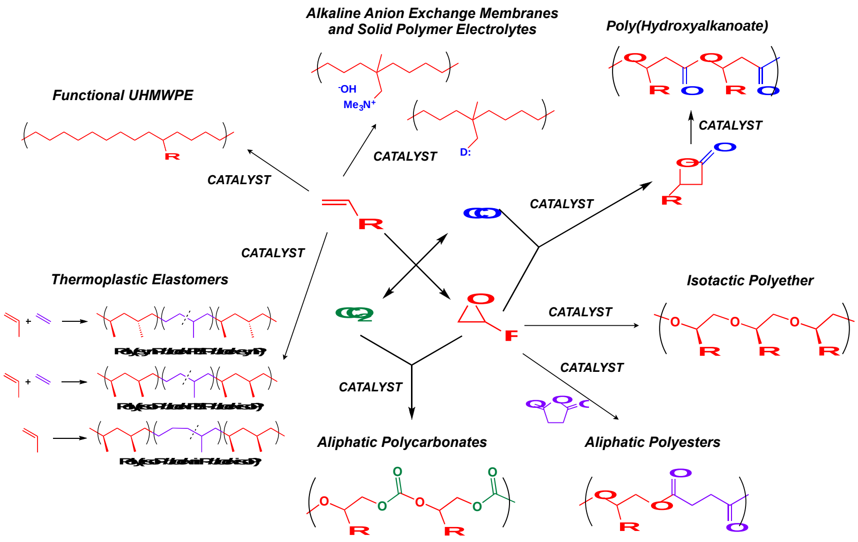
Abstract

Society depends on polymeric materials now more than at any other time in history. Although synthetic polymers are indispensable in a diverse array of applications, ranging from commodity packaging and structural materials to technologically complex biomedical and electronic devices, their synthesis and post-use fate pose important environmental challenges. The focus of our research is the development of routes to polymers with reduced environmental impact. In this work, we aim to transition from fossil fuels to renewable resources, and are developing synthetic methods that limit energy and raw-material consumption. In addition, we are designing materials that will eventually degrade into non-toxic materials, and have properties comparable to current commodity plastics. In this lecture, the development of catalytic routes to polyolefins, polyesters, polycarbonates, and polyethers will be presented.



References

[1] Noonan, K. J. T.; Hugar, K. M.; Kostalik IV, H. A.; Lobkovsky, E. B.; Abruña, H. D.; Coates, G. W. "Phosphonium Functionalized Polyethylene: A New Class of Base Stable Alkaline Anion Exchange Membranes" *J. Am. Chem. Soc.* **2012**, *134*, 18161-18164.

[2] DiCiccio, A. M.; Coates, G. W. "Ring-Opening Copolymerization of Maleic Anhydride with Epoxides: A Chain-Growth Approach to Unsaturated Polyesters" *J. Am. Chem. Soc.* **2011**, *133*, 10724–10727.

[3] Dunn, E. W.; Coates, G. W. "Carbonylative Polymerization of Propylene Oxide: A Multicatalytic Approach to the Synthesis of Poly(3-Hydroxybutyrate)" *J. Am. Chem. Soc.* **2010**, *132*, 11412–11413.

[4] Thomas, R. M.; Widger, P. C. B.; Ahmed, S. M.; Jeske, R. C.; Hirahata, W.; Lobkovsky, E. B.; Coates, G. W. "Enantioselective Epoxide Polymerization Using a Bimetallic Cobalt Catalyst" *J. Am. Chem. Soc.* **2010**, *132*, 16520-16525.

LONG-CHAIN BRANCHING CHARACTERIZED BY ADVANCED CHROMATOGRPHIC AND RHEOLOGICAL METHODS

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Abstract

To infer long-chain branching level from rheological data, we are developing theory and computer software based on the "tube model" to predict linear viscoelastic properties for mixtures of unbranched and branched polymers with arbitrary lengths and positions of branch points. To test and improve these predictive methods, model anionic polymers with one or two branches (i.e., star or H polymers) of the same or different lengths are synthesized and thoroughly characterized by both size exclusion chromatography (SEC) and temperature gradient interaction chromatography (TGIC). [1] It is found that even carefully synthesized polymers that show nearly monodisperse molecular weight distributions by SEC nevertheless contain impurities that can be identified and quantified by TGIC. While these impurities cannot be completely eliminated by fractionation, their effect on the rheology can be accounted for by theory. The accuracy of the theory is demonstrated not only by prediction of the rheology of the final product branched polymer, but also by its prediction of the rheology of blends of this polymer with linear or star-shaped "impurities" deliberately introduced. To illustrate the power of rheology to detect tiny levels of long-chain branching, we formulate a series of metallocene polymers with nearly the same weight averaged molecular weights, Mw = 115,000 and 116,400, respectively, and nearly the same polydispersity, Mw/Mn = 2.2, but with levels of long-chain branching ranging from 15 down to less than 0.3 long chain branches per million backbone atoms. We find that we can detect and predict differences in the rheology produced by less than branch per million backbone atoms, and show how to account for variations in rheological properties due to both the long-chain and short-chain branches, the latter produced by different choices of co-monomers.

SABIC: THE SUCCESS STORY OF INNOVATION

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Abstract

Saudi Basic Industries corporation (SABIC) was established in 1976 on the basis of converting petroleum-associated gas to value added products. The company has expanded remarkably to become the world second largest diversified chemical company.

This presentation gives an overview on the successful business march of SABIC with special emphasis on the critical role of technology and innovation in delivering on the company’s strategic objectives and contributing to its substantial growth. Examples of SABIC innovative solutions in polymers will be shared.

LIVING RADICAL POLYMER SYNTHESIS IN AQUEOUS MEDIA

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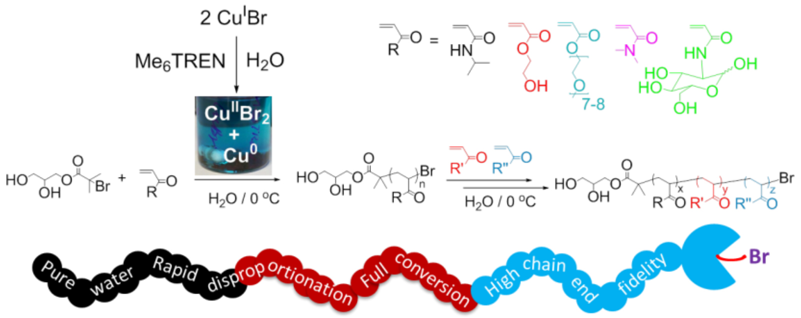
Abstract

A new approach to perform single-electron transfer living radical polymerization (SET-LRP) in water will be described [1]. The key step in this process is to allow full disproportionation of CuBr/Me6TREN to Cu(0) powder and CuBr2 in water prior to addition of both monomer and initiator. This provides an extremely powerful tool for the synthesis of functional water-soluble polymers with controlled chain length and narrow molecular weight distributions (PDI approx. 1.10), including poly- NIPAM, DMA, acrylamide, zwiterionic monomers, PEG acrylate, HEA and an acrylamido glyco monomer. The polymerizations are performed at or below ambient temperature with quantitative conversions attained in minutes. Polymers have high chain end fidelity capable of undergoing chain extensions to full conversion or multi-block copolymerization via iterative monomer addition after full conversion. Activator generated by electron transfer atom transfer radical polymerization (AGET ATRP) of NIPAM in water was also conducted as a comparison with the SET-LRP system. This shows that the addition sequence of L-ascorbic acid is crucial in determining the onset of disproportionation, or otherwise. Finally, this robust technique was applied to polymerizations under biologically relevant conditions (PBS buffer, serum) and complex ethanol/water mixtures (Tequila, beers and wines). Polymerisation is also effective in biological media, sheep serum [3].

SET-LRP has also been used for the preparation of sequence controlled glycopolymers [2] and the demonstration of their binding to the human lectin DC-SIGN. We have utilized a successful sequence controlled polymerization technique, single electron transfer living radical polymerization (SET-LRP), to polymerize glycomonomers, which are prepared by copper catalyzed azide-alkyne click (CuAAc) reaction prior to polymerization. A series of glycomonomers were prepared by reaction of 3-azidopropylacrylate (APA) and alkylated mannose, glucose and fucose, as synthesized via Fischer-Helferich glycosylation. The CuAAc reaction was performed in the presence of CuSO4 and sodium ascorbate in methanol/water mixture. The obtained sequence controlled glycopolymers were examined for their binding behaviour to DC-SIGN.



References (please use the format shown below, Arial, Font Size 10; line space 1 line)

[1] Q. Zhang, et. al. *J. Amer. Chem. Soc.* **2013**, 135(19), 7355-7363.
[2] Q. Zhang, et. al. *Angew. Chem.*, **2013,** 52(16), 4435-4439.
[3] Q. Zhang, et. al. Chem. Commun., 2013, 49, 6608-6610.

DISCOVERING USEFUL POLYOLEFIN MATERIALS BASED ON POLYMER PHYSICS PRINCIPLES

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Abstract

The likelihood of success in the development of new polymer products and processes can be greatly improved by the use of the insights derived from polymer physics. While it is possible to discover innovations simply through the correlation of data, this can be done much more quickly and with a greater chance to succeed when rigorously derived principles are employed. This is because such relations allow the researcher to solve the “inverse problem” of, for instance, how to predict the chain structure needed to produce a given property, and not just what property a given structure will have. Both the higher rate of success and the speed of development can be crucial in commercial development. I will illustrate the use of such physical principles to develop new products in several areas – controlling the miscibility and compatibility of polyolefin blends[1,2], and modifying the backbone and long-chain-branching structure of polyolefins to control their rheology and other performance properties[1,3].

References

[1] D. J. Lohse,. Journal of Macromolecular Science – Reviews 2005, 45, 289-308.
[2] D. J. Lohse, S. Datta, E. N. Kresge, Macromolecules 1991, 24, 561-566.
[3] D. J. Lohse, S. T. Milner, L. J. Fetters, M. Xenidou, N. Hadjichristidis, R. A. Mendelson, C. A. García-Franco, M. K. Lyon, Macromolecules 2002, 35, 3066-3075.

A MATERIALS GENOME APPROACH TO COMPLEX SYSTEMS AND SYNTHETIC METHODS

Virgil Percec

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Abstract

A materials genome approach to the design of programmed primary structures of self-assembling dendrons, dendrimers and other building blocks that are instructed to undergo intramolecular and intermolecular self-assembly, self-organization and the other sequences of events involved in the emergence of complex chiral functional systems will be presented. Materials genome uses the first principles commonly employed in biology to design the tertiary structure responsible for a particular function. Since the mechanism of transfer of structural information is not understood, and also according to the definition of complex systems, theoretically the primary structures responsible for the creation of complex functional systems characterized by adaptation, self-control, self-organization, emergence, self-repair and memory, cannot be designed. This lecture will first introduce the generational and deconstruction library approaches to the discovery, prediction and design of dendron and dendrimer primary structures responsible for the generation of a tertiary structure (1). Subsequently these primary structures will be used to demonstrate their synthetic capabilities by changing the chemical reactivity and chemoselectivity that subsequently will be used in the design of new concepts in polymerization methodology and nanomechanical functions (2). Additional examples of new fundamental concepts in supramolecular electronics (3), transmembrane proteins that act as Aquaporin mimics, address the role of chirality in functional materials, and provide new hypothesis for the origins of chirality will follow (4). Finally mimics of biological cell membranes and their use in biomedical applications including glycan-ligands for sugar-binding proteins (lectins), and drug delivery devices will also be discussed (5). Elaboration of novel synthetic methods via the same principles will be discussed.

References:

[1] (a) Rosen, B.M.; Wilson, C.J.; Wilson, D.A.; Peterca, M.; Imam, M.R.; Percec, V. Chem. Rev. 2009, 109, 6275-6540. (b) Rosen, B.M.; Wilson, D.A.; Wilson, C.J.; Peterca, M.; Won, B.C.; Huang, C.H.; Lipski, L.R.; Zeng. X.B.; Ungar, G.; Heiney, P.A.: Percec, V. J. Am. Chem. Soc. 2009, 131, 17500-17521. (c) Rosen, B.M.; Peterca, M.; Huang, C.H.; Zeng, X.B.; Ungar, G.; Percec, V. Angew. Chem. Int. Ed. 2010, 49, 7002-7005.

[2] (a) Percec, V.; Ahn, C.H.; Ungar, G.; Yeardley, D.J.P.; Moeller, M.; Sheiko, S.S. Nature 1998, 391, 161-164. (b) Percec, V.; Rudick, J.G.; Peterca, M; Wagner, M.; Obata, M.; Mitchell, C.M.; Cho, W.D.; Balagurusamy, V.S.K.; Heiney, P.A. J. Am. Chem. Soc. 2005, 127, 15257-15264. (c) Percec, V.; Rudick, J.G.; Peterca, M.; Heiney, P.A. J. Am. Chem. Soc. 2008, 130, 7503-7508. (d) Percec, V.; Imam, M.R.; Peterca, M.; Leowanawat, P. J. Am. Chem. Soc. 2012, 134, 4408-4420.

[3] (a) Percec, V.; Glodde, M.; Bera, T.K.; Miura, Y.; Shiyanovska, I.; Singer, K.D.; Balagurusamy, V.S.K.; Heiney, P.A.; Schnell, I.; Rapp, A.; Spiess, H.W.; Hudson, S.D.; Duan, H. Nature 2002, 419, 384-387. (b) Percec, V.; Sun, H.J.; Leowanawat, P.; Peterca, M.; Graf, R.; Spiess, H.W.; Zeng, X.B.; Ungar, G.; Heiney, P.A. J. Am. Chem. Soc. 2013, 135, 4129-4148.

[4] (a) Percec, V.; Dulcey, A.E.; Balagurusamy, V.S.K.; Miura, Y.; Smidrkal, J.; Peterca, M.; Edlund, U.; Hudson, S.D.; Heiney, P.A.; Hu, D.A.; Magonov, S.N.; Vinogradov, S.A. Nature 2004, 430, 764-768. (b) Rosen, B.M.; Peterca, M.; Morimitsu, K.; Dulcey, A.E.; Leowanawat, P.; Resmerita, A.-M.; Imam, M.R.; Percec, V. J. Am. Chem. Soc. 2011, 133, 5135-5151. (c) Roche, C.; Percec, V. Israel J. Chem. 2013, 53, 30-44.

[5] (a) Percec, V.; Wilson, D.A.; Leowanawat, P.; Wilson, C.J.; Hugh, A.D.; Kaucher, M.S.; Hammer, D.A.; Levine, D.H.; Kim, A.J.; Bates, F.S.; Davis, K.P.; Lodge, T.P.; Klein, M.L.; DeVane, RT.H.; Aqad, E.; Rosen, B.M.; Argintaru, A.O.; Sienkowska, M.J.; Rissanen, K.; Nummelin, S.; Roponen, J. Science 2010, 328, 1009-1014. (b) Peterca, M.; Percec, V. Leowanawat, P.; Bertin, A. J. Am. Chem. Soc. 2011, 133, 20507-20520. (c) Percec, V. et al. J. Am. Chem. Soc. 2013, 135, 9055-9077.

FROM HIERARCHICAL SELFORGANISATION TOWARDS POLYMER SYSTEMS WITH FUNCTIONAL AND ACTIVE PROPERTIES

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Abstract

Polymer science focuses more than ever on mastering increasingly complex molecular structures and supramolecular assemblies for advanced functionalities such as nanoprogrammed structure formation, molecular recognition, meta- and multistability, adaptive structures, shape memory properties, self-healing properties, molecular motility, molecular energy conversion systems and replication.

The work presented here focuses on the spontaneous formation of functional monolayers with a high charge carrier mobility and a high tolerance on the substrate structure. These polymers can also form single and multilayer vesicles and hierarchically ordered ultrathin films with well defined lateral nanopattern and a thickness corresponding to that of lipids. With a focus on switchability, we will present examples on switchable adhesion properties, switchable stabilisation of emulsions based on the variation of pH, temperature and solvents. Moreover we will present examples where small objects can be switched between different states by NIR-light. This way it has been possible to design a light driven microfluidic pump. For this purposes we take advantage of the fact that hydrogels and microgels respond critically to the change of pH, temperature and solvent, but also that the state of ordering of liquid crystal can be switched and used to achieve actuation. A key aspect of the light-driven molecular devices is that beyond photoisomerisation, it has been possible to effect fast and highly localized temperature jumps in a material by incorporation of suitable nanoscopic IR-antennae.

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References

[1] J. Wang, W.H. de Jeu, M. Speiser, A. Kreyes, U. Ziener, D. Magerl, M. Philipp, P. Müller-Buschbaum, M. Möller, A. Mourran, *Soft Matter* **2013**, DOI: 10.1039/C2SM27209A
[2] L. Li, M. Rosenthal, H. Zhang, J.J. Hernandez, M. Drechsler, K.H. Phan, S. Rütten, X.-M. Zhu, D.A. Ivanov, M. Möller, *Angew. Chem.*, Int. Ed. **2012**, *51*, 11616
[3] M. Defaux, F. Gholamrezaie, J. Wang,A. Kreyes, U. Ziener, D.V. Anokhin, D.A. Ivanov, A. Moser, A. Neuhold, I. Salzmann, R. Reselm, D.M. de Leeuw, S.C. J. Meskers, M. Möller, A. Mourran, Advanced Materials **2012,** *24*, 973

SELF-ORGANIZED MULTICOMPARTMENT NANOSTRUCTURES FROM TRIBLOCK TERPOLYMERS

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Compartmentalization of nanostructures is an important issue since different compartments can have different functions, e.g. loading of different payloads, such as drugs or inorganic nanoparticles. The self-assembly of triblock terpolymers (also known as ABC triblock copolymers) in solution and in the bulk are ideally suited for such a task. A typical example is polystyrene-block-polybutadiene- block-poly(methyl methacrylate) (SBM). Compartmentalization can occur either in the corona or in the core.

We have prepared corona-compartmentalized nanoparticles (Janus spheres, cylinders, or disks) by crosslinking domains in the bulk nanostructures of triblock terpolymers. These Janus micelles have superior properties as interfacial agents, as stabilizers in emulsion polymerization, as compatibilizers of polymer blends, or for the solubilization of carbon nanotubes [1,2].

We present a flexible route for the hierarchical, guided self-assembly of triblock terpolymers into multicompartment micelles (MCMs) of different shapes and sizes, simply by choosing the right solvent conditions and solvent sequences. These MCMs can have spherical shapes, like hamburgers, clovers, or footballs. However, by choosing the right terpolymers composition we ca n also trigger the shapes in a way that they reversibly form worm-like structures with alternating compartments of, e.g. polystyrene and polybutadiene, with a corona of PMMA. The different compartments can be loaded with various nanoparticles [3]. Co-assembly of AB- and ABA-style building blocks for MCMs leads to new, complex linear structures at a further level of hierarchy and allows control of the chain length up to 30 μm [4].

We also demonstrate a novel, solution-based approach to Janus micelles by crosslinking the patches on a spherical MCM. In contrast to our former bulk morphology approach this new approach for the first time provides soft Janus micelles with adjustable Janus balance, i.e. adjustable fraction of polymer chains forming one face [5]. This balance is important, e.g., for their use as dispersants of carbon nanotubes.

A new triblock terpolymer, polybutadiene-block-poly(quaternized 2-vinylpyridene)-block-poly-(methacrylic acid) (PVqMAA) forms multicompartement micelles in water with patches of an interpolyelectrolyte complex (IPEC) between the shorter cationic and a part of the longer anionic block [6]. Interaction of the PMAA corona of these micelles with block copolymer of a polycation and Poly(ethylene oxide) leads to complex core-shell-shell-corona micelles [7] or even “paddle-wheel” structures.

References

[1] A. Walther, A.H.E. Müller Soft Matter 2008, 4, 663; Chem. Rev. 2013, 113, 5194-5261
[2] A. H. Gröschel, P. D. Petrov, T. I. Löbling, M. Müllner, F. Wieberger, C. Kuttner, A. H. E. Müller Angew. Chem. Int. Ed. 2013, 52, 3602.
[3] A. H. Gröschel, F. H. Schacher, H. Schmalz, O. V. Borisov, E. B. Zhulina, A. Walther, A. H. E. Müller , Nature Commun. 2012, 3, 710.
[4] A. H. Gröschel, A. Walther, T. I. Löbling, F. H. Schacher, H. Schmalz, A. H. E. Müller, Nature 2013, published online on November 3, 2013. DOI: 10.1038/nature12610.
[5] A. H. Gröschel, A. Walther, T. I. Löbling, J. Schmelz, A. Hanisch, H. Schmalz, A. H. E. Müller J. Am. Chem. Soc. 2012, 134, 13850
[6] F. Schacher, A. Walther, A. H. E. Müller, Langmuir 2009, 25, 10962
[7] C. V. Synatschke, F. H. Schacher, M. Förtsch, M. Drechsler, A.H.E. Müller, Soft Matter 7, 1714 (2011).

SUPRAMOLECULAR POLYMERS IN ACTION; A MODULAR APPROACH TO FUNCTIONALITY

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Abstract

The intriguing prospects of molecular electronics, nanotechnology, biomaterials, and the aim to close the gap between synthetic and biological molecular systems are important ingredients to study the cooperative action of molecules in the self-assembly towards functional supramolecular systems. The design and synthesis of well-defined supramolecular polymers requires a balanced choice between covalent synthesis and the self-assembly of the fragments prepared. The current self-assembly processes are primarily controlled by solvent, temperature or concentration. For synthetic chemists, the non-covalent synthesis of these supramolecular architectures is regarded as one of the most challenging objectives in science: How far can we push chemical self-assembly and can we get control over the kinetic instabilities of the non-covalent architectures made? How can we go from self-assembly to self-organization? Where the number of different components is increasing the complexity of the system is increasing as well. Mastering this complexity is a prerequisite to achieve the challenges in creating functional systems. In the lecture we illustrate our approach using a number of examples out of our own laboratories, with the aim to come to new strategies for multi-step non-covalent synthesis of functional supramolecular systems.

In the lecture we will use functional supramolecular polymers [1] as the main component of the architecture and like to show the scope and limitations of this area of polymer science.

References

[1] T. Aida, E.W. Meijer, S.I. Stupp *Science,* **2012***, 335,* 813-817.

SYNTHESIS AND CHARACTERIZATION OF ASYMMETRIC H-SHAPED POLYBUTADIENES

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Abstract

A new type of model branched polymer, asymmetric H-shaped polybutadienes, consisting of central crossbars having various combinations of short and long arms attached to the ends of the crossbars, was synthesized using living anionic polymerization and chlorosilane linking chemistry. The linking agent 4-(dichloromethylsilyl)diphenylethylene provides selective reactivity to attach short or long arms on one side or both sides as desired. The samples were characterized thoroughly by size exclusion chromatography with light scattering detection (SEC-LS) and found to exhibit controlled molecular weights, as well as narrow polydispersity indices (PDIs of 1.01 to 1.06). Temperature gradient interaction chromatography, a method with far superior resolution as compared to SEC, also shows that these materials are well-defined, with minimal and identifiable impurities.

MULTIBLOCK POLYMERS: PANACEA OR PANDORA'S BOX?

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Abstract

Synthetic polymers impact nearly every segment of science and engineering with applications in commodity and value added plastics and elastomers, medical and separation technologies, the microelectronics industry, and a host of products that facilitate energy conversion and storage. Recent advances in polymer chemistry provide economically tractable strategies for combining two or more types of macromolecules into multiblock polymers capable of generating almost any imaginable nanoscale structure endowed with remarkable properties. However, increasing the number (n) and type (k) of discrete blocks leads to an explosion in sequencing possibilities, each capable of producing myriad morphologies, similar to the dilemma faced when designing new proteins for biological application. For example, just three sequences are possible with $n = 3$ and $k = 3$ (ABC, ACB and BAC) while $n = 4$ and $k = 3$ results in 9 distinct linear combinations. A modest increase in molecular complexity, $n = 6$ and $k = 4$, results in 300 unique possibilities. What engineering strategies are available for selecting among the multitude of choices? This lecture outlines the basic principles underpinning multiblock polymer science and engineering including modern synthetic approaches, how molecular architecture influences structure and properties, contemporary characterizations methods, and the current state of predictive statistical theories. Several commercially successful examples will be used to highlight the unparalleled opportunities for creating new materials and products presented by this emerging class of polymers.

RHEOLOGY OF ENTANGLED BRNACHED POLYMERS WITH VARYING NUMBER ANS SIZE OF BRANCHES

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Abstract

We present a systematic investigation of the rheology of model, well-characterized entangled branched polymers. We focus on the transient response of comb polymers in simple shear and uniaxial extensional flow. The combs were anionically synthesized polystyrenes and polyisoprenes, with varying number of branches (5-30) and length of branches (1 to 8 entanglements). Using a cone-partitioned plate set-up we have observed that, beyond a certain shear rate, the start-up shear stress develops an overshoot which is associated with the backbone orientation and stretching [1]. The peak strain became rate-independent and at a given rate it appeared to scale with the number of backbone entanglements when the dynamic dilution due to branches is accounted for. For longer branches, within the rate-independent region the start-up shear stress displayed a double overshoot [2]. We have associated the faster, weaker overshoot with the withdrawal of branches into the backbone tube, in line with pom-pom dynamics. We have also examined the relaxation of stress upon cessation of steady shear flow, and found that the fast relaxation rate increases with the applied shear rate. By comparing against respective data with entangled linear and star polymers, we propose that this rheological test sensitively probes the action of convected constraint release in different macromolecular architectures [3]. The strain hardening observed in uniaxial extension was found to strongly depend on the size of the (entangled) branches, as well as on the backbone segment between branches [4]. We have quantified the onset of strain hardening with a simple scaling argument accounting for dynamic dilution and the fact that, eventually a diluted comb behaves as an effective linear polymer with the same number of entanglements.

We propose that this unique data set can help improving our molecular understanding of polymer response in flow. Finally, we discuss some open experimental challenges in the field.

References

[1] F. Snijkers et al., *J.Rheol,* **2013***, 57,* 1079-1100.
[2] F. Snijkers et al., *ACS Macro Lett*., **2013**, *2*, 601-604.
[3] F. Snijkers et al., *Macromolecules*, **2013**, *46*, 5702-5713.
[4] H. Lentzakis et al., *J.Rheol*, **2013**, 57, 605-625.

SUGAR-BASED BLOCK COPOLYMER THIN FILMS FOR OPTO- AND BIO-ELECTRONIC DEVICES

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Abstract

Current knowledge in macromolecular engineering allows for the preparation of a myriad of tailored block copolymer morphologies, which play distinguished, multifaceted roles in nanoscience and technology (nanolithography, photonics, pharmaceutical, biomedical…). Such systems exhibit a remarkable ability to self-assemble into a great variety of supra-macromolecular structures both in solution (nanoparticles: micelles, vesicles...) and in solid state (thick and thin films: lamellae, cylinders, gyroids, spheres...), whose domain spacing span from few to hundred nanometers. Their final nano-organization results from the interaction between the molecular “elementary bricks” and architectures, the block composition or volume fraction and, in the case of solvent annealing, the affinity of the solvent with the different blocks. Most of those systems are, however, derived from petroleum: A resource that is being rapidly depleted!

While the self-assembly of synthetic block copolymer systems is limited today to 20 nm features (domain and size spacing) and in some cases to less than 10nm with “heavy” chemical modification, we have recently developed a versatile hierarchical self-assembly approach of novel multi-functional glycopolymer (carbohydrate) leading by self-assembly process to thin thin films shooting down to few nm-high-resolution nanoscale pattern. Such thin films found a number of key applications, spanning from next generation nanolithography, memory devices, pharmaceutical, biomedical and generally in flexible opto- and bio-electronic devices where the feature size (domain spacing) as well as its control at the 2 and 3D nanoscale level is of great importance.

The talk will focus on the design and the nanofabrication of new hybrid nano-organized thin films made from bio-sourced macromolecules (oligo or polysaccharides) for potential applications in “green” flexible electronics. Recent results will be presented on the self-assemblies of sugar-based block copolymer leading to ultra-thin films (sub-10nm resolution) for next generation of flexible opto- and bio-electronic devices.

References

[1] Giacomelli, C., Schmidt, V., Aissou, K. and Borsali, Langmuir 2010, 26, 15734-15744
[2] K. Aissou, I. Otsuka, C. Rochas, S. Fort, S. Halila, & R. Borsali Langmuir, 2011, 27(7), 4098-4103
[3] L.C. Porto, K. Aissou, C. Giacomelli, T. Baron, C. Rochas,.P. Armes, A.L. Lewis, V. Soldi & R. Borsali Macromolecules, 2011, 44(7), 2240-2244
[4] Aissou, K.; R. Borsali, Fort, S.; Halila,T. Baron, Patent (CNRS) 2010, World Extension 2011,
[5] Cushen, JD; Otsuka, I; Bates, CM; Halila, S; Fort, S; Rochas, C; Easley, JA; Rausch, EL; Thio, A; Borsali, R; Willson, CG; Ellison, CJ ACS NANO, 2012, 6, 4 ,3424-3433
[6] Otsuka, I ; Tallegas, S; Sakai, Y; Rochas, C; Halila, S; Fort, S; Bsiesy, A; Baron, T; Borsali, R Nanoscale 2013, 5, 7, 2637-2641
[7] Otsuka, I; Isono, T; Rochas, C; Halila, S; Fort, S; Satoh, T; Kakuchi, T; Borsali, R ACS Macro Letters 2013, 1,12, 1379-1382

THE METATHESIS OF ALKANES AND RELATED REACTIONS WITH OLEFINS VIA SURFACE ORGANOMETALLIC CHEMISTRY

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Abstract

"Surface Organometallic Chemistry" (SOMC) leads to a predictive and conceptual approach of heterogeneous catalysis. The accuracy of the grafting directly onto the surfaces of oxides and not at a remote distance from the surface, has been made possible thanks to the number of physical and chemical tools to prepare surface "single sites". Because these species are directly bonded to the surface they are relevant to the understanding of heterogeneous catalysis. The synthesis and characterization of these species, allowed us to discover and or predict new catalytic reactions derived from alkane or olefin metathesis:

- Metathesis of alkanes (with Tantalum and Tungsten hydrides)
- Methane-olysis of alkanes (with Tantalum hydrides)
- Coupling of methane to ethane and hydrogen (with Tungsten hydrides)
- Hydrometathesis of olefins (with Tantalum hydrides)
- Direct transformation of ethylene to propylene (with Tungsten hydrides)

It has also been possible to obtain extremely high activity in the field of:

- Olefin metathesis
- Olefin polymerization
- Alkyne metathesis

It has also been possible to cleave di-nitrogen on an isolated tantalum atom at the surface of silica.

References

[1] Modern Surface Organometallic Chemistry, Jean -Marie Basset, Rinaldo Psaro, Dominique Roberto et Renato Ugo (Editor), (Wiley) (2009)

[2] Development of the first well-defined tungsten oxo alkyl derivatives supported on silica by SOMC: towards a model of WO3/SiO2 olefin metathesis catalyst , Mazoyer, E; Merle, N; de Mallmann, A, et al., Chem. Comm., 46,(2010) 8944-8946

[3] "Hydro-metathesis" of olefins: A Catalytic Reaction Using a Bifunctional Single-Site Tantalum Hydride Catalyst Supported on Fibrous Silica (KCC-1) Nanospheres , Polshettiwar, V; Thivolle-Cazat, J; Taoufik, M; Basset J.M., Angew. Chem. Int. Ed. Eng., 50(2011) 2747-2751

[4] Revisiting the Metathesis of C-13-Monolabeled Ethane , Maury, O; Lefort, L; Vidal, V, et al., Organometallics 29(2010) 6612-6614

[5] A well-defined silica-supported aluminium alkyl through an unprecedented, consecutive two-step protonolysis-alkyl transfer mechanism , Pelletier, J; Espinas, J; Vu, N, et al., Chem. Comm., 47(2011) 2979-2981

[6] Non-oxidative coupling reaction of methane to ethane and hydrogen catalyzed by the silica-supported tantalum hydride: ([triple bond]SiO)2Ta-H. , Soulivong, D.; Norsic, S.; Taoufik, M.; Coperet, C.; Thivolle-Cazat, J.; Chakka, S.; Basset, J.-M., J Am Chem Soc, (2008), 130, (15), 5044-5.

[7] Direct transformation of ethylene into propylene catalyzed by a tungsten hydride supported on alumina: trifunctional single-site catalysis. , Taoufik, M.; Le Roux, E.; Thivolle-Cazat, J.; Basset, J.-M., Angew. Chem. Int. Ed. Eng., (2007), 46, (38), 7202-7205.

[8] Dinitrogen Dissociation on an Isolated Surface Tantalum Atom. , Avenier, P.; Taoufik, M.; Lesage, A.; Solans-Monfort, X.; Baudouin, A.; De Mallmann, A.; Veyre, L.; Basset, J. M.; Eisenstein, O.; Emsley, L.; Quadrelli, E. A., Science (2007), 317, (5841), 1056-1060.

POLYMERS OF INTRINSIC MICROPOROSITY FOR MEMBRANE-BASED GAS SEPARATIONS

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Abstract

High-performance polymeric gas separation membranes have important applications in hydrogen recovery, natural gas purification, on-site nitrogen production from air as well as carbon dioxide capture/separation. Ideal membranes should be both highly permeable and selective. However, there is an inherent trade-off between permeability (P) and selectivity (α), as illustrated by the Robeson upper-bound relationship that is frequently updated according to the performance of state-of-the-art membranes [1]. Rational molecular design of solution-processable polymeric materials is the key to creating new membranes with superior gas separation properties. To enhance gas permeability, an effective strategy is to introduce intrinsic micropores into highly rigid, glassy polymers that can increase both gas solubility and gas diffusivity. Polymers with intrinsic microporosity have been known since the development of di-substituted polyacetylenes in the 1980s [2]. These highly rigid glassy polymers contain alternating double bonds in the main chain and bulky side-chain substituents that prevent efficient chain packing, leading to high free volume. As a result, they exhibit the following general properties: (i) extremely high gas permeability and low selectivity for separation of small permanent gases; (ii) extremely high organic vapor permeability and high organic-vapor/permanent-gas selectivity; (iii) blocking of permanent gases by preferential sorption of condensable organic vapors in gas mixture permeation experiments; (iv) negative activation energy of permeation (e.g. increase in permeability with decreasing temperature); and (v) very high BET surface area (up to 1000 m2/g). Specifically, microporous poly(1-trimethylsilyl-1-propyne) (PTMSP) exhibits the highest gas- and organic vapor permeabilities of all known glassy polymers to date [3]. In addition, PTMSP shows the highest mixture organic-vapor/permanent-gas selectivities of all currently existing polymers.

Recently, a new class of polymers of intrinsic microporosity (PIMs) was reported [4]. These materials contain contorted ladder-like backbones consisting of spiro-centers and fused dioxane rings that prevent close polymer chain packing. The ladder-type PIMs exhibit excellent gas separation performance because their molecular structure gives rise to remarkable microporosity in a suitable pore size range of 6−10 Å, combining high permeability with moderate selectivity for separation of permanent gases, such as O2/N2 and CO2/N2.

In this study, a newly designed diamine monomer, 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5'-diamino-6,6'-diol, was successfully used to synthesize two types of spiro-based polyimides for membrane-based gas separation applications. The novel polymers integrate significant microporosity and polar hydroxyl groups, showing the combined features of polymers of intrinsic microporosity (PIMs) and functional polyimides (PIs) [5].

References

[1] L.M. Robeson, *J. Membr. Sci.,* **2008**, *320,* 390-400.
[2] T. Masuda, Y. Iguchi, B.Z. Tang, T. Higashimura, *Polymer,* **1988**, *29*, 2041-2049.
[3] K. Nagai, T. Masuda, T. Nakagawa, B.D. Freeman, I. Pinnau, *Prog. Polym. Sci.*, **2001**, *26*, 721-798.
[4] P.M. Budd, B.S. Ghanem, S. Makhseed, N.B. McKeown, K.J. Msayib, C.E. Tettershall, *Chem. Comm.*, **2004**, 230-231.
[5] X. Ma, R. Swaidan, Y. Belmabkhout, Y.H. Zhu, E. Litwiller, M. Jouiad, I. Pinnau, Y. Han, *Macromolecules*, *45*, **2012**, 3841-3849.

CONCEPTS FOR THE STEREOSELECTIVE POLYMERIZATION OF POLAR MONOMERS

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Abstract

The regularity of stereocenters in a macromolecule can profoundly affect the macroscopic material properties. This is illustrated most impressively by isotactic polypropylene, produced on the 10^6 tons/year scale, basically using heterogeneous $MgCl_2/TiCl_4$ based catalysts. The development of well defined homogeneous catalysts for non-polar olefins polymerization has dominated the last 20 years, and has allowed to develop a highly detailed knowledge of the key parameters leading to polymers with the desired macromolecular architecture, in terms of molecular mass and stereoregularity. In the last years, the challenge has been shifted to develop a similar control over the polymerization of polar monomers to highly stereoregular polymers with high molecular mass.[1,2]

In this contribution we will present the current mechanistic understanding in the stereoselective polymerization of monomers of the acrylate family. The focus will be on the successful polymerization of methylmethacrylate to highly iso and syndiotactic PMMA by early transition metal cataysts,[3,4] and on the challenges still open in the stereoselctive polymerization of methacrylate by late transition metal catalysts.[5] Finally, a short insight will be given on the mechanism of the stereoselective polymerization of propylene oxide by bimetallic catalysts.[6]

References

[1] A. Nakamura, S. Ito, K. Nozaki, Chem. Rev., 2009, 109, 5251.
[2] E. Y.-X. Chen Chem. Rev., 2009, 109, 5157.
[3] L. Caporaso, J. G. Budrìa, L. Cavallo, J. Am. Chem. Soc., 2006, 128, 16649
[4] Y. Zhang, Y. Ning, L. Caporaso, L. Cavallo, E. Y.-X. Chen, J. Am. Chem. Soc., 2010, 132, 2695.
[5] B. Neuwald, L. Caporaso, L. Cavallo, S. Mecking, J. Am. Chem. Soc., 2013, 135, 1026.
[6] S. M. Ahmed, A. Poater, M. I. Childers, P. C. B. Widger, A. M. LaPointe, E. B. Lobkovsky, G. W. Coates, L. Cavallo, submitted

MULTICOMPONENT POLYMERIC MEMBRANES: FROM MULTILAYER TO SELF-ASSEMBLED STRUCTURES

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Abstract

The majority of todays commercial polymeric membranes are composite sructures. A simple example is a non-selective porous support covered by a thin selective layer of a different polymer. But in other cases a multilayer membrane can be more than just the sum of its different layers. A composite membrane built from two non-sective layers might surprisingly show a high selectivity [1]. Several examples will be shown in this lecture. Polymers can be laminated or they can be mixed forming homogeneous or heterogeneous blends. Different polymers can be covalently linked forming block copolymers. A well-known multiblock copolymer for membrane application is Pebax™, which consists of polyamide and polythylene oxide blocks. Pebax™ is one one of the best commercial polymers for separation of polar gases like hydrogen sulfide, carbon dioxide or water water from inert gases. It can be easily produced into high-flux composite membranes with very thin layers [2]. A more defined multiblock copolymer designed for membrane applications is the pentablock polymer poly(t-butylstyrene-*b*-hydrogenated isoprene-*b*-sulfonated styrene-*b*-hydrogenated isoprene-*b*-t-butylstyrene) commerzialised under the trade name Nexar™ by Kraton Performance Polymers, Inc. When cast from solution this polymer self-assembles into non-equilibrium morphologies with interconnected sulfonated styrene microdomains leading to very high water vapor permeability [3]. The self-assembly of diblock copolymers into non-equilibrium morphogies can result in interesting and often unexpected asymmetric membrane structures. Our work in this field was focused on the combination of macrophase separation by non-solvent precipitation and microphase separation by self-assembly. This process is fast and can easily be up-scaled [4]. Examples with diblocks containing polyvinylpyridine, polyethylene glycol and polyacrylic acid will be shown. Potential technical applications will be discussed.

References

[1] S. Shishatskiy, S Nistor, C. Popa, S. P. Nunes, K.-V. Peinemann, Advanced Eng. Mat., 2006, 8, 390-397
[2] W. Yave, A. Car, J. Wind, K.-V. Peinemann, Nanotechnology, 2010, 21, 395303-395310
[3] J.-H. Choi, C. L. Willis, K. I. Winey, J. Membr, Sci., 2012, 394-395, 169-174
[4] S. P. Nunes, A. R. Behzad, K.-V. Peinemann, J. Mater. Res., 2013, (first view article), DOI: 10.1557/jmr.2013.253

PORE FORMATION IN BLOCK COPOLYMER MEMBRANES

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Abstract

We have demonstrated that, by combining block copolymers self-assembly and macroscopic phase separation, membranes with very regular pores and high porosity can be manufactured [1,2]. The mechanism of pore formation has been investigated and understood with help of cryo-electron microscopy[3], small angle x-ray scattering analysis (SAXS)[4] and time-resolved grazing incidence SAXS. By choosing solvent mixtures with selective thermodynamic interaction with the polymer blocks, a micelle supra-molecular assembly is tailored with hexagonal, body-centered cubic or lamellar order. When the solution layer is immersed in water, a solvent-non-solvent exchange drastically decreases the quality of the polymer interaction with the surrounded environment. The micelles become strongly interlinked and the order is frozen, forming regular pores between them. The same order observed in solution is reflected in the final pore distribution. The process was simulated with dissipative particle dynamics modeling. The structure formation can be induced or controlled by addition of complexing agents, which lead to σ or π bonding (metal coordination) or hydrogen bonding (organic complexing agents)[5]. They affect the solution rheology and the final pore morphology (Figure 1).

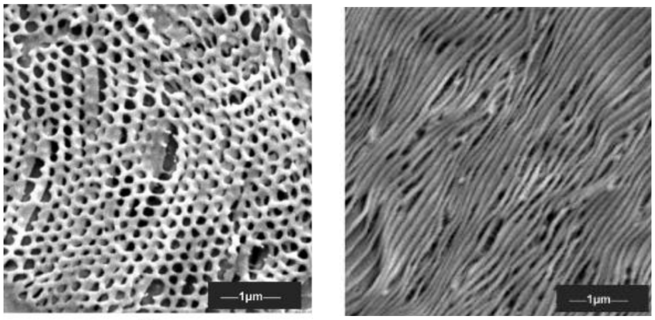

Figure 1. PS-b-P4VP membranes formed in the presence of 9-anthracenemethanol (*left)* and 1,3,5-tris(4'carboxy(1,1-biphenyl)-4-yl) benzene (*right*)

References

[1] S. P. Nunes et al., *Macromolecules*, **2010**, *43*, 8079-8085.
[2] S. P. Nunes et al., *ACS Nano* **2011**, *5*, 3516-3522.
[3] S.P. Nunes et al. Langmuir **2011**, *27*, 10184-10190.
[4] D. S. Marques et al. *Soft Matter* **2013**, 9, 5557-5564.
[5] P. Madhavan et al. *Appl. Materials Interfaces* **2013**, 5, 7152-7159.

MOLECULAR DESIGN AND ORDERING EFFECTS IN π-FUNCTIONAL POLYMERS FOR EFFICIENT SOLAR CELLS

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Abstract

Among *Organic Electronics*, solution-processable π-conjugated polymers are proving particularly promising in bulk-heterojunction (BHJ) solar cells with fullerene acceptors such as PCBM.[1] In the past few years, we have found that varying the size and branching of solubilizing side-chains in π-conjugated polymers impacts their self-assembling properties in thin-films. Beyond film-forming properties, nanoscale ordering in the active layer governs material and device performance. For example, in poly(benzo[1,2-*b*:4,5-*b'*]dithiophene–thieno[3,4-*c*]pyrrole-4,6-dione) (PBDTTPD), TPD substituents of various size and branching impart distinct molecular packing distances (i.e., π–π stacking and lamellar spacing),[2] varying degrees of nanostructural order in thin films,[2] and preferential backbone orientation relative to the device substrate.[3] These structural variations have been found to correlate with solar cell performance, with power conversion efficiencies ranging from 4% to 8.5%.[2-4] (Fig. 1) In parallel, discrete backbone modifications in PBDTTPD can impact polymer backbone conformations and self-assembly,[5] and various ring-substituents directly appended to the π-conjugated backbone can induce morphological effects and may also affect polymer performance in BHJ solar cells with PCBM.[6] Our recent developments emphasize how systematic structure-property relationship studies impact the design of efficient polymer donors for BHJ solar cell applications.

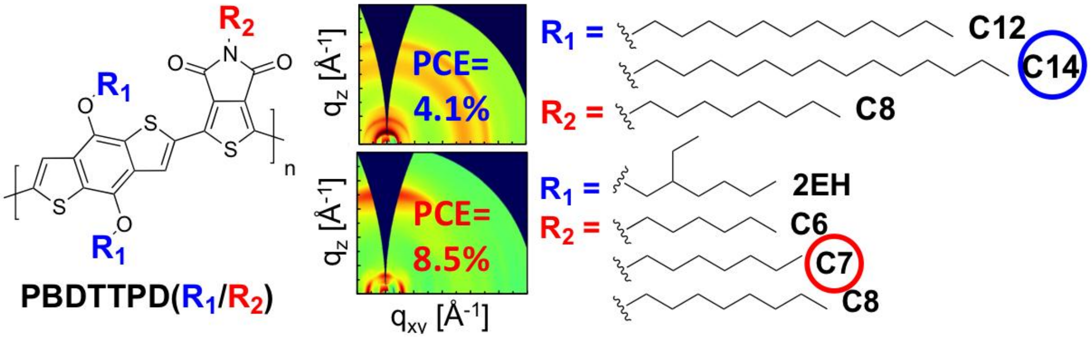

Figure 1.

References

[1] P. M. Beaujuge, and J. M. J. Fréchet, JACS, 2011, 133, 20009.
[2] C. Piliego, T. W. Holcombe, J. D. Douglas, C. H. Woo, P. M. Beaujuge, and J. M. J. Fréchet, JACS, 2010, 132, 7595.
[3] C. Cabanetos, A. El Labban, J. A. Bartelt, J. D. Douglas, W. R. Mateker, J. M. J. Fréchet, M. D. McGehee, and P. M. Beaujuge, JACS, 2013, 135, 4656.
[4] J. A. Bartelt, J. D. Douglas, W. R. Mateker, A. El Labban, C. J. Tassone, M. F. Toney, J. M. J. Fréchet, P. M. Beaujuge, and M. D. McGehee, 2013, Submitted this Fall.
[5] J. Warnan, C. Cabanetos, A. El Labban, M. R. Hansen, C. Tassone, M. F. Toney, and P. M. Beaujuge, 2013, Submitted this Fall.
[6] J. Warnan, A. El Labban, C. Cabanetos, E. Hoke, C. Risko, J-L. Brédas, M. D. McGehee, and P. M. Beaujuge, 2013, Submitted this Fall.

STIMULI RESPONSIVE POLYMERIC CAPSULES FOR CONTROLLED RELEASE AND IMAGING APPLICATIONS

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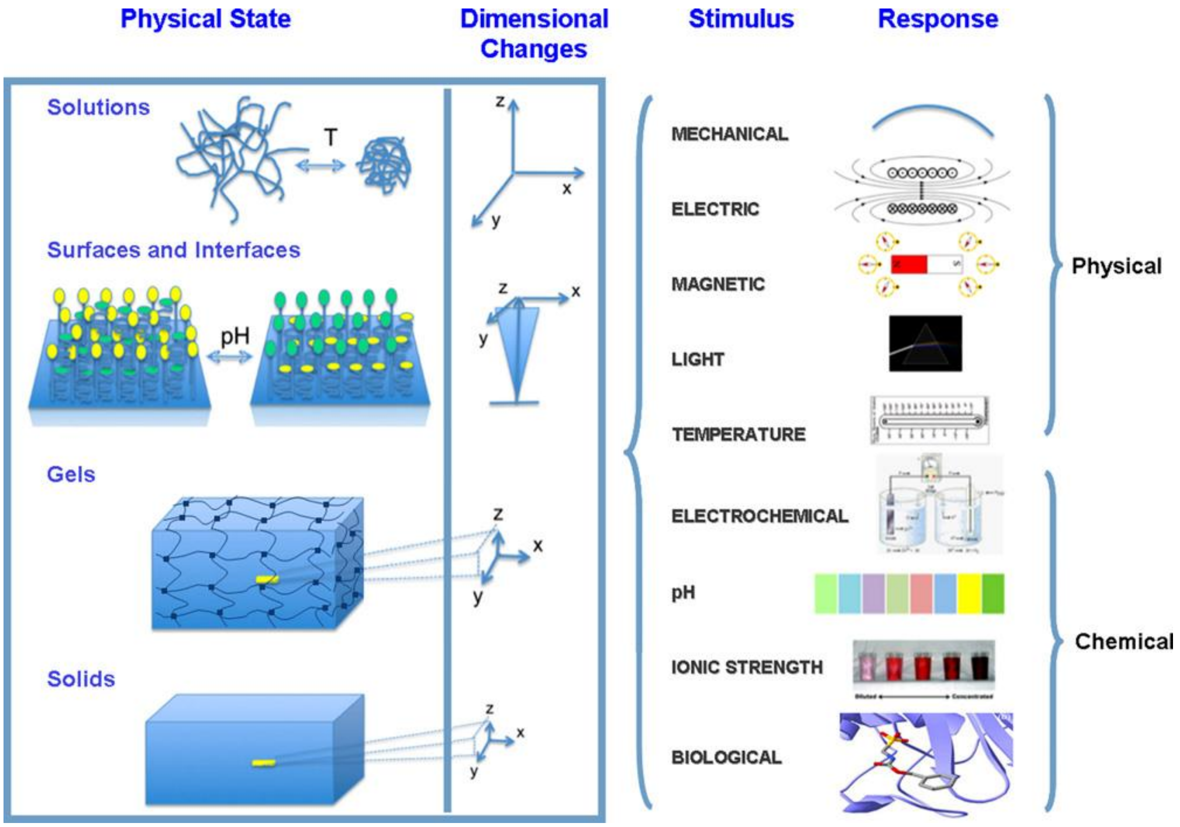
Abstract

A responsive or “smart” material is one in which a key material property is altered in a controlled fashion in response to the introduction of a pre-determined external stimulus. These stimuli-responsive materials might be utilized to undergo such changes as specimen shape, mechanical rigidity/flexibility, opacity, porosity, or may even be used for the controlled release of a specified molecular component for drug delivery purposes. Nowadays, there is an increasing interest in functional materials with reversibly switchable physicochemical properties for which mass transfer and interfacial properties can be adjusted using external stimuli such as temperature, pH, solution ionic strength, light, electric and magnetic fields, and chemical cues. Herein, an overview of our contribution to theses “smart” systems is presented with direct illustration of their possible applications in controlled release and imaging.



Dimensional changes depending on the physical state of the responsive material under different physical and chemical stimuli.

CATALYSIS WITH SOLUBLE POLYMERS: TOWARDS ENZYME-LIKE MATERIALS

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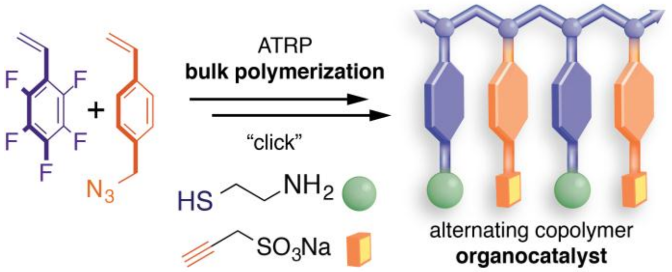

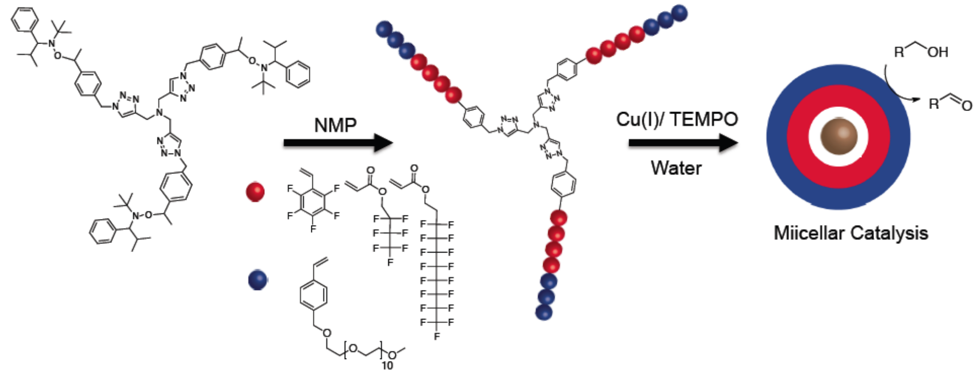

Abstract

The defining features of Nature's catalysts are their size, nanometer-scale, and precise three-dimensional structures, achieved through meticulous, programmed folding of linear polymer chains. Inspired by Nature, we use catalytic macromolecules with simple topologies (linear or star) and predictable self-assembly properties as conceptual enzyme mimics. In this presentation, I shall describe our current progress towards several enzyme-inspired macromolecules, both organocatalytic and bearing metal catalytic sites.[1,2]

References

[1] O'Shea J-.P., Solovyeva V., Guo X., Zhao J., Hadjichristidis N., and Rodionov V. *submitted*.

[2] Mugemana C., Chen B., Bukhryakov K. and Rodionov V. *in preparation*.

WELL-DEFINED POLYETHYLENES AND POLYETHYLENE-BASED BLOCK COPOLYMERS BY ANIONIC POLYMERIZATION AND POLYHOMOLOGATION

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Abstract

Access to model (high degree of structural, molecular weight and compositional homogeneity) polyethylenes (PEs) and PE-based block copolymers is necessary in order to elucidate the structure-properties relationships, which are very important for polymer performance. The synthesis of such polymers requires a truly living process. These approaches usually require high vacuum techniques, which are demanding, time consuming and leads to a small quantities of products. Nevertheless, this is a small price to pay given the tremendous potential of model macromolecules for selecting the appropriate structures needed for specific applications. Our group is using the following two methodologies to synthesize PEs and PE-based block copolymers:

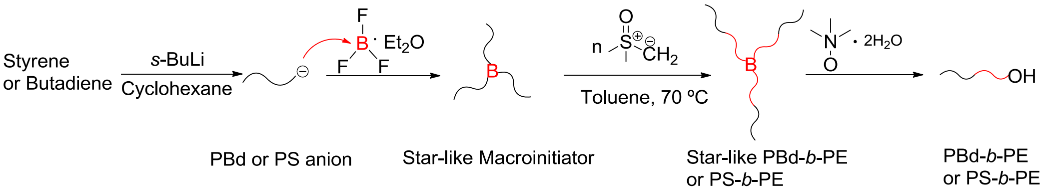
a) Anionic polymerization and Hydrogenation

Hydrogenation of 1,4-polybutadiene with various architectures (star, comb, dendritic, etc.) synthesized by anionic polymerization high vacuum techniques and appropriate post polymerization chemistry [1]. A few examples will be given, showing the importance of access to a variety of well-defined structures for a deeper understanding of polyethylene performance.

b). Combination of Anionic polymerization and Polyhomologation

Recently, Shea developed a novel polymerization methodology leading to perfectly linear PEs [2]. The general reaction scheme involves the formation of an organoboron zwitterionic complex between a methylide (monomer) and a trialkylborane Lewis acid (initiator) which breaks down by the intramolecular 1,2-migration. As a consequence, the methylene group of methylide is randomly inserted one by one into the three branches of the trialkylborane leading to a 3-arm PE star. The resulting star is subsequently oxidized/hydrolysed to give perfectly OH-end-capped linear PEs.

By combining anionic polymerization and polyhomologation, through a "bridge" molecule (BF_3OEt_2), a novel one-pot methodology was developed for the synthesis of PE-based block copolymers [3]. The anionically synthesized macroanion reacts with the "bridge" molecule to afford a 3-arm star (trimacromolecular borane) which serves as an initiator for the polyhomologation (Scheme 1).



Scheme 1. Synthesis of PE-based diblock copolymers by combining anionic polymerization and polyhomologation

References

[1] N. Hadjichristidis et al., *Macromolecules* **2000**, 33, 2424-2436.
[2] J. Luo, K. J. Shea, *Acc. Chem. Res*. **2010**, *43*, 1420-1433.
[3] H. Zhang, N. Alkayal, Y. Gnanou, N. Hadjichristidis, *Chem. Commun.* **2013**, 49, 8952-8954.

FROM STATIC SELF-ASSEMBLIES, HIERARCHIES AND BIOMIMETIC MATERIALS TO DYNAMIC SELF-ASSEMBLIES

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Abstract

Biological materials characteristically involve self-assembled structures at different length scales using subtle combinations of supramolecular interactions of various strengths. Inspired by them, we have pursued towards hierarchical static and responsive self-assemblies for various functions using simpler tectons, thus allowing rational constructs. Among the most straightforward approaches for hierarchies is to use structural units of different sizes, ranging from low molecular weights to polymers and to colloids and beyond, connected by physical interactions, such as hydrogen bonds, coordinations, ionic bonds and multivalent interactions to mimick sacrificial bonds of natural materials. Combining polymeric and low molecular weight supramolecular adducts leads to a wide variety of hierarchies.[1] Selecting polypeptidic blocks therein allows to additionally control the secondary structure to be α-helical, β-sheet, and random coil within the self-assemblies.[2-4] On the other hand, combining colloidal level units, such as nanoclay sheets or nanocellulose nanofibers, with polymers leads to biomimetic nanocomposites which open routes for feasible mechanical properties and functional materials.[5-7] One can combine colloidal, polymeric, and low molecular weight units in supramolecular constructs, leading to biomimetic structures, providing sacrificial bonds for tailored toughness.[8,9] Colloidal nanofibers and nanorods allow functional networks and surface self-assemblies.[10-11] Finally a model system is presented allowing to investigate adaptive patterns, complexity and emergent properties in static self-assemblies and switching to dynamic dissipative self-assemblies, suggesting new approaches for several polymer assemblies.[12]

References

[1] O. Ikkala, G. ten Brinke, *Science*, **2002**, 295, 2407-2409.

[2] S. Junnila, N. Houbenov, S. Hanski, H. Iatrou, N. Hadjichristidis, O. Ikkala, *Macromolecules*, **2010**, 43, 9071-9076.

[3] N. Houbenov, J. S. Haataja, H. Iatrou, N. Hadjichristidis, J. Ruokolainen, C. F. J. Faul, O. Ikkala, *Angew. Chem., Int. Ed*., **2011**, 50, 2516–2520.

[4] S. Hanski, S. Junnila, A. J. Soininen, J. Ruokolainen, O. Ikkala, *Biomacromolecules*, **2010**, 11, 3440-3447.

[5] T. Verho, M. Karesoja, P. Das, L. Martikainen, R. Lund, A. Alegría, A. Walther, O. Ikkala, *Adv. Mat.* **2013** early view.

[6] M. Wang, A. Olszewska, A. Walther, J.-M. Malho, F. H. Schacher, J. Ruokolainen, M. Ankerfors, J. Laine, L. A. Berglund, M. Österberg, O. Ikkala, *Biomacromolecules*, **2011**, 12, 2074-2081.

[7] H. Rosilo, E. Kontturi, J. Seitsonen, E. Kolehmainen, O. Ikkala, *Biomacromolecules*, **2013**, 14, 1547–1554.

[8] L. Martikainen, A. Walther, J. Seitsonen, L. Berglund, O. Ikkala, *Biomacromolecules* **2013** 14, 2531-2535.

[9] J. R. McKee, E. A. Appel, J. Seitsonen, E. Kontturi, O. A. Scherman, O. Ikkala, **2013**, submitted.

[10] A.R. Lokanathan, A. Nykänen, J. Seitsonen, L.-S. Johansson, J. Campbell, O. J. Rojas, O. Ikkala, J. Laine, *Biomacromolecules* **2013** 14, 2807-2813.

[11] R. T. Olsson, M. A. S. Azizi Samir, G. Salazar-Alvarez, L. Belova, V. Ström, L. A. Berglund, O. Ikkala, J. Nogués, U.W. Gedde, *Nature Nanotechnology*, **2010,** 5, 584-588.

[12] J. V. I. Timonen, M. Latikka, L. Leibler, R. H. A. Ras, O. Ikkala, *Science* **2013**, 341, 253-257.

METAL-CATALYZED LIVING RADICAL POLYMERIZATION: FROM CATALYSTS TO FUNCTIONAL POLYMERS

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Abstract

This lecture will discuss recent progresses in metal-catalyzed living radical polymerization that the authors have been developing [1]. Following an overview of catalyst development coupled with a general principle for precision control of chain-growth polymerization ("dormant" species), the lecture will highlight "sequence-controlled" polymers and functional "microgel" star polymers.

Green Metal Catalysts. Two catalyst familes will be presented for precision polymerization of functionalized monomers: Water-soluble, robust, verstaile, and highly active Ru(II) catalysts; and Functionality-tolerant, tunable, and active Fe(II) and Fe(III) catalysts [2].

Sequence-Controlled Polymers (Fig. 1). Sequence conrtol, as the authors believe, is among the most challenging subjects in polymer synthesis, and interest in this area has apparently been rising [3,4]. We are developing a variety of methodologies that could potentially enable to achieve sequence control, and a particularly interesting method is directed to the "iterative single monomer-addition" of designed "bulky", non-polymerizable methacrylates that can be converted into pendent-functionalized units by simple acidolysis/esterification.

Functional Microgel Star Polymers (Fig. 2). With designed binfunctional alkenes (linking agents), linear living polymers could be linked into "microgel" star polymers, a family of multi-armed, completely soluble, globular macromolecules where the "core" is a spherical microgel (localized gel) derived from the linking agent. With use of functional co-linking agents, the microgel core could enbed an extremely large nubmer of selected functionalities (esters, amides, ions, flurorine atoms, phosphine ligands, chiral ligands, etc.) [5]. The lecture will highlight recent examples in synthesis and functions of these stars such as flurorous molecular recognition.

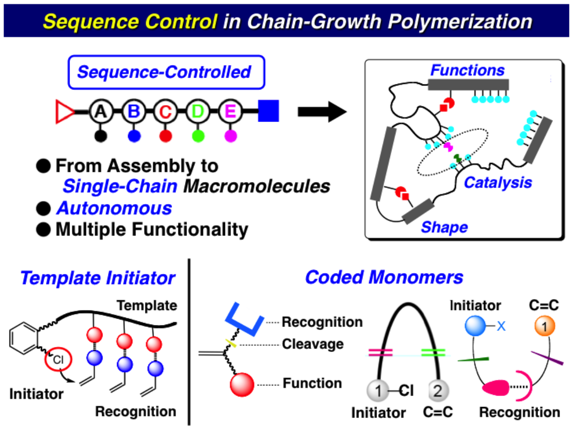

Fig. 1. Sequence-controlled polymers.

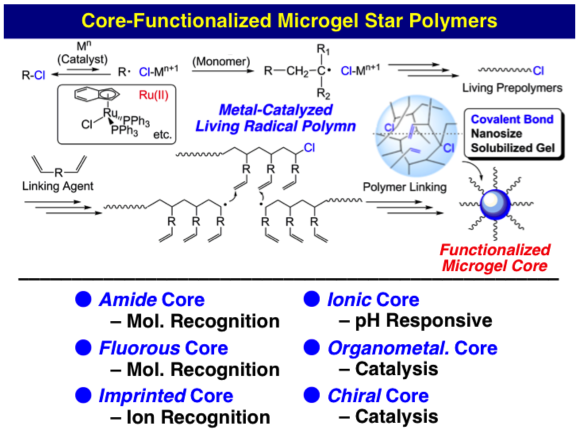

Fig. 2. Functional microgel star polymers.

References

[1] M. Sawamoto et al., *Chem. Rev.* **2009**, *109*, 4963; *Acc. Chem. Res.* **2008**, *41*, 1120.

[2] K. Fujimura, M. Ouchi, M. Sawamoto, *ACS Macro. Lett.* **2012**, *1*, 321.

[3] M. Ouchi, N. Badi, J.-F. Lutz, M. Sawamoto, *Nat. Chem.* **2011**, *3*, 917.

[4] Y. Hibi, M. Ouchi, M. Sawamoto, *Polym. Chem.* **2011**, *2*, 341; *Angew. Chem.* **2011**, *50*, 7434.

[5] T. Terashima et al., *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 373; **2011**, *49*, 1061; *Angew. Chem.* **2011**, *50*, 7892.

Poster Contributions

#	Presenter Name	Poster Title
1	Abdulrahman El Labban	TUNING THE SELF-ASSEMBLY OF POLY(BENZO[1,2-b:4,5-b']DITHIOPHENE-THIENO[3,4-c]PYRROLE-4,6-DIONE) (PBDTTPD) FOR EFFICIENT SOLAR CELLS
2	Athina Anastasaki	PHOTO ENHANCED-RAPID COPPER-MEDIATED LIVING RADICAL POLYMERIZATION OF ACRYLATES
3	Christianus Leenders	SUPRAMOLECULAR POLYMERS IN WATER; DESIGN, SYNTHESIS, CHARACTERIZATION AND APPLICATIONS
4	Christopher Waldron	COPPER-MEDIATED LIVING RADICAL POLYMERIZATION (SET-LRP) OF LIPOPHILIC MONOMERS FROM MULTI-FUNCTIONAL INITIATORS: REDUCING STAR-STAR COUPLING AT HIGH MOLECULAR WEIGHTS AND HIGH MONOMER CONVERSIONS
5	Clement Mugemana	THREE-ARM BLOCK COPOLYMER STARS: TAILORED POLYMER ARCHITECTURES FOR OXIDATION CATALYSIS IN WATER
6	Dirong Gong	NOVEL PN3-TYPE PINCER COMPLEXES FOR ETHYLENE AND 1,3-BUTADIENE POLYMERIZATIONS
7	Haleema Alamri	METAL-FREE POLYMERIZATION OF ε-CAPROLACTONE USING a PHOSPHAZENE CATALYST
8	Hassan Bouchekif	SYNTHESIS AND CHARACTERIZATION OF POLYVINYLETHER-BASED BLOCK AND GRAFT COPOLYMERS BY COMBINATION OF LIVING POLYMERIZATION TECHNIQUES
9	Hefeng Zhang	POLYETHYLENE-BASED COPOLYMERS SYNTHESIZED BY COMBINING POLYHOMOLOGATION AND LIVING ANIONIC/ATOM TRANSFER RADICAL POLYMERIZATION
10	Ioannis Marakis	GLASSY STATES IN ASYMMETRIC MIXTURES OF SOFT AND HARD COLLOIDS
11	Jagadeesh Malineni	AN EFFICIENT N-HETEROCYCLIC CARBENE BASED RUTHENIUM-CATALYST: APPLICATION TOWARDS THE SYNTHESIS OF POLYESTERS AND POLYAMIDES
12	Johannes S. Haataja	ELECTRON MICROSCOPY TOMOGRAPHY OF PENTABLOCK QUINTOPOLYMER MULTICOMPARTMENT MICELLES
13	John-Paul O'Shea	SEQUENCE-CONTROLLED COPOLYMERS OF 2,3,4,5-PENTAFLUOROSTYRENE: A MECHANISTIC INSIGHT AND APPLICATION TO ORGANOCATALYSIS
14	Julien Warnan	POLY(BENZO[1,2-b:4,5-b']DITHIOPHENE-THIENO[3,4-C]PYRROLE-4,6-DIONE) (PBDTTPD) ANALOGS FOR EFFICIENT SOLAR CELLS

15	Junpeng Zhao	A FACILE METAL-FREE “GRAFTING-FROM” ROUTE FROM ACRYLAMIDE-BASED SUBSTRATE TOWARD COMPLEX MACROMOLECULAR COMBS
16	Junpeng Zhao - David Pahovnik	PHOSPHAZENE-PROMOTED METAL-FREE RING-OPENING POLYMERIZATION OF ETHYLENE OXIDE INITIATED BY CARBOXYLIC ACID
17	Konstantin Bukhriakov	CATALYSIS WITH BLOCK-COPOLYMER MICELLES: A COMBINATORIAL STUDY
18	Laurent Chabanne	CONTROLLED SELF-ASSEMBLY AND HIERARCHICAL SELF-ASSEMBLY OF BLOCK COPOLYMERS IN SOLUTION
19	Luis Francisco Villalobosa	POLY-THIOSEMICARBAZIDE MEMBRANE FOR GOLD RECOVERY
20	Mary Welch	APPLICATIONS FOR POLYMER BRUSHES IN BIOSENSORS
21	Miguel Garcia Iglesias	SUPRAMOLECULAR ELECTRONIC MATERIALS BASED ON VINYLIDENE FLUORIDE OLIGOMERS.
22	Mikko Poutanen	COLLOID-POLYMER ASSEMBLIES FOR BIOMIMETIC COMPOSITES
23	Nicolas Moreno-Chaparro	MESO-SCALE SIMULATION OF SELF-ASSEMBLED DIBLOCK COPOLYMERS IN SOLUTION
24	Nik Fernandes	CORONA-FREE NANOPARTICLE IONIC MATERIALS: SYNTHESIS, PROPERTIES, AND APPLICATIONS
25	Poornima Madhavan	ASYMMETRIC BLOCK COPOLYMER MEMBRANES WITH POROSITY INDUCED BY H-BOND COMPLEX FORMATION
26	Sai V. C. Vummaleti	INSIGHTS INTO THE MECHANISM OF POLYHOMOLOGATION REACTION OF YLIDES (CH2S(O)Me2 and CH(Ph)S(O)Me2)
27	Sayed Z. Mohammady	IMPACT OF MOLECULAR ARCHITECTURE ON THE DYNAMICS OF THE GLASS RELAXATION PROCESSES IN BLOCK COPOLYMERS OF THE TYPE S-SB-S
28	Yihui Xie	POLYSULFONE-TRIAZOLE ULTRAFILTRATION MEMBRANES
29	Zulkifli Merican	NANOCAPSULES WITH FLUOROUS FILLING: PROGRESS TOWARDS SELF-ASSEMBLED NANOREACTORS

TUNING THE SELF-ASSEMBLY OF POLY(BENZO[1,2-*b*:4,5-*b'*]DITHIOPHENE-THIENO[3,4-*c*]PYRROLE-4,6-DIONE) (PBDTTPD) FOR EFFICIENT SOLAR CELLS

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Abstract

Solution-processable π-conjugated polymers are promising systems in bulk-heterojunction (BHJ) solar cells with fullerene acceptors.[1] Of all recently reported polymer donors, poly(benzo[1,2-*b*:4,5-b']-dithiophene−thieno[3,4-c]pyrrole-4,6-dione) (PBDTTPD) polymers can reach >8% power-conversion efficiency (PCE) in conventional BHJ devices.[2,3] In these systems, varying the size and branching of the solubilizing side-chain pattern,[3] together with tuning the polymer molecular weight,[4] can greatly impact the polymer self-assembly both in solution and in thin films. In parallel, various PBDTTPD analogs yield distinct nanoscale morphologies in BHJs with PCBM, leading to a broad range of solar cell efficiencies (Fig. 1). Our recent work emphasizes the critical role of linear alkyl substitutions in the development of ordered π-aggregates in blends of PBDTTPD and PCBM.[3,5]

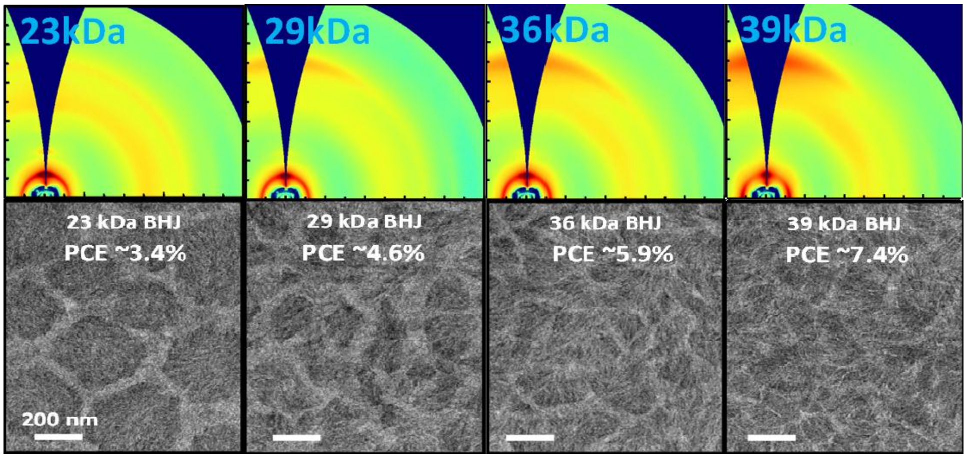

Figure 1. Grazing incidence X-ray diffraction (GIXD) images of neat PBDTTPD films with number-average molecular weights of 23 kDa, 29 kDa, 36 kDa, and 39 kDa. Top-down bright-field transmission electron microscope (TEM) images of PBDTTPD BHJs with PCBM (no additive used).

References

[1] P. M. Beaujuge, and J. M. J. Fréchet, *JACS*, **2011**, *133*, 20009.

[2] C. Piliego, T. W. Holcombe, J. D. Douglas, C. H. Woo, P. M. Beaujuge, and J. M. J. Fréchet, *JACS*, **2010**, *132*, 7595.

[3] C. Cabanetos, A. El Labban, J. A. Bartelt, J. D. Douglas, W. R. Mateker, J. M. J. Fréchet, M. D. McGehee, and P. M. Beaujuge, *JACS*, **2013**, *135*, 4656.

[4] J. A. Bartelt, J. D. Douglas, W. R. Mateker, A. El Labban, C. J. Tassone, M. F. Toney, J. M. J. Fréchet, P. M. Beaujuge, and M. D. McGehee, **2013**, *Submitted this Fall*. A. El Labban *et al.*, **2013**, *Manuscript submitted this Fall*.

PHOTO ENHANCED-RAPID COPPER-MEDIATED LIVING RADICAL POLYMERIZATION OF ACRYLATES

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Abstract

Recently, considerable interest has been directed towards controlling the activation and deactivation steps of living polymerizations (particularly CLRP) using a range of stimuli such as photo[1,2], pressure[3] and electronic[4] inducements. In an ideal synthesis such stimuli should result in lower activation energies for crucial steps such as initiation and repeated activations, allowing *in situ* generation of more active catalysts[5,6] and thus faster CLRP under milder conditions. The current contribution sets forth our experimental observations of a significantly increased polymerization rate for the copper-mediated living radical polymerization of acrylates to near quantitative conversion under UV exposure, and associated characterization detailing precise control over molecular weight, PDi, end-group fidelity, chain extension *etc*.

References

[1] Fors, B. P.; Hawker, C. J. *Angew.Chem.Int.Ed.,* **2012**, *51*, 8850.
[2] Konkolewicz, D.; Schröder, K.; Buback, J.; Bernhard, S.; Matyjaszewski, K. ACS Macro Lett **2012**, *1*, 1219.
[3] Rzayev, J.; Penelle, J. *Angew.Chem.Int.Ed.,* **2004**, *43*, 1691.
[4] Magenau, A. J. D.; Strandwitz, N. C.; Gennaro, A.; Matyjaszewski, K. *Science* **2011**, *332*, 81.
[5] Yoon, H. J.; Kuwabara, J.; Kim, J.-H.; Mirkin, C. A. *Science* **2010**, *330*, 66.
[6] Gregson, C. K. A.; Gibson, V. C.; Long, N. J.; Marshall, E. L.; Oxford, P. J.; White, A. J. P. *J. Am. Chem. Soc*

SUPRAMOLECULAR POLYMERS IN WATER; DESIGN, SYNTHESIS CHARACTERISATION AND APPLICATIONS.

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Supramolecular chemistry, and more specifically the self-assembly of small molecules into supramolecular polymers, has developed into an active field of research over the last decades. Because of the importance of water as solvent, more and more examples of self-assembly in water are reported in literature.[1,2] However, it is still difficult to design and predict the self-assembly behaviour of small molecules in water. In water, the hydrophobic effect provides an important additional driving force for self-assembly, and hydrogen bonding arrays need to be shielded from the surrounding water, for example by providing a hydrophobic pocket. These additional aspects make the step from apolar organic solvents to water anything but trivial. Our research focuses on the self-assembly of the benzene-1,3,5-tricarboxamide (BTA) unit, which in organic solvents self-assembles into highly dynamic, one dimensional columnar helical aggregates in a cooperative fashion driven by threefold hydrogen bonding.[3] We rationally redesigned the BTA unit to self-assemble in water harnessing both hydrophobic effects and hydrogen bonds to drive self-assembly.[4] By introducing an aliphatic spacer, the hydrogen bonding array is shielded from the surrounding water, while peripheral ethylene glycol units provide water solubility (Figure 1). BTA derivatives designed by this strategy form long supramolecular polymers in water, of micrometers in length and of a diameter of approximately 5 nanometers. Interestingly, small changes in the molecular design can strongly influence the self-assembly. Furthermore, by connecting two BTA units by a polyethylene glycol (PEG) linker visco-elastic hydrogel materials can be obtained which can find applications as modular and rationally designed biomaterials.

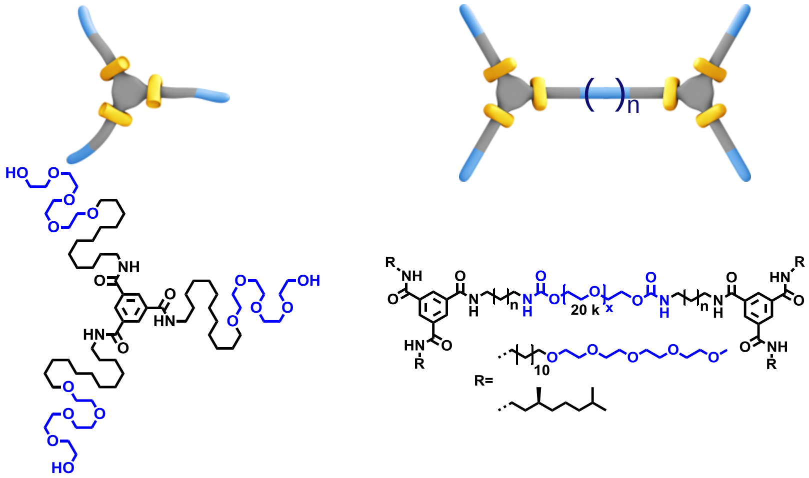

Figure 1: *Schematical representation and molecular structure of the BTA derivatives under investigation.*

[1] J.D. Hartgerink, E. Beniash and S.I. Stupp, *Science*, **2001**, 294, 1684-1688.
[2] J. Boekhoven, A.M. Brizard, P. van Rijn, M.C.A. Stuart, R. Eelkema and J.H. van Esch, *Angew. Chem. Int. Ed.*, **2011**, 50, 12285-12289.
[3] S. Cantekin, T.F.A. de Greef and A.R.A. Palmans, *Chem. Soc. Rev.*, **2012**, 41, 6125-6137.
[4] C.M.A. Leenders, L. Albertazzi, T. Mes, M.M.E. Koenigs, A.R.A. Palmans and E.W. Meijer, *Chem. Commun.*, **2013**, 49, 1963-1965.

COPPER-MEDIATED LIVING RADICAL POLYMERIZATION (SET-LRP) OF LIPOPHILIC MONOMERS FROM MULTI-FUNCTIONAL INITIATORS: REDUCING STAR-STAR COUPLING AT HIGH MOLECULAR WEIGHTS AND HIGH MONOMER CONVERSIONS

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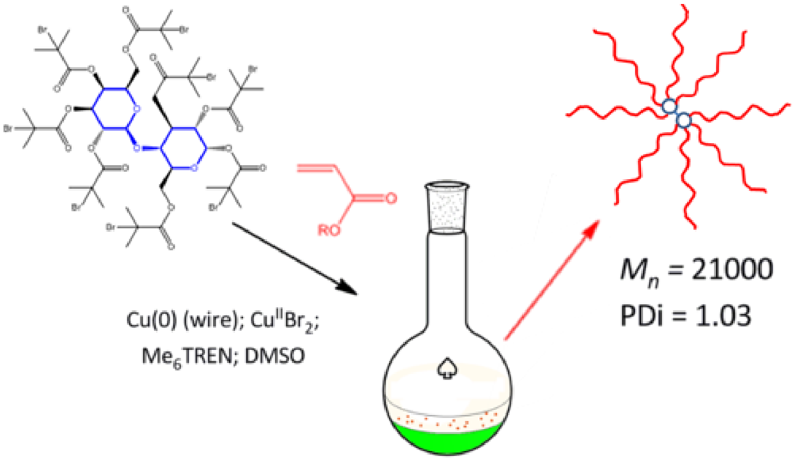
Abstract

The SET-LRP of lipophilic monomers (*n*-butyl and lauryl acrylate) from a lactose based octa-functional initiator is described. A range of highly defined lipophilic poly(acrylate) stars are prepared to relatively high molecular weights (*Mn*,target >100,000 g/mol in some cases) and high monomer conversions (≥99%) with excellent control retained over molecular weight distributions (PDi values as low as 1.03). Phase separation of star polymers from the reaction media during polymerization is seen to occur which is advantageous in reducing star-star coupling in certain cases, without limiting the attainment of near quantitative conversions. A comparison is made between heterogeneous and homogeneous polymerization protocols to illustrate this finding.



THREE-ARM BLOCK COPOLYMER STARS: TAILORED POLYMER ARCHITECTURES FOR OXIDATION CATALYSIS IN WATER

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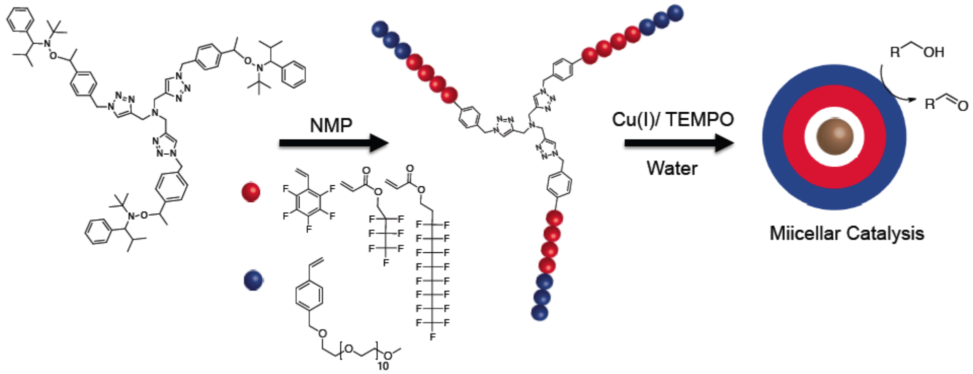

Abstract

Oxygen is rarely a reagent of choice for oxidations of organic compounds, due to challenges of activating the O_2 molecule. Furthermore, the safety implications of combining O_2 with standard organic solvents are far from trivial. Recently, a highly active Cu(I)/TEMPO catalyst system that effects selective aerobic oxidation of a broad range of primary alcohols to the corresponding aldehydes has been reported, with the limitation of being effective only in organic solvents.[1] The use of dendrimers[2] and branched polymers[3,4] has been a successful strategy for improving catalyst dispersion properties and creating optimal local solvent environment. Starting with a tripodal, TBTA – inspired[5] NMP initiator, we synthesized a range of well-defined three-arm block-copolymer stars. Self-assembly of the star polymers resulted in micelles and vesicular assemblies with evidence for microphase separation. The micelles, and especially vesicles are catalytically active in water for Cu(I)/TEMPO catalyzed oxidation of primary alcohols to aldehydes.

References

[1] Hoover, J. M.; Stahl, S. S. *J. Am. Chem. Soc.* **2011**, *133*, 16901-16910.
[2] Kreiter, R.; Kleij, A. W.; Gebbink, R. J. M. K.; van Koten, G. *Top. Curr. Chem.* **2001**, *217*, 163-199; Hecht, S.; Frechet, J. M. J. *Angew Chem Int Edit* **2001**, *40*, 74-91.
[3] Helms, B.; Liang, C. O.; Hawker, C. J.; Frechet, J. M. J. *Macromolecules* **2005**, *38*, 5411-5415.
[4] Helms, B.; Guillaudeu, S.; Xie, Y.; Mcmurdo, M.; Hawker, C.; Fréchet, J. *Angew. Chem. Int. Ed.* **2005**, *44*, 6384-6387.
[5] Chan, T. R.; Hilgraf, R.; Sharpless, K. B.; Fokin, V. V. *Org. Lett.* **2004**, *6*, 2853-2855.

NOVEL PN3-TYPE PINCER COMPLEXES FOR ETHYLENE AND 1,3-BUTADIENE POLYMERIZATIONS

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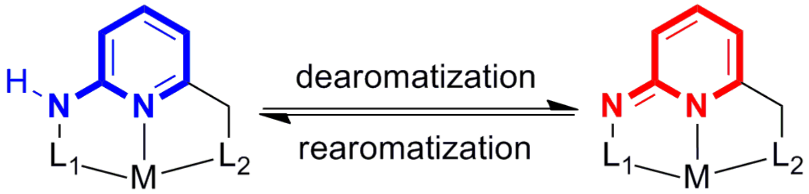
Abstract

Pincer transition metal complexes have versatile reactivities to catalyze many organic transformations and to activate strong chemical bonds. In particular, complexes with ligand derived from tridentate pyridine-based framework exhibit interesting reactivities. It has been demonstrated that unique bond activation reactions can be achieved through aromatization–dearomatization of the central pyridine ring. A new class of pincer ligands that have a unique disubstituted phosphinoamino (NH-PR_2) arm were synthesized and a series of Chromium (III) and Cobalt (II) complexes bearing this family of novel PN3-type pincer ligands have been prepared. The molecular structures of selected compounds were further elucidated by X-ray crystallographic analysis. Upon treatment with MAO or alkylaluminum, ethylene polymerization can be catalyzed by Cr complexes to afford exclusively linear low molecular weight solid PE without any detectable oligomers, and polymerization of 1,3-butadene can be catalyszed by Co complexes to generate polybutadiene with high 1,4-cis selectivity up to 99.7%.



References

[1] L.-P. He, T. Chen, D. Gong, Z.-P. Lai, K.-W. Huang, *Organometallics* **2012**, *31*, 5208-5211
[2] G. Zeng, T. Chen, L.-P. He, I. Pinnau, Z.-P. Lai; K.-W. Huang *Chem. Eur. J.* **2012**, *18*, 15940-15943.
[3] L.-P. He, T. Chen, D. Xue, M. Eddaoudi, K.-W. Huang, *J. Organomet. Chem.* **2012**, *700*, 202-206.
[4] D. Gong, W. Jia, T. Chen, K.-W. Huang, *Appl. Catal. A Gen.* **2013**, *464-465*, 35-42.
[5] K.-W. Huang *et al*, US 13/528,481 (2012),“Phospho-Amino Pincer-Type Ligands and Catalytic Metal Complexes Thereof”

METAL-FREE POLYMERIZATION OF ε-CAPROLACTONE USING a PHOSPHAZENE CATALYST

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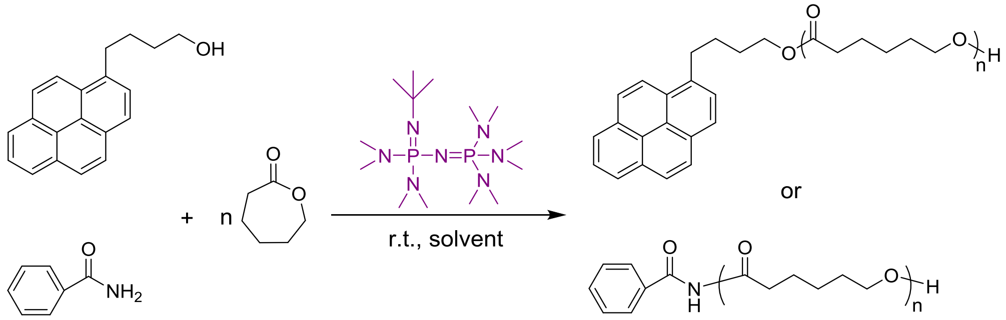
Abstract

Phosphazene base (P_2) catalyzed metal-free ring-opening polymerization (ROP) of *ε*-caprolactone (*ε*-CL) with 1-pyrenealcohol (PyOH) and benzamide (BAM) as the initiators in different solvents at room temperature was investigated (Scheme 1). The homogeneous polymerization proceeded to afford, in most cases, poly(*ε*-caprolactone) (PCL) with low polydispersities and controlled molecular weight. Kinetics study revealed that the polymerization rate in different solvents followed the order of dichloromethane>toluene>tetrahydrofuran (THF) (Figure 1, left), which was most probably the consequence of different interactions between the solvent and the active species. The kinetics could also be regulated by other factors such as monomer/initiator concentration or quantity of the catalyst used (Figure 1, right). In addition to alcohol, the feasibility of using BAM as initiator was also demonstrated. However, relatively high molecular weight with low conversion was obtained, indicating a slow initiation mode. These studies provided important information for the route design toward the metal-free synthesis of polyester-based materials.



Scheme 1. Synthetic scheme of phosphazene-catalysed ROP of ε-CL using either PyOH or BAM as the initiator.

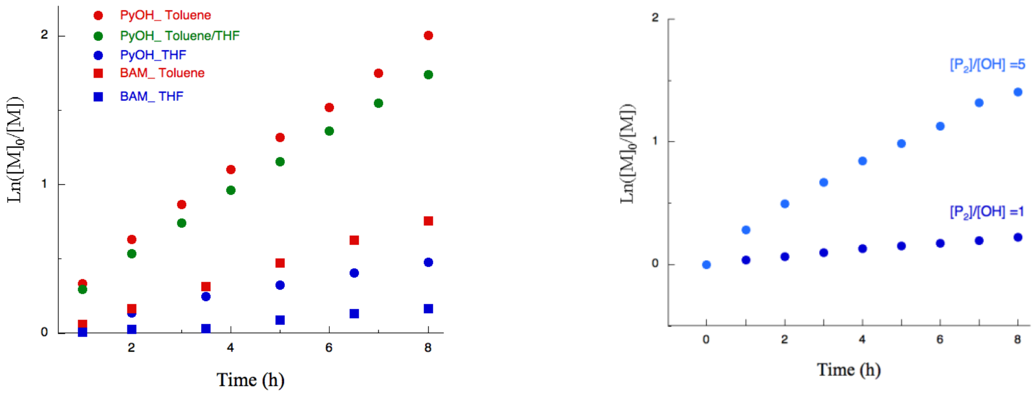


Figure 1. Kinetic plots of phosphazene-catalysed ROP of ε-CL in different solvents with either PyOH or BAM as initiator (left) and in THF with PyOH as initiator at different $[P_2]/[OH]$ ratio (right).

SYNTHESIS AND CHARACTERIZATION OF POLYVINYLETHER-BASED BLOCK AND GRAFT COPOLYMERS BY COMBINATION OF LIVING POLYMERIZATION TECHNIQUES

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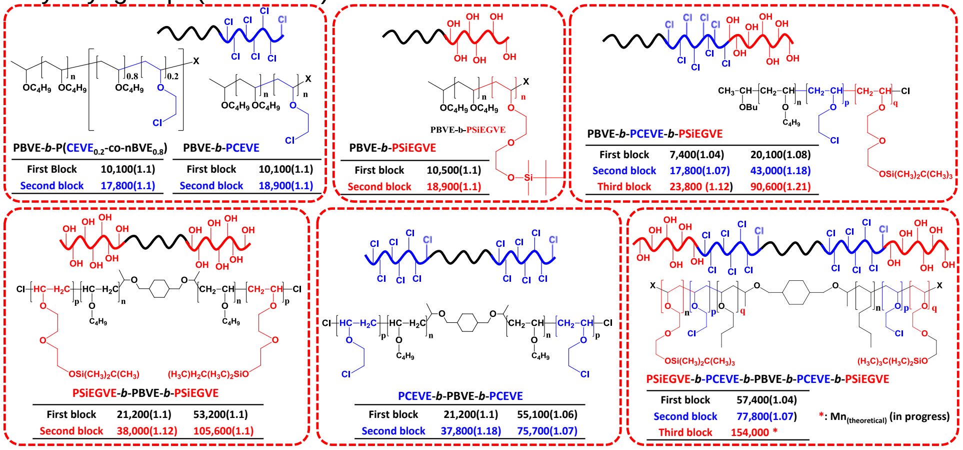
Abstract

The discovery of living anionic polymerization by Szwarc in 1956,[1] opened the way to the synthesis model polymers[2] with different macromolecular architectures (multiblocks, star blocks, miktoarms star, etc.) and rich variety of morphological microstructures (lamella, gyroid, hexagonal-packed cylinders, etc.). This ground-breaking discovery inspired many researchers to develop controlled/living routes for a plethora of monomers including those not compatible with anionic polymerization. This work presents our attempt to synthesis complex macromolecular architectures by combination of living cationic polymerization of vinyl ether[3] with other living polymerization techniques.

In this study, well-defined AB, BAB, ABC and CBABC block copolymers containing hydroxyl and chloro pendant groups (Scheme 1) were synthesized by sequential living cationic polymerization of n-butyl vinyl ether (nBVE), 2-chloroethyl vinyl ether (CEVE) and Si-containing vinyl ether monomer (t-butyldimethylsilyl ethylene glycol vinyl ether (SiEGVE)) using mono-functional (n-butoxyethyl acetate) and di-functional (1,4-Cyclohexanedimethanol di(1-ethyl acetate)) initiators. The living cationic polymerizations of those monomers were conducted in the presence of $Et_3Al_2Cl_3$ in hexane at -20°C. The quantitative desilylation of the poly(2-ethoxyethanol vinyl ether) protected by silyl group (PSiEGVE) were carried out with HCl-Ethanol-THF at 0°C.



PBVE-*b*-P(CEVE$_{0.2}$-co-nBVE$_{0.8}$)

First Block	10,100(1.1)
Second block	17,800(1.1)

PBVE-*b*-PCEVE

First block	10,100(1.1)
Second block	18,900(1.1)

PBVE-*b*-PSiEGVE

First block	10,500(1.1)
Second block	18,900(1.1)

PBVE-*b*-PCEVE-*b*-PSiEGVE

First block	7,400(1.04)	20,100(1.08)
Second block	17,800(1.07)	43,000(1.18)
Third block	23,800 (1.12)	90,600(1.21)

PSiEGVE-*b*-PBVE-*b*-PSiEGVE

First block	21,200(1.1)	53,200(1.1)
Second block	38,000(1.12)	105,600(1.1)

PCEVE-*b*-PBVE-*b*-PCEVE

First block	21,200(1.1)	55,100(1.06)
Second block	37,800(1.18)	75,700(1.07)

PSiEGVE-*b*-PCEVE-*b*-PBVE-*b*-PCEVE-*b*-PSiEGVE

First block	57,400(1.04)
Second block	77,800(1.07)
Third block	154,000 *

*: $Mn_{(theoretical)}$ (in progress)

Scheme 1. *Block copolymers obtained by living cationic polymerization of vinyl ethers monomers*

The synthesis of graft arms from the “grafting from” and “grafting onto” methods using other living polymerization techniques will be discussed during the poster session.

References

[1] M. Szwarc, *Nature*, **1956**, 178, 1168.
[2] N. Hadjichristidis, H. Iatroua, M. Pitsikalisa, J. Mays, *Prog. Polym. Sci.,* **2006**, 31, 1068–1132.
[3] S. Aoshima, S. Kanaoka, *Chem. Rev.,* **2009,** *109,* 5245–528.

POLYETHYLENE-BASED COPOLYMERS SYNTHESIZED BY COMBINING POLYHOMOLOGATION AND LIVING ANIONIC/ATOM TRANSFER RADICAL POLYMERIZATION

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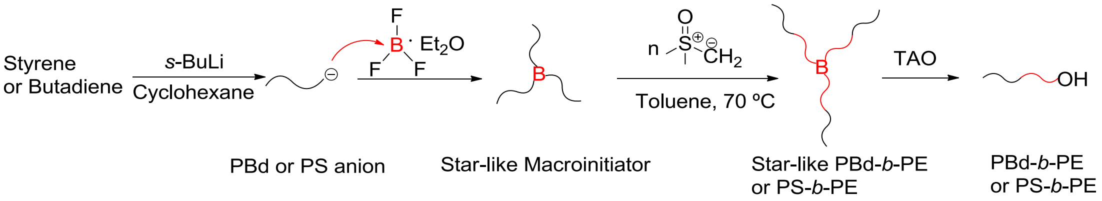
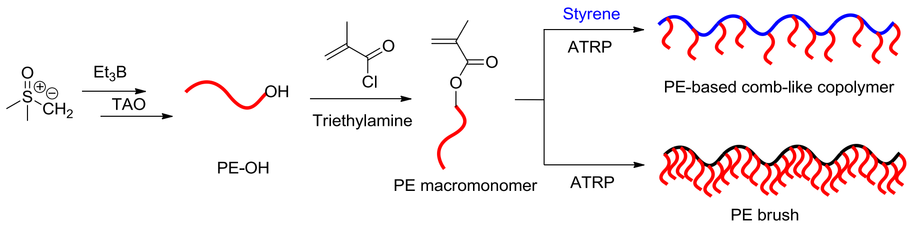
Abstract

In order to better understand the physical behavior and improve the performance of PE-based materials (PE: polyethylene), well-defined PE-based copolymers are needed. Polyhomologation, developed by Shea, has emerged as a powerful tool to synthesize PE using non-olefin monomer (ylide) in presence of organoborane as initiator.[1] Recently, we developed a novel method by combining anionic polymerization and polyhomologation to synthesize narrow dispersed PE-based block copolymers such as PS-*b*-PE and PB-*b*-PE (PS: polystyrene, PB: polybutadiene)(Scheme 1).[2] The synthesis was performed in one-pot: the anionically synthesized macroanion reacts with a "bridge" molecule (BF_3OEt_2) to afford the 3-arm star (trimacromolecular borane) which serves as macroinitiator for the further polyhomologation *in situ*. The resulting PE-based copolymers showed narrow polydispersities (PDI < 1.1). Using the same strategy multiblock copolymers can be synthesized,such as PS-*b*-PI-*b*-PE and PS-*b*-PI-*b*-PE-*b*-PEO (PI: polyisoprene, PEO: polyethylene oxide).



Scheme 1. Synthesis of PE-based block copolymers by combining anionic polymerization and polyhomologation

Furthermore, PE macromonomers with controllable molecular weight and narrow polydispersity (PDI < 1.10) have been successfully prepared by reacting the hydroxyl-terminated PE with methacryloyl chloride. The resulting PE-macromonomer was employed to synthesize PE-graft copolymers (copolymerization with styrene) and PE-brushes (homopolymerization) *via* atom transfer radical polymerization (ATRP) (Scheme 2).



Scheme 2 Synthesis of PE-based graft and brush copolymers by combining polyhomologation and atom transfer polymerization

References

[1] J. Luo, K. J. Shea. *Acc. Chem. Res*. **2010**, *43*, 1420-1433.
[2] H. Zhang**,** N. Alkayal**,** Y. Gnanou**,** N. Hadjichristidis**.** *Chem. Commun.* **2013**, *49*, 8952-8954.

GLASSY STATES IN ASYMMETRIC MIXTURES OF SOFT AND HARD COLLOIDS

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Abstract

Colloidal binary mixtures involving large hard spherical particles and small non-adsorbing depletant additives have emerged as the lead paradigm of sticky hard sphere (HS) systems, i.e. a tunable composite system with a very reach morphology diagram exhibiting a range of dynamic states [1], hence offering immense opportunities for tailoring final product properties and processing conditions. The softness of colloidal particles already showed to be a key element with respect to the melting of an initial repulsive glassy state and in general on the specific features of the depletion induced attractions [2].

We show that hard particles can induce multiple transitions in a soft colloidal glass. HS-like star polymers were added into a glassy solution of softer and bigger stars. The progressive addition of HS particles induced melting of the glassy state and eventually led to an arrested phase separation. The results on star/HS systems have been successfully described by Mode Coupling Theory based on colloid-star effective potential that has been recently developed [3] and by MD simulations.

References

[1] F. Sciortino, *Nat. Mat.*, **2002**, 1, 145-146.
[2] E. Stiakakis, D. Vlassopoulos, C. N. Likos, J. Roovers, and G. Meier, *Phys. Rev. Lett.*, **2001**, 89, 208302.
[3] D. Marzi, C. N. Likos, and B. Capone, *J. Chem. Phys.*, **2012**, 137, 014902.

AN EFFICIENT N-HETEROCYCLIC CARBENE BASED RUTHENIUM-CATALYST: APPLICATION TOWARDS THE SYNTHESIS OF POLYESTERS AND POLYAMIDES

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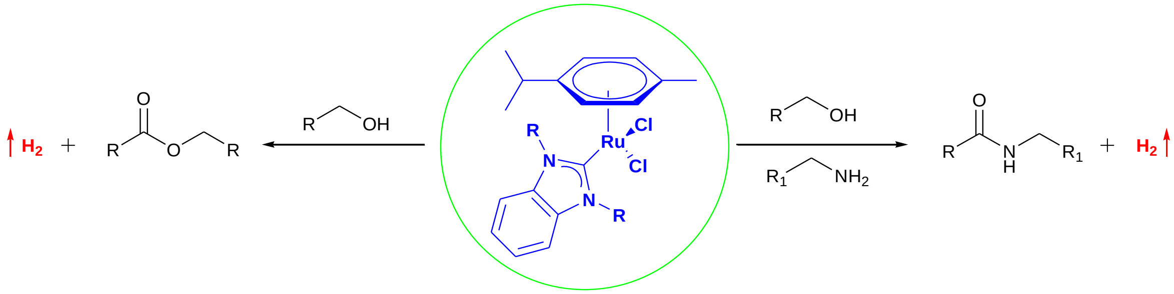
Abstract

A highly stable benzimidazolylidene based *N*-heterocyclic carbene (NHC) Ruthenium catalyst was prepared starting with readily accessible starting materials. Under inert gas atmosphere and in air the catalyst showed high activity for the direct synthesis of esters from primary alcohols and of amides from primary alcohols and amines. Due to highly stabile and sustainable nature the NHC Ruthenium complex allows for direct synthesis of polyester and polyamides by catalytic dehydrogenation of diols and diamines.



ELECTRON MICROSCOPY TOMOGRAPHY OF PENTABLOCK QUINTOPOLYMER MULTICOMPARTMENT MICELLES

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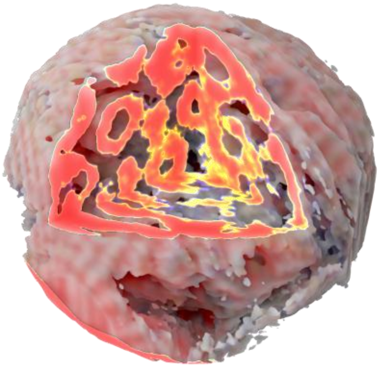
Abstract

Multicompartment micelles, i.e., multicompartment core micelles (MCMs) are 10-1000 nm diameter block copolymeric self-assemblies involving complex microphase-separated internal structures [1,2]. MCMs have been extensively studied e.g. because they are potential drug delivery candidates and because they resemble biological systems due to their ability to incorporate distinct chemical environments in close proximity within one nanostructure [3].

Current research has emphasized understanding how polymer block compositions and solvent treatments can be utilized to produce MCMs with well-defined structures and narrow size distributions, and how these structures can be stabilized in aqueous media [4,5]. Furthermore, there is a keen interest to develop MCMs that are responsive to external stimuli.



In this work we report the characterization of pentablock quintopolymers PS-*b*-PI-*b*-PDMS-*b*-P*t*BMA-*b*-P2VP [PS: Polystyrene; PI: Polyisoprene-1,4; PDMS: Polydimethyl siloxane); P*t*BMS: Poly(*t*-butyl methactylate; P2VP: Poly(2-vinyl pyridine)] [6] MCMs in acetone solution. Since such and related pentablock quintopolymers have so far been almost unprecedented in polymer science, the material at hand offers us new possibilities to investigate polymer block interactions and interfaces. Our main methods of study are transmission electron microscopy (TEM) combined with electron tomography (ET) (Figure) and selective staining of the polymer blocks. Due to the fact that our system is much more complex than the currently reported MCMs formed by AB, ABC and ABCA di-, tri- and tetra-block co/terpolymers, a wide variety of structures is available. Here, we will concentrate on the methodologies how to identify the different microphases and compartments.

References

[1] F. H. Schacher, A. Walther, M. Ruppel, M. Drechsler, A. H. E. Müller, *Macromolecules*, **2009**, 42, 3540-3548.
[2] *Y. Gao, Y. Wang, M. Jiang, D. Chen, ACS Macro Lett.,* **2012**, *1*, 1312-1316.
[3] A.O. Moughton, M.A. Hillmyer, T.P. Lodge, *Macromolecules*, **2012,** 45, 2-19.
[4] F. H. Schacher, T. Rudolph, M. Drechsler, A. H. E. Müller, *Nanoscale*, **2011**, 3, 288-297.
[5] A.H. Gröschel, F. H. Schacher, H. Schmalz, O. V. Borisov, E. B. Zhulina, A. Walther, A.H. E. Müller, Nat. Commun., 2012, 3, 710.
[6] P. Fragouli, H. Iatrou, D.Lohse, N.Hadjichristidis, *J. Polym Sci-Polym Chem,* **2008**, 46,3938

SEQUENCE-CONTROLLED COPOLYMERS OF 2,3,4,5-PENTAFLUOROSTYRENE: A MECHANISTIC INSIGHT AND APPLICATION TO ORGANOCATALYSIS

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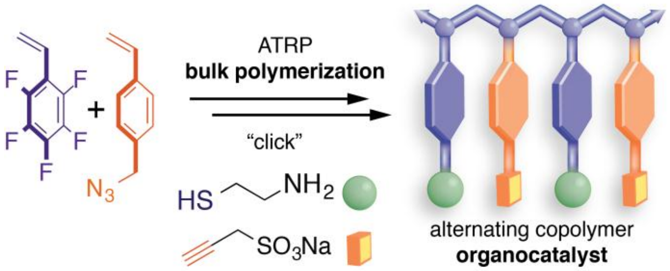

Abstract

A number of copolymers between styrene (St) or 4-azidomethylstyrene (N_3St) and 2,3,4,5,6-pentafluorostyrene (FSt) have been prepared by atom-transfer radical polymerization (ATRP) and conventional free radical polymerization (FRP). The mode of monomer alternation in copolymers has been established unambiguously using heteronuclear multiple bond correlation (HMBC) NMR. The degree and nature of monomer alternation was found to be strongly dependent both on the solvent (or lack thereof) and the polymerization initiator. These results stand in contrast with previously published works,[1,2] which rely primarily on classic analysis of monomer reactivity ratios.[3] We proceeded to independently functionalize the N_3St and FSt moieties using orthogonal "click" chemistries: copper-catalyzed azide-alkyne cycloaddition (CuAAC) [4] and fluoroarene-thiol coupling (FTC).[5] An alternating copolymer bearing $-NH_2$ and $-SO_3^-$ functional groups was found to be a competent organocatalyst for a Henry reaction between benzaldehyde and nitromethane.

References

[1] Pryor, W. A.; Huang, T.-L. *Macromolecules* **1969**, *2*, 70-77.
[2] Pugh, C.; Tang, C. N.; Paz-Pazos, M.; Samtani, O.; Dao, A. H. *Macromolecules* **2007**, *40*, 8178-8188.
[3] Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*, 259-262.
[4] Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596-2599.
[5] Becer, C. R.; Babiuch, K.; Pilz, D.; Hornig, S.; Heinze, T.; Gottschaldt, M.; Schubert, U. S. *Macromolecules* **2009**, *42*, 2387-2394.

POLY(BENZO[1,2-b:4,5-b′]DITHIOPHENE-THIENO[3,4-C]PYRROLE-4,6-DIONE) (PBDTTPD) ANALOGS FOR EFFICIENT SOLAR CELLS

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Abstract

Bulk heterojunction (BHJ) solar cells based on several polymer donors and PCBM acceptors can achieve power conversion efficiencies (PCEs) >7%.[1] Relying on donor-acceptor (D-A) principles, π-conjugated polymers based on benzo[1,2-*b*:4,5-*b′*]dithiophene (BDT) and thieno[3,4-*c*]pyrrole-4,6-dione (TPD) motifs (Fig. 1) are some of the best-performing systems, with PCEs >8% recently reported in conventional BHJ devices.[2]

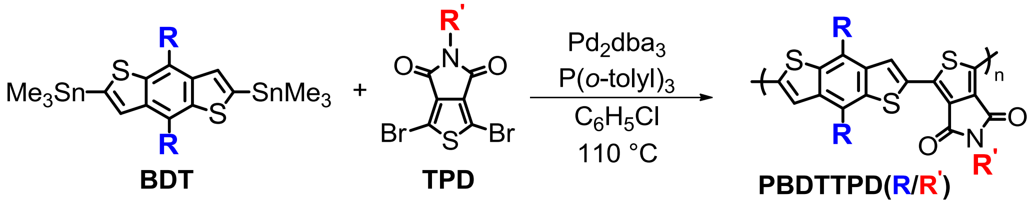

Figure 1. General method for the polymerization of PBDTTPD polymer analogs

In these D-A systems, energetic factors such as the HOMO and LUMO energy levels, and the corresponding band-gap (E_g), are governed by the electron-rich and -deficient motifs that compose the π-conjugated backbone, as well as by the conjugation length of the polymer.[1] Our recent developments show that replacing BDT and TPD by other analogous electron-rich motifs, such as benzo[1,2-*b*:4,5-*b′*]difuran (BDF), various ring-substituted BDT units, or *N*-alkyloyl TPD moieties (Fig. 2) affects both the optoelectronic properties of the polymers and their nanoscale morphologies in BHJs with PCBM.[3]

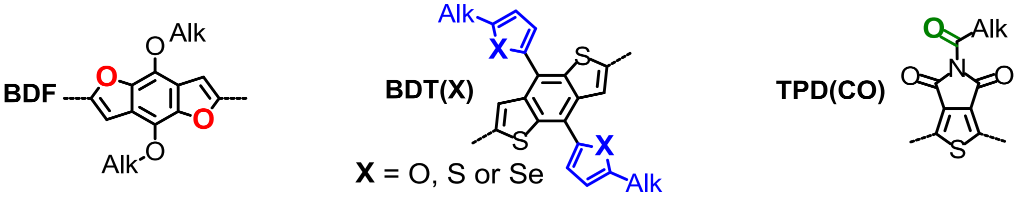

Figure 2. Discrete synthetic modifications in the BDT and TPD motifs

References

[1] P. M. Beaujuge, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2011**, *133*, 20009.

[2] C. Cabanetos, A. El Labban, J. A. Bartelt, J. D. Douglas, W. R. Mateker, J. M. J. Fréchet, M. D. McGehee, P. M. Beaujuge, *J. Am. Chem. Soc.* **2013**, *135*, 4656.

[3] J. Warnan *et al.*, **2013**, *Manuscripts (x3) submitted this Fall*.

A FACILE METAL-FREE “GRAFTING-FROM” ROUTE FROM ACRYLAMIDE-BASED SUBSTRATE TOWARD COMPLEX MACROMOLECULAR COMBS

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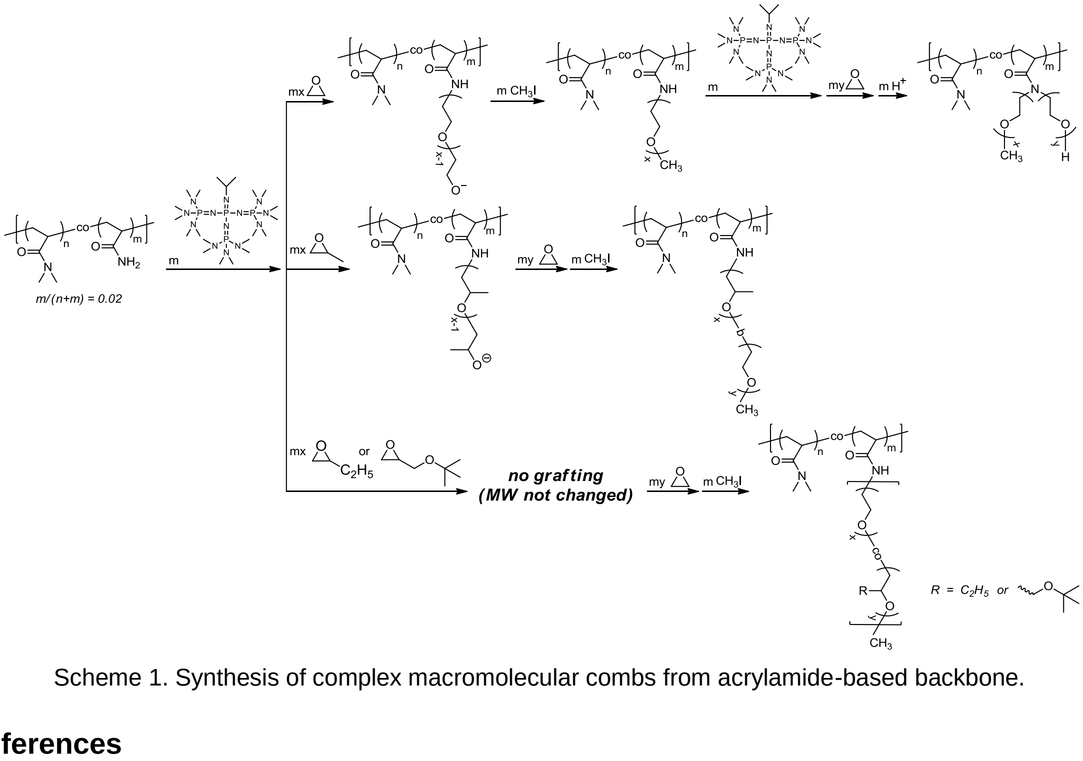
Abstract

In the recent surge of metal-free polymerization techniques,[1] a strong phosphazene base (t-BuP$_4$) has shown its remarkable strength as the promoter for the anionic polymerization of various types of monomers, especially epoxides.[2] The in-situ activation/polymerization mechanism has allowed facile achievement of a wide variety of polyether-based macromolecular structures. In the present work, we have employed primary amide moieties as initiating sites, instead of conventional hydroxyl groups, to further strengthen this polymer synthesis strategy. High-molecular-weight poly(*N*,*N*-dimethylacrylamide-*co*-acrylamide) has been used as a model functional substrate (backbone), and t-BuP$_4$-promoted anionic ring-opening graft polymerizations are conducted directly from the activated primary amide moieties (Scheme 1). The (co)polymerizations of ethylene oxide and propylene oxide have been proven to be effective, leading to macromolecular combs with single homopolymer, double homopolymer and block copolymer side chains. Larger epoxide monomers cannot be homopolymerized, while the copolymerizations with ethylene oxide are successful, leading to statistical copolymer side chains.



Scheme 1. Synthesis of complex macromolecular combs from acrylamide-based backbone.

References

[1] M. K. Kiesewetter, E. J. Shin, J. L. Hedrick, R. M. Waymouth, *Macromolecules*, **2010**, *43*, 2093-2107.
[2] S. Boileau, N. Illy, *Prog. Polym. Sci.*, **2011**, *36,* 1132-1151.

PHOSPHAZENE-PROMOTED METAL-FREE RING-OPENING POLYMERIZATION OF ETHYLENE OXIDE INITIATED BY CARBOXYLIC ACID

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Abstract

The phosphazenes, a class of organic superbases, have shown their remarkable potential as promoter/catalyst for the anionic polymerization of various types of monomers. Phosphazene bases improve the nucleophilicity of the initiator/chain-end significantly by complexation with the counterion (e.g. proton or lithium cation), resulting in a rapid and usually controlled anionic polymerization. Hydroxyl based initiators have been most commonly used with phosphazene bases, however other protic functionalities, e.g. amide, can be used as well [1, 2]. Using new initiating sites enables us to develop new methodologies toward facile macromolecular engineering from substrates with various functionalities.

We have studied the polymerization of ethylene oxide (EO) using 1-pyrenebutyric acid as initiator together with a phosphazene superbase, *t*-BuP$_4$. With 10% *t*-BuP$_4$ (with regard to carboxyl groups), we have successfully polymerized EO with practically 100% initiation efficiency and full monomer conversion. SEC and NMR results confirm the effectiveness of initiation from carboxylic groups, as the polymer have low dispersity (M_w/M_n = 1.05) and expected molecular weight. MALDI-TOF MS reveals that, while the main product is the expected species, bearing one pyrenyl and one hydroxyl end group, there are two more populations, which belong to the species bearing no pyrenyl moiety at either end and the species with ester-bound pyrenyl moieties on both ends (Figure 1). However, the degree of polymerization for the apexes of all three distributions is the same and the apex positions are different only due to the different numbers (0, 1, or 2) of pyrenyl moieties. The formation of these two extra species is caused by the simultaneous and fast intermolecular transesterification reaction, which, however, doesn't affect the polymer's dispersity and molecular weight.

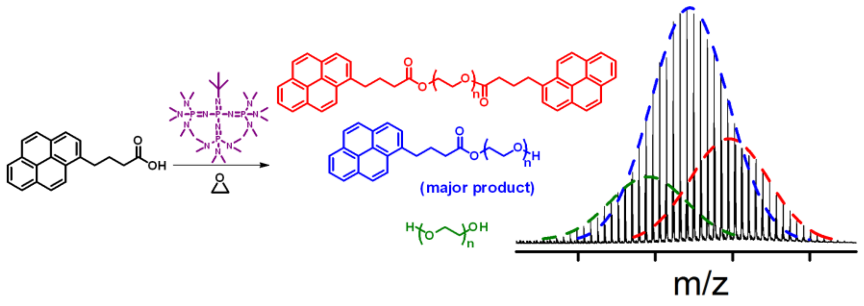

Figure 1. Metal-free anionic polymerization of ethylene oxide initiated by 1-pyrenebutyric acid and the MALDI TOF spectrum of a typical product.

References

[1] J. Zhao, H. Schlaad, Macromolecules, 2011, 44, 5861-5864.
[2] J. Zhao, H. Alamri, N. Hadjichristidis, Chem. Commun., 2013, 49, 7079-7081.

CATALYSIS WITH BLOCK-COPOLYMER MICELLES: A COMBINATORIAL STUDY

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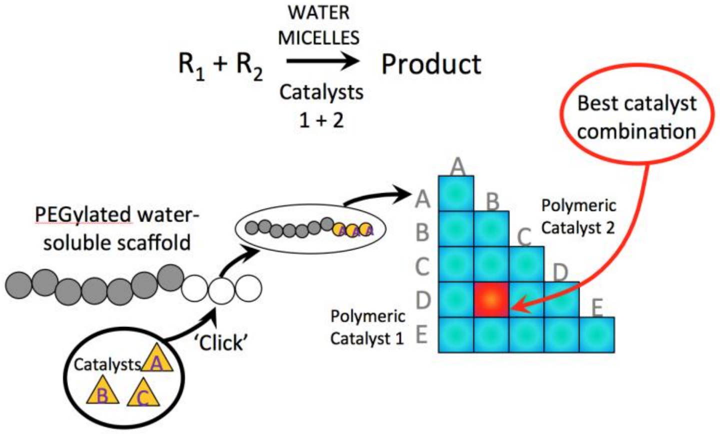

Abstract

A key step in a number of important reactions, such as Mannich, Michael, Friedel-Crafts, and conjugate additions is the activation of electrophilic reagents by Lewis acids or H-bond donors. Nature's enzymes perform these reactions in water effortlessly, by positioning the reactants and catalytic moieties within hydrophobic binding pockets.1 Water is rarely the solvent of choice for chemist-designed reactions: it is not suitable for hydrophobic substrates or catalysts, and is highly competitive as a hydrogen bond acceptor and a Lewis base. In this presentation, we shall describe our current progress towards enzyme-inspired catalysts. We prepared a number of "clickable" amphiphilic block-copolymer scaffolds, which we proceeded to functionalize with a number of potentially catalytic or activating functional groups.2 When the polymers were screened in systematically varied pairs, a number of effective catalytic systems were identified. This approach to catalyst discovery is general, and can be extended to other chemistries, polymer scaffolds and catalytic moieties.

References

[1] Fersht, A. Structure and Mechanism in Protein Science: A Guide to Enzyme Catalysis and Protein Folding; W. H. Freeman: 1998;
[2] For a related approach to catalyst discovery, see: Menger, F. M.; Eliseev, A. V.; Migulin, V. A. *J. Org. Chem.* **1995**, *60*, 6666-6667.

CONTROLLED SELF-ASSEMBLY AND HIERARCHICAL SELF-ASSEMBLY OF BLOCK COPOLYMERS IN SOLUTION

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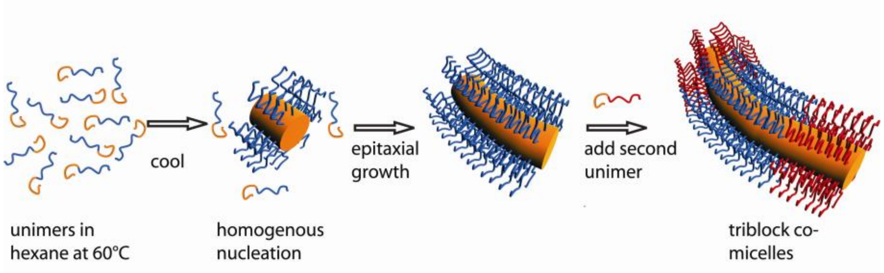
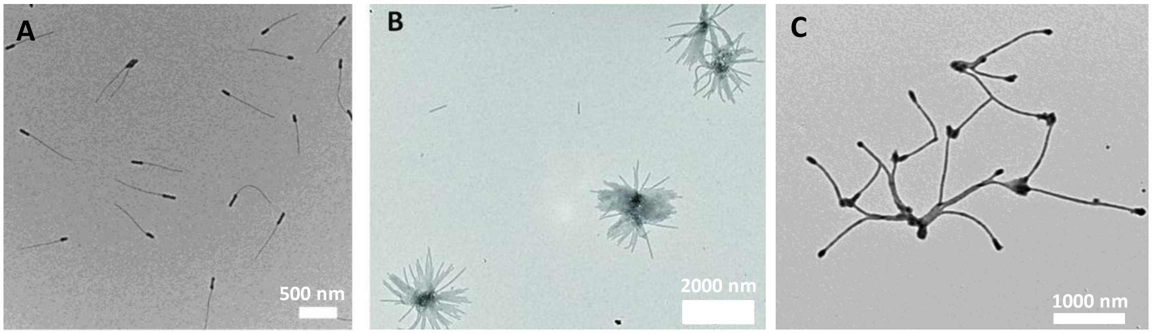
Abstract

It is known that block copolymers containing a crystalline poly(ferrocenylsilane) (PFS) block undergo crystallization-driven self-assembly in selective solvents. The size and polydispersity of the resulting cylindrical or lamellar micelles can be precisely controlled thanks to the living character of this epitaxial growth.[1,2,3] In addition, block co-micelles were prepared from PFS block copolymer unimers with various corona-forming blocks.



This poster will discuss recent strategies for the precise control of micelle architectures and the assembly of these micelles into hierarchical structures.[4,5 and unpublished results]

TEM images



A: asymmetric micelles **B**: spherical supermicelles **C**: micelle network

References

[1] X. S. Wang, G. Guerin, H. Wang, Y. S. Wang, I. Manners, M. A. Winnik, *Science* **2007**, *317*, 644.

[2] T. Gädt, N. S Ieong, G. Cambridge, M. A. Winnik, I. Manners, *Nature Mat.* **2009**, *8*, 144.

[3] J. B. Gilroy, T. Gädt, G. R. Whittell, L. Chabanne, J. M. Mitchels, R. M. Richardson, M. A. Winnik, I. Manners *Nature Chem.* **2010**, *2*, 566.

[4] H. Qiu, G. Russo, P. A. Rupar, L. Chabanne M. A. Winnik, I. Manners, *Angewandte Chemie* **2012**, *124*, 12052

[5] P. A. Rupar, L. Chabanne M. A. Winnik, I. Manners, *Science* **2012**, *337*, 559.

POLY-THIOSEMICARBAZIDE MEMBRANE FOR GOLD RECOVERY

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Abstract

The current exponential demand of gold for electronics has encouraged the development of efficient processes to recycle it. Several adsorbents used to recover gold from acidic solutions can be found in the literature with outstanding maximum uptakes, yet, poor kinetics lead to an overall inefficient process. A solution to this issue could be the use of membrane adsorbers that can achieve higher adsorption rates. These membranes operate using a pressure-driven flow through the pores that eliminates the diffusion limitations commonly present in packed column adsorption processes. When a solution is forced to pass through the porous membrane, the molecules travel by convective flow through the membrane pores, promoting the contact of the metal ions with the adsorbing sites [1].

The biggest challenge for the fabrication of membrane adsorbers, is the efficient and stable incorporation of adsorption sites inside the membrane matrix. In this work we propose the use of poly-thiosemicarbazide (PTSC) [2,3] for the fabrication of asymmetric membranes to recover gold(III) from a solution. Each monomeric unit of this polymer contains two thiosemicarbazide groups that form a chelate site capable of forming strong complexes with several metal ions. This site contains several groups that can contribute to the formation of complexes with metal ions as can be seen in the structure presented below. To our knowledge, this membrane presents the most efficient method to recover gold from acidic solutions. The membrane permeation process is able to selectively capture gold in a simple, efficient and continuous process.

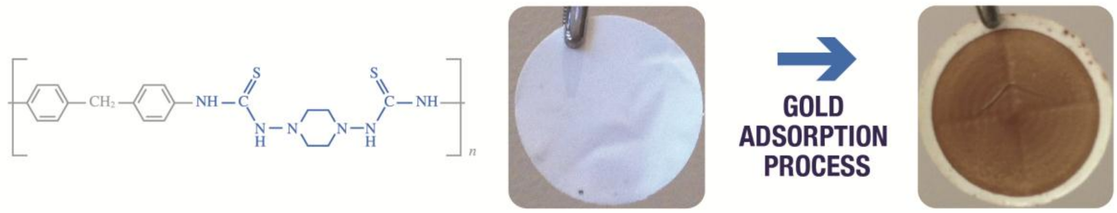

Fig 1. Structure of poly-thiosemicarbazide and photos of the membrane before and after the adsorption process.

Acknowledgements

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References

[1] E. Klein, Affinity membranes: their chemistry and performance in adsorptive separation processes, Wiley New York, **1991**.
[2] E.A. Tomic, V.S. Foldi, T.W. Campbell, J. Polym. Sci., **1962,** 62, 387-399.
[3] T.W. Campbell, E.A. Tomic, J. Polym. Sci., **1962,** 62, 379-386

APPLICATIONS FOR POLYMER BRUSHES IN BIOSENSORS

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Abstract

Polymer brushes have many desirable characteristics such as the ability to tether molecules to a substrate, or change the properties of a surface. In the past few years they have garnered much attention for their involvement in microelectronics, nanofluidic devices, biosensing, and other areas of nanotechnology.[1-4] We are investigating several types of biosensors that can be enhanced through the incorporation of polymer brushes. Two examples are given here.

The ability to detect selective antibodies is essential for diagnosing infectious diseases. We report an electrochemical detection system based on an antibody catalyzed water oxidation pathway (ACWOP) which takes advantage of the intrinsic ability of the primary antibody to generate hydrogen peroxide when in the presence of singlet oxygen and water.[5] Using a simple solution assay and amplified electrochemical detection, we can measure the H_2O_2 produced and thus all antibodies that bind to the antigen coated electrode. As a means of amplifying the signal, polymer brushes have been integrated to bind the antibodies to the surface as well as to prevent non-specific adsorption of other antibodies or contaminants that may be present in the test fluid. Because of the ability to tailor the polymer brushes to specific antibodies, a broad range of viruses can be investigated.

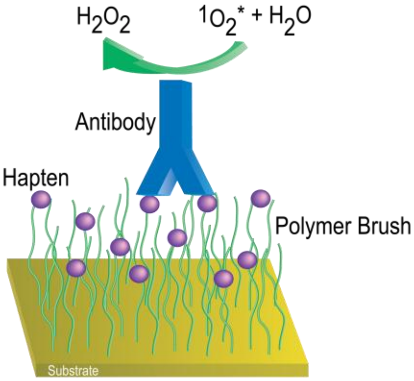

Figure 1. Schematic depiction of immunosensor polymer brush platform based on the ACWOP.

A second biosensor includes a PEDOT:PSS based microelectrode which measures neuronal activities *in vivo*. This device requires the tethering of glucose oxidase for specific charge exchange reactions to occur between the biological media and the conducting polymer sensor. Our goal is to use polymer brushes as a way of anchoring these molecules to the electrode surface without altering the conductivity of the transistor.

References

[1] M.A.C. Stuart, W.T.S. Huck, J. Genzer, M. Muller, C. Ober, M. Stamm, G.B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, and S. Minko, *Nat. Mater.,* **2010,** 9,101-113.
[2] M. Welch, A. Rastogi, C. K. Ober, *Soft Matter,* **2011,** *7, 297-302*.
[3] E. N. Chiang, R. Dong, C. K. Ober, B. A. Baird, *Langmuir*, **2011,** 27, 7016-7023.
[4] O. Hollmann, T. Gutberlet, C. Czeslik, *Langmuir*, **2007,** 23, 1347-1353.
[5] P. Wentworth, P. et al. *Science,* **2001,** 293, 1806-1811.

SUPRAMOLECULAR ELECTRONIC MATERIALS BASED ON VINYLIDENE FLUORIDE OLIGOMERS.

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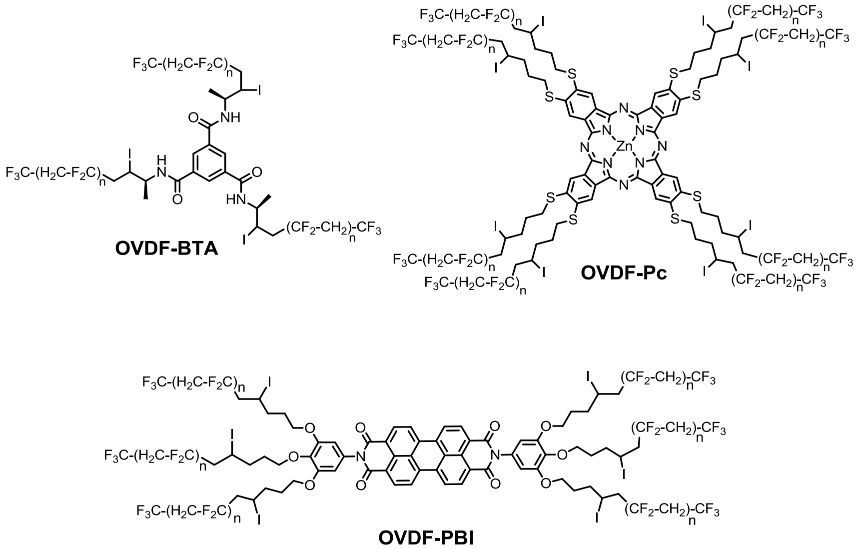
Abstract

Polymers consisting of vinylidenefluoride monomer units (CF_2CH_2) are known to be a ferroelectric polymer with large dipole moments oriented perpendicular to the molecular chain. Dipole moments can be aligned with an applied field giving rise to materials which can potentially be used to construct piezoelectric devices and flexible nonvolatile memories.[1,2] More recently, oligomers (OVDF) have shown to have the same type of dipole orientation.[3] This opens the way to use these oligomers in supramolecular chemistry.

Our work aims at the synthesis and characterization of nanometer-sized self-assembled non-centrosymmetric architectures exhibiting intrinsic permanent polarization and among others, ferroelectric and piezoelectric properties. To that aim OVDF chains of about 10 carbons length have been incorporated to different central cores whose self-assembling properties are well known. The coupling of the central cores and OVDF has been carried out using a new synthetic method for the end-functionalization of I-OVDF[4] by means of radical-based chemistry.

Regarding the central cores, we are primarily interested in using benzene-1,3,5-tricarboxamide (BTA) derivatives as a model structure and π-conjugated discotics like phthalocyanine (Pc) or perylene bisimide (PBI) to introduce further functionality, such as light-harvesting, luminescence or semiconducting properties. (Figure 1).



OVDF-BTA

OVDF-Pc

OVDF-PBI

Figure 1: Molecular structure of the discotic molecules synthetized.

The liquid crystalline properties of the materials as well as the formation of the antiparallel intrachain arrangement originates from the zig-zag all-anti conformation in OVDF have been studied exhaustively using different techniques.

References

[1] C. Chang, V. H. Tran, J. Wang, Y.-K. Fuh, L. Lin, Nano Lett. 2010, 10, 726-731.
[2] R. C. G. Naber, K. Asadi, P. W. M. Blom, D.M. de Leeuw, B. de Boer, Adv. Mater. 2010, 22, 933-945.
[3] K. Noda, K. Ishida, A. Kubono, T. Horiuchi, H. Yamada, J. Appl. Phys, 2003, 93, 2866-2870.
[4] Product provided by DAIKIN INDUSTRIES.

COLLOID-POLYMER ASSEMBLIES FOR BIOMIMETIC COMPOSITES

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Abstract

The classic engineering polymer composites consist of disordered small weight fraction of reinforcing units in matrix polymers. This approach allows high strength and stiffness. However, toughness remains more challenging. Biological nanocomposites (like pearl of nacre, silk, insect exoskeletons, and bone) allow toughness in combination with strength and stiffness. In contrast to engineering nanocomposites, the biological nanocomposites involve high weight fraction of self-assembled reinforcing units separated by soft domains involving sacrificial fracture energy dissipating units and hidden length scales. Here we will present biomimetic approaches towards them. First, we will use pearl of nacre as inspiration, when we construct nanoclay (montmorillonite)/polymer self-assemblies using one-step processes, using nanoclays coated with polymers.[1-4] We e.g. show that nanoclay coated by polyvinylalcohol will allow controlled crack propagation in the hydrated state.[3] We will describe supramolecular constructs towards sacrificial bonds, using DNA-like supramolecular interactions.[4] We will describe related approaches based on using polymer-coated colloidal nanocellulose fibrils.[5,6] Nanobrillated cellulose, having steel-strong mechanical properties and diameter in the nanometer range, is coated using adsorbed copolymer layers based on electrostatic interactions. In-depth characterization is shown describing the effect of soft polymer coatings on the mechanical properties.

References

[1] A. Walther, I. Bjurhager, J.-M. Malho, J. Pere, J. Ruokolainen, L. Berglund, O. Ikkala, Nano Letters, 2010, 10, 2742–2748.
[2] A. Walther, I. Bjurhager, J.-M. Malho, J. Ruokolainen, L. Berglund, O. Ikkala, Angew. Chem., Int. Ed., 2010, 49, 6448 –6453.
[3] T. Verho, M. Karesoja, P. Das, L. Martikainen, R. Lund, A. Alegría, A. Walther, O. Ikkala, Adv. Mat., 2013, 25, 5055-5059.
[4] L. Martikainen, A. Walther, J. Seitsonen, L. Berglund, O. Ikkala, Biomacromolecules 2013, 14, 2531-2535.
[5] M. Wang, A. Olszewska, A. Walther, J.-M. Malho, F. H. Schacher, J. Ruokolainen, M. Ankerfors, J. Laine, L. A. Berglund, M. Österberg, O. Ikkala, Biomacromolecules, 2011, 12, 2074-2081.
[6] M. Poutanen, M. Sc. Thesis, 2013, article in preparation.

MESO-SCALE SIMULATION OF SELF-ASSEMBLED DIBLOCK COPOLYMERS IN SOLUTION

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Abstract

Successful production of isoporous membranes by self-assembly of block copolymers, such as PS-b-P4VP, has been recently reported by our group [1, 2]. Experimental data on the self-assembly of block copolymers demonstrates that the existence of order in solution drives the final membrane structure [2]. However, a complete picture of the mechanisms governing the multi-scale phenomena of self-assembly in solution has not been achieved yet. To accelerate the process of understanding of the membrane structure formation, we complement the experimental evidence of micelle assembly to form the pores obtained by small-angle x-ray scattering and cryo electron microscopy [2] with computational modeling and simulation. We used a stochastic particle model, Dissipative Particle Dynamics (DPD), to study self-assembly of di-block copolymers in solution, at different concentrations and solvent-polymer interactions that emulate our experimental data setups. The model was able to capture the relevant features, governing the self-assembly of di-block copolymers in solution, reproducing both 2D hexagonal and lamellar configurations observed in solution and in the final membrane structur

References

[1] S. P. Nunes et al. Langmuir 2011, 27, 10184-10190.
[2] D. S. Marques et al. Soft Matter 2013, 9, 5503-5658.

CORONA-FREE NANOPARTICLE IONIC MATERIALS: SYNTHESIS, PROPERTIES, AND APPLICATIONS

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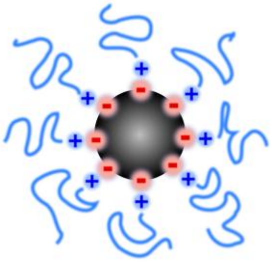
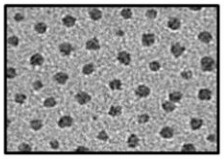
Abstract

We report an ionic hybrid based on silica nanoparticles as the anion and amine-terminated poly(ethylene oxide) (PEO) as a cation. The charge on the nanoparticle anion is carried by the surface hydroxyls. SAXS and TEM reveal an exceptional degree of dispersion of the silica in the polymer and high degree of order in both thin film and bulk forms. The synthesis is highly scalable due to straightforward chemistry involved, and is extensible to a variety of systems. In addition to better dispersion, the ionic hybrid shows improved flow characteristics compared to silica/PEO mixtures in which the ionic interactions are absent. In addition to forming a highly dispersed system of particles, this scalable approach to synthesis opens avenues to number of application areas where hybrid materials are desirable but until now were unfeasible for widespread use, including battery electrolytes and lubricants.





References

[1] N. J. Fernandes, J. Akbarzadeh, H. Peterlik, E. P. Giannelis, ACS Nano 2013, 7, 1265-1271.
[2] N. J. Fernandes, H. Koerner, E. P. Giannelis, R. A. Vaia, MRS Commun. 2013, 3, 13-29.
[3] N. J. Fernandes, T. J. Wallin, R. A. Vaia, H. Koerner, E. P. Giannelis, Chem. Mater. 2013 (DOI: 10.1021/cm402372q)

ASYMMETRIC BLOCK COPOLYMER MEMBRANES WITH POROSITY INDUCED BY H-BOND COMPLEX FORMATION

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Abstract

Isoporous asymmetric nanoporous membranes have been manufactured by simultaneous self-assembly of poly (styrene-b-4-vinylpyridine) in different solvent mixtures followed by nonsolvent induced phase separation[1]. The morphology depends on the chosen solvent, as well as on the copolymer block sizes and ratios. Here we propose how the addition of small amounts of hydrogen-bond forming agents can be used to tailor the pore morphology, while keeping the same solvent and block copolymer composition. Different -OH and –COOH functionalized organic molecules were used as complexing agents. The morphology was investigated by scanning electron and atomic force microscopy. A detailed rheological investigation was conducted, measuring the storage and loss moduli, to understand the role of each complexing molecule in solution[2]. Infra red spectroscopy supplied information on the strength of the hydrogen bond and dynamic light scattering informed the size of micelles and aggregates in solution. The following series of additives led to pores with hexagonal order with increasing pore size: terephthalic acid (COOH-bifunctionalized) < rutin (OH-multifunctionalized) < 9-anthracenemethanol (OH-monofunctional- ized) < 3,5-dihydroxybenzyl alcohol (OH-trifunctionalized)

References

[1] S. P. Nunes, A. R. Behzad, B. Hooghan, R. Sougrat, M. Karunakaran, N. Pradeep, U. Vainio, K. V. Peinemann, ACS Nano 2011, 5, 3516-3522.

[2] P. Madhavan, K.-V. Peinemann and S. P. Nunes, Applied Materials and Interfaces 2013, 5, 7152-7159.

INSIGHTS INTO THE MECHANISM OF POLYHOMOLOGATION REACTION OF YLIDES ($CH_2S(O)Me_2$ and $CH(Ph)S(O)Me_2$)

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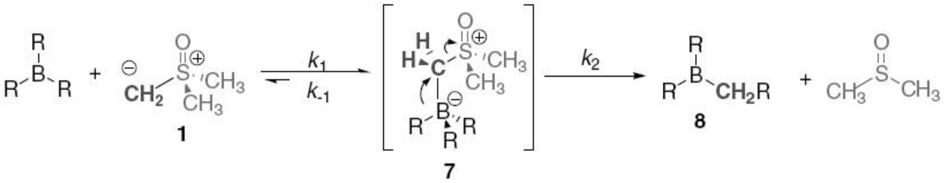
Abstract

Recently, Shea et al described a new approach for the controlled synthesis of polymethylene, named polyhomologation.[3] The polyhomologation reaction uses an organoborane as the initiator/catalyst and dimethylsulfoxonium methylide **1** as the monomer to produce perfectly linear polymethylene. The general reaction mechanism (see Figure below) involves association of ylide and trialkylborane to form a zwitterionic complex **7**, which subsequently undergoes a rate-limiting 1,2-migration step to insert a methylene unit into a boron-terminated polymer chain **8**. The polymer backbone is built up one carbon at a time. This step also regenerates the Lewis-acid site. Very recently, Hadjichristidis et al developed a novel one-pot methodology for the synthesis of PE-based block copolymers with a well defined 3-arms star macromolecular architecture. [4]



To shed light on the mecanism of polyhomologation of methylene based ylides, and to explore the potential of more substituted ylide monomers, in the present study, we investigated the mechanism of one complete polyhomologation cycle for ylide monomers $CH_2S(O)Me_2$ and $CH(Ph)S(O)Me_2$ using a density function theory (DFT) calculations. A complete cycle refers to the addition of three CH_2= or PhCH= groups to the three ends of the $B(CH_3)_3$ polymer chain. Additionally, we evaluated the influence of steric repulsion on the second cycle of polyhomologation due to the presence of bulky CH-Ph groups. Comparison of the thermodynamics of the first polyhomologation cycle indicates that for both monomers, $CH_2S(O)Me_2$ and $CH(Ph)S(O)Me_2$, the addition step is largely exothermic. Differently, our calculations suggest a remarkable difference in second polyhomologation step, which becomes difficult with the bulky $CH(Ph)S(O)Me_2$ monomer.

References

[1] O. G. Piringer, A. L. Baner, VCH Verlagsgessellschaft, Weinheim, Germany, New York, **2008**.
[2] K. Ziegler, E. Holzkamp, H. Breil, H. Martin, *Angew. Chem.*, **1995**, *67*,541–547.
[3] J. Luo, K. J. Shea, John Wiley & Sons (Asia) Pte. Ltd, Singapore, **2011**, 349-376.
[4] H. Zhang, N. Alkayal, Y. Gnanou, N. Hadjichristidis, *Chem. Comm.*, **2013**, *49*, 8952-8954.

IMPACT OF MOLECULAR ARCHITECTURE ON THE DYNAMICS OF THE GLASS RELAXATION PROCESSES IN BLOCK COPOLYMERS OF THE TYPE S-SB-S

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Abstract

To determine the impact of molecular architecture on the molecular dynamics of the glass relaxation processes of hard blocks in different types of block copolymers, model block copolymers with a variation in both molecular architecture and chemical composition were investigated. Four samples of the type styrene–styrene butadiene–styrene (S-SB-S) were selected. Two are linear triblock and the other are star asymmetric. For the sake of comparison, different polystyrene (PS) homopolymer samples, having comparable chain lengths of the PS blocks present in the S-SB-S block copolymers, have been investigated. Dynamic mechanical measurements have been carried out for the complex shear modulus in the temperature and frequency ranges from 30 to 220 °C and from 10−2 to 30 Hz, respectively. Complete master curves have been constructed for all samples investigated. Moreover, broadband dielectric spectroscopy has been carried out to cover wide temperature and frequency windows, 20 to 150 °C and 10−1 to 107 Hz, respectively. The morphology of samples were determined by transmission electron microscopy (TEM) (Figure 1). The results showed that the molecular dynamics of the glass relaxation process of the PS phases in the block copolymers is dramatically changed when compared to the PS homopolymers. The results are discussed in terms of the applied confinement of the counter soft phase, block lengths, domain thicknesses and the type of end-to-end junctions between the different polymeric blocks.

Keywords: Dynamic mechanical and dielectric spectroscopy, triblock and star asymmetric block copolymers, glass relaxation process, hard and soft confinement.

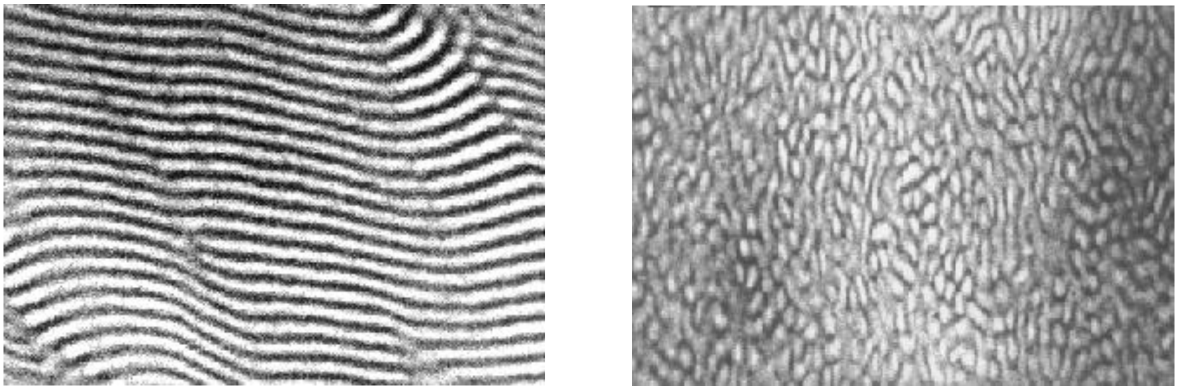

Figure 1 (a) *Figure (1 b)*

Figure 1 (a, b) represents the morphologies of S-SB-S linear triblock (a) S-SB-S star asymmetric (b) copolymer TEM

References

[1] S. Z. Mohammady, *Rheol. Acta,* **2007**, *64*, 1109-1119.
[2] S. Z. Mohammady, Macromol. Chem. Phys., **2001**, 202, 2732-2741.

POLYSULFONE-TRIAZOLE ULTRAFILTRATION MEMBRANES

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Abstract

One of the most relevant drawbacks of membranes for water application is fouling and flux reduction during operation. While hydrophilic surfaces are known to reduce fouling, ultrafiltration membranes are frequently prepared from rather hydrophobic polymers like polysulfone. Strategies to keep the good pore forming characteristics of polysulfone, but increasing the hydrofilicity are proposed to improve the membrane performance. Modified polysulfone 1,2,3-triazole ring substituents containing OH groups was successfully synthesized through click reaction. The structures of the polymers were confirmed using NMR spectroscopy and FTIR. High thermal stability (> 280°C) was observed by TGA. Elemental analysis showed the presence of nitrogen containing triazole group as well as the variation of degree of functionalization (28%, 34%, 40% and 45%), which was achieved by changing synthesis conditions. Being affected by triazole pendant group which increased the flexibility of the polymer chain, the glass transition temperature shifted from 190°C (unmodified) to 183°C (28%), 180°C (34%), 178°C (40%) and 171°C (45%). Ultrafiltration membranes were prepared via phase inversion by immersion in different coagulation baths (NMP/water mixtures with volume ratios from 0/100 to 40/60). The morphologies of these membranes were studied by field emission scanning electron microscopy. The optimized PSU-g-Triazole membranes exhibited water permeability up to 236 $L*m^{-2}*h^{-1}*bar^{-1}$, which is 80 times higher than the unmodified polysulfone membrane (3 $L*m^{-2}*h^{-1}*bar^{-1}$) prepared under the same conditions. This result agrees with the increased hydrophilicity, which can be seen from the lower contact angle (70°) of the modified membrane compared to that of pure polysulfone membrane (79°). The morphologies play an important role in permeability as well. The results of gamma-globulin rejection test indicated that protein anti-fouling property of PSU membranes was improved after modification, and the rejection ration was higher than 99% for all the membranes.

NANOCAPSULES WITH FLUOROUS FILLING: PROGRESS TOWARDS SELF-ASSEMBLED NANOREACTORS

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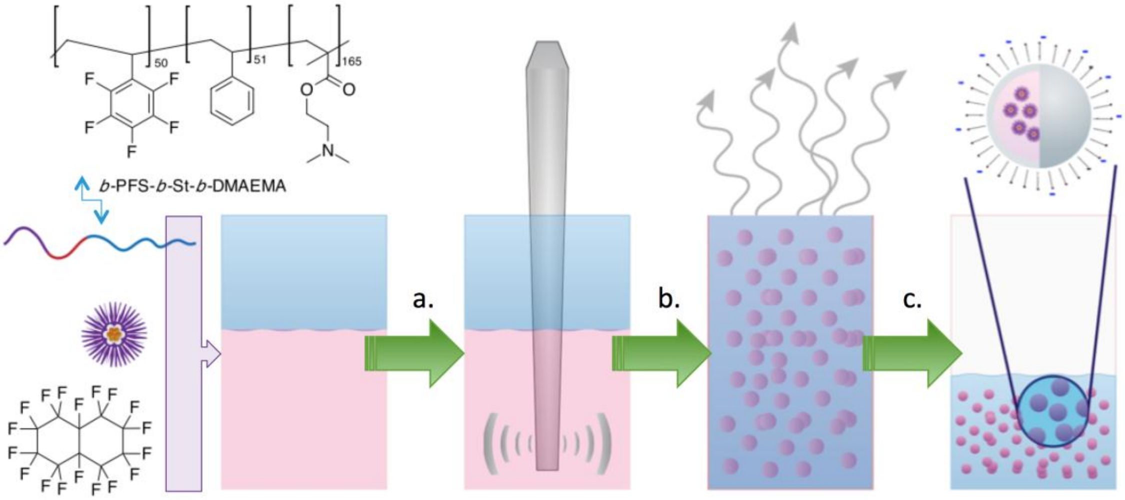


Abstract

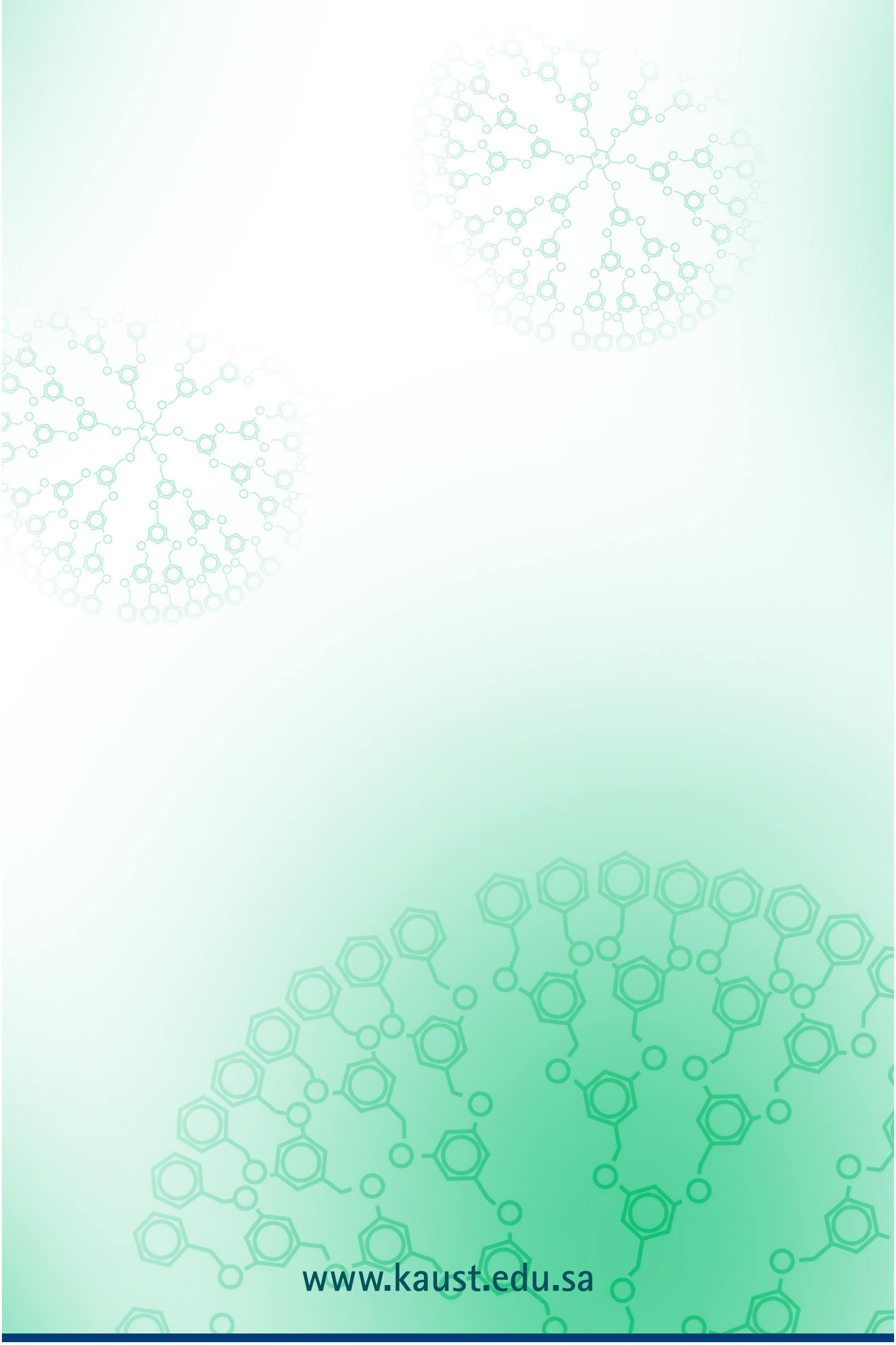
In this presentation, we shall describe the fabrication of water-dispersible nanocapsules filled with superhydrophobic solvents, such as perfluorodecalin. The capsules have been prepared through self-assembly of a variety of amphiphilic block-copolymers around miniemulsion droplets using a simple solvent evaporation technique.1,2 We investigated a range of block-copolymer architectures, varying the block length, monomer nature, and length. The capsules prepared in this way show promise as gas transport vehicles, due to anomalously high solubility of both O2 and CO2 in perfluorinated solvents.3 Furthermore, we were able to entrap metal nanoparticles coated with fluorous coronas into the capsules. The catalytic activity of nanocapsule materials is being actively explored.

References

[1] Fickert, J.; Wohnhaas, C.; Turshatov, A.; Landfester, K.; Crespy, D. *Macromolecules* **2013**, *46*, 573-579.

[2] Diou, O.; Tsapis, N.; Giraudeau, C.; Valette, J.; Gueutin, C.; Bourasset, F.; Zanna, S.; Vauthier, C.; Fattal, E. *Biomaterials* **2012**, *33*, 5593-5602.

[3] Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; Wiley-VCH: Fachbereich Chemie der Philipps-Universität Marburg Hans-Meerwein-Straße 35032 Marburg Germany, 2003; pp 1-645.



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