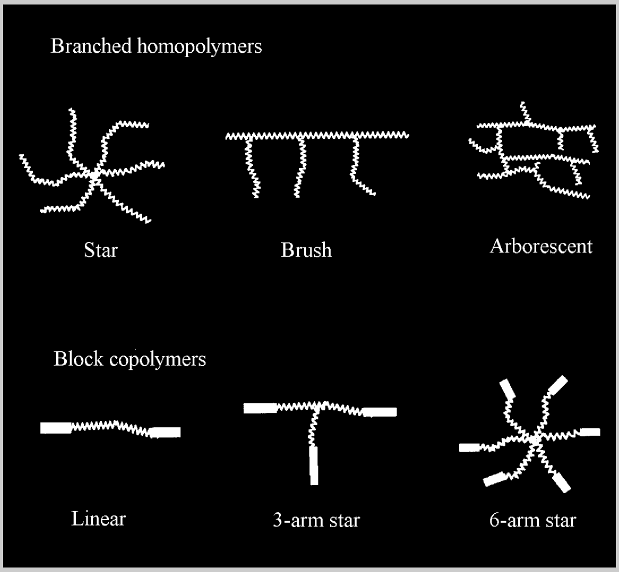
Macromol. Mater. Eng. **2001,** *286,* 565–582

Macromolecular Materials and Engineering

Feature Article: This article features macromolecular engineering via carbocationic polymerization, the focus of research of the recently established Macromolecular Engineering Research Centre (MERC) at the University of Western Ontario. The fundamental philosophy of MERC is interdisciplinary research with a strong industrial orientation, while emphasizing the quest for fundamental understanding of polymerization processes and polymer structure-property relationships. First, a brief overview of living polymerizations in general, and living carbocationic polymerizations in particular will be given. This latter technique is of interest because some monomers (e.g., isobutylene) can be polymerized by cationic techniques only, to yield polymers with unique properties (e.g., polyisobutylene with superior chemical and oxidative stability, low permeability and high damping). This will be followed by an overview of our research strategy and a summary of our latest results. These include the development of a fiber-optic mid-FTIR method for the real-time monitoring of low temperature polymerization processes, the discovery that selected epoxides initiate effectively the living carbocationic polymerization of isobutylene, fundamental studies into the mechanism and kinetics of living carbocationic polymerization, and the design and synthesis of various polymer architectures (e.g., branched homo- and block copolymers) with improved properties and nanostructured phase morphologies.



Star, brush-like and hyperbranched structures and block copolymers.

Macromolecular Engineering via Carbocationic Polymerization: Branched Structures, Block Copolymers and Nanostructures

Judit E. Puskas,[1] Prince Antony,[1] Yongmoon Kwon,[1] Christophe Paulo,[1] Milan Kovar,[2] Peter R. Norton,[2] Gabor Kaszas,[3] Volker Altstädt[4]*

[1] Macromolecular Engineering Research Center, Department of Chemical and Biochemical Engineering, University of Western Ontario, London, Ontario, N6A 5B9, Canada
[2] Department of Chemistry, University of Western Ontario, London, Ontario, N6A 5B9, Canada
[3] Rubber Division, Bayer Inc., 1265 Vidal St. South, Sarnia, Ontario, N7T 7M6, Canada
[4] University of Bayreuth, Faculty for Applied Natural Science, Department of Polymer Engineering, IMA II, Universitätstr. 30, D-95440 Bayreuth, Germany

Introduction

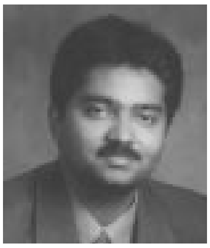
Macromolecular engineering is a relatively new term, and is used to describe the ability to have control over polymerization processes in order to design and make well-defined and complex macromolecular architectures. It has been recognized that changing the molecular architecture of well-known polymers can lead to improved and/or new properties, opening avenues for new applications.[1–5] These new structures can be stars, brush-like chains, hyperbranched and arborescent structures, or self-assembling block copolymers with various molecular architectures (Figure 1). There is considerable industrial and academic interest in synthesizing various polymer architectures and establishing structure-property relationships. Industry has also a vested interest in designing commercially feasible processes to produce polymeric structures

1438-7492/2001/1010–0565$17.50+.50/0

with improved properties. Research and development in macromolecular engineering need to be a collaborative effort between academe and industry, achieving a synergy that neither side could achieve alone. The Macromolecular Engineering Research Centre (MERC) was founded in 1996 at the University of Western Ontario, Canada, to foster such synergistic research. As the director of MERC and the principal author of this feature article, I will try to give an overview of our research philosophy as well as our latest results in macromolecular engineering. Having transferred from industry into academe, I feel that I have a good understanding of industry's needs, which I try to highlight to our students. At the same time, I have a quest for fundamental understanding, which cannot always be accommodated by the time constraints of industry. I believe that the results presented here will demonstrate the success of our approach to macromolecular engineering through collaboration. This approach is very broad based, and spans process research, product characterization, chemical engineering, chemistry, materials research and applications ranging from commodity to specialty medical applications. While this approach is broad, the collaborative efforts of outstanding individuals ensure that it is not shallow. The results will speak for themselves.

In macromolecular engineering, it is recognized that living polymerization is the only viable technique avail-

Judit E. Puskas received a PhD in plastics and rubber technology in 1985, and an M. E. Sc in organic and biochemical engineering in 1977, from the Technical University of Budapest, Hungary. Her advisors were Professors Ferenc Tüdös and Tibor Kelen of Hungary, and Professor Joseph P. Kennedy at the University of Akron, Ohio, USA, in the framework of collaboration between the National Science Foundation of the USA and the Hungarian Academy of Sciences. She started her academic career in 1996. Before that she was involved in polymer research and development in the microelectronic, paint and rubber industries. Her present interests include environmentally benign polymerization processes, polymerization mechanisms and kinetics, polymer structure/property relationships, the biomedical application of polymers and the combination of biopolymers and synthetic polymers. She has been published in more than 170 publications, including technical reports and is an inventor or co-inventor of 14 U.S. patents and applications. She is a member of the Advisory Board of the European Polymer Journal. She holds the Bayer/NSERC (Natural Science and Engineering Research Council of Canada) Industrial Research Chair in Elastomer technology. She is the Director of the Macromolecular Engineering Research Centre at UWO, and her research group presently has 11 coworkers. She is member of the IUPAC Working Party IV.2.1 "Structure-property relationships of commercial polymers". She is the recipient of several awards, including the 1999 PEO (Professional Engineers of Ontario, Canada) Medal in Research&Development, and a 2000 Premier's Research Excellence Award.



Prince Antony received his Ph.D. degree in the field of Rubber Technology in 1999 from the Indian Institute of Technology, Kharagpur, and an M.Sc. degree in Chemistry in 1995 from Mahatma Gandhi University, Kerala, India. From 2000 to early 2001, he was a Postdoctoral Research Fellow at the Macromolecular Engineering Research Center in the Department of Chemical and Biochemical Engineering of the University of Western Ontario, Canada. Since April of this year he is employed in 3M Canada Company as a Senior Rubber Technologist. His research expertise includes polymer blends and processing, thermoplastic elastomers, ion-containing polymers, dynamic vulcanization, rubber compounding and reinforcement, polymer modification, viscoelastic properties of elastomers, adhesion science and technology, polymer recycling and composites. He has published more than 20 research papers and is the co-inventor of one patent application.

Yongmoon Kwon is a Ph.D. student in the Department of Chemical and Biochemical Engineering of the University of Western Ontario. He obtained an MSc in Chemical Engineering at Yeungnam University, Korea in 1993. He was then involved in research and development of polymer binders for glass fibers at Owens-Corning Korea Co. He worked as a research engineer at McMaster University in the field of dispersed air effects in brownstock washing in the Pulp and Paper Research Centre. He joined the Macromolecular Engineering Research Centre (MERC), directed by Dr. Puskas, at the University of Western Ontario, as a Ph.D. candidate in February of 2000. His research interests include the synthesis, mechanical properties and phase morphology of multiarm-star and arborescent polyisobutylene-polystyrene block copolymers.

Christophe Paulo received his Ph.D. in Engineering Science from the University of Western Ontario in 2000, and his Master's Degree in Organic Chemistry from the University of Bordeaux I, France, in 1997. His advisor was Professor Puskas at the Macromolecular Engineering Research Centre at UWO, in the framework of collaboration between Bayer, the Natural Science and Engineering Research Council of Canada and UWO. His research involved branched polymers (comb, star and hyperbranched or arborescent structures), polymerization mechanisms and kinetics, and polymer structure/ property/ rheology relationships. Presently he is employed by Rhodia Research (Applications Des Polymères Et Spécialités, Centre De Recherche De Lyon, Lyon, France). He has 7 publications, including technical reports, and is a co-inventor of French and Canadian patents and applications. His field of interest is new functional textiles and fibers that are environmentally friendly, lighter and elastic, offering better comfort and easy care.

able to control molecular architecture.[1–6] We have been using this technique, more specifically, living carbocationic polymerization, in our research. In the next sections, living polymerization in general and living carbocationic polymerization in particular will be discussed.

Living Polymerization

The term, 'living polymerization', was introduced by Szwarc.[7] He used this term to distinguish polymerizations in which chain breaking processes such as termination and transfer reactions are absent. Living polymerization provides control over the molecular weight (MW) and molecular weight distribution (MWD) of the polymers produced. The number-average molecular weight ($\overline{M}_n$) at any given conversion can be calculated from Equation (1):

$$\overline{M}_n\ (\mathrm{g/mol}) = \Delta \mathrm{M}\ (\mathrm{g})/\mathrm{I}\ (\mathrm{mol}) \qquad (1)$$

where ΔM is the amount of monomer converted into polymer, and I is the molar amount of initiator. In living polymerizations, $\overline{M}_n$ increases linearly with conversion, and in the case of instantaneous initiation, the polymers

Peter R. Norton is a Professor of Chemistry at the University of Western Ontario. His specialization is the study of surfaces and interfaces in modern materials and particularly the study of nanoscale phenomena. His current interests include surfaces and interfaces relevant to the properties of metals, alloys, polymers, composites, organic light emitting diodes, semiconductors, biomaterials and biological materials, such as cells. His group houses a wide range of techniques, some unique to his laboratory, such as interfacial force microscopy (IFM), a technique capable not only of nm-scale imaging, but also of making quantitative measurements of interfacial forces, moduli, hardness etc. with ~ 20 nm spatial and < 1 nm depth resolution. In the polymer area he is using IFM to determine localized moduli of polymer surfaces and, potentially, localized storage and loss moduli, and microscopic adhesion phenomena. He is currently developing sub-microsecond IR techniques to determine relaxation times of polymer components subject to periodic mechanical stresses. The relationship between chemical structure and composition and the nanometre scale mechanical properties of materials is a central theme of his group.

Milan Kovar is a Research Associate with Professor Peter Norton in the Chemistry Department of the University of Western Ontario. He trained at the Czech Academy of Sciences and is a specialist in surface and interface science, particularly in IR spectroscopy and nanoscale phenomena in polymer science, such as the molecular origins of stress cracking. He has worked at Cambridge University and the University of Texas before coming to UWO. He is currently developing sub-microsecond time resolved broad band IR for studies of materials and interfaces, including the relaxation of polymer side-chains to periodic stress. He is also actively developing new nanoscale mechanical probes of surfaces and interfaces.

Gabor Kaszas received his M. E. Sc in organic and biochemical engineering in 1977 and a Ph.D. in plastics and rubber technology in 1991 from the Technical University of Budapest, Hungary. In the initial years of his professional carrier, he worked for the Central Research Institute for Chemistry of the Hungarian Academy of Sciences, studying the kinetics and mechanism of the radical polymerization of butyl-acrylate and styrene. He obtained a Candidate of Chemical Sciences degree from the Hungarian Academy of Sciences in 1986. He worked for a total of five years at the University of Akron as a visiting scientist in Professor Kennedy's lab before joining Polysar (now Bayer) in 1989. Presently he works as a Science Advisor in the Butyl Technology Group of the Technology Department of Bayer Inc. His research interest is broad. It includes the study of the kinetics and mechanism of polymerization and polymer analog reactions, design of new products by controlling the chemical and physical pathway of the reactions, establishment of structure/property (physical and rheological) relationships, including the cure and cured properties of elastomers. He has published 38 papers in various journals and is the inventor or co-inventor of 10 patents.

Volker Altstädt: Since October 1, 2000, the Department for Polymer Engineering at the Faculty of Applied Natural Science at the University of Bayreuth is led by Prof. Dr.-Ing. Volker Altstädt. After completing his studies in Physics and his Ph.D at the Department of Mechanical Engineering under the supervision of Professor Dr. Ing. G.W. Ehrenstein at the University of Kassel, he was employed in the Polymer Research Division of BASF-AG in Ludwigshafen (Germany), where he continued his research for 8 years. Before his move to the University Bayreuth he was qualified for professorship in 1995 and became a faculty member at the Technical University Hamburg-Harburg where he was appointed as Head of the Department of Polymers and Polymer Composites. Professor Altstädt has conducted research in the field of polymers and polymer composites and has made major contributions to both basic science and applied technology during his 16-year scientific career in industry and in government research. His main research expertise is in the field of polymer blends, polymer foams and the fatigue of polymers. He has authored or coauthored more than 60 papers and 7 patents. He is a member of the IUPAC Working Party IV.2.1 "Structure property relationships of commercial polymers". He is also a member of the advisory board of the German Engineering Unification VDI-K and of the Editorial Board of Journal of Polymers and Composites.

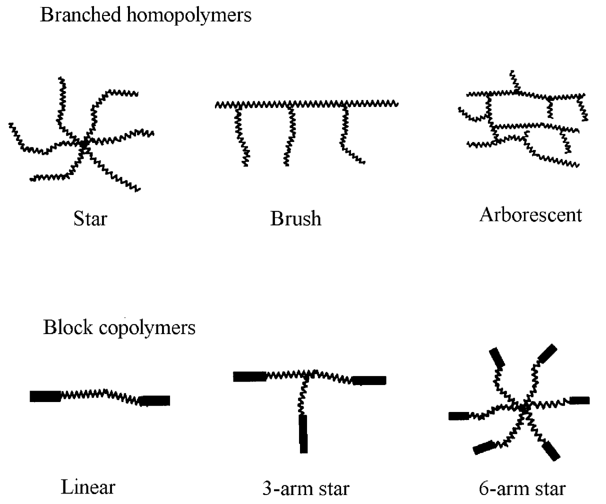


Figure 1. Star, brush-like and hyperbranched structures and block copolymers.

produced in a batch reactor will have a polydispersity described by the Poisson distribution:

$$\overline{M}_w/\overline{M}_n = DP_w/DP_n = 1 + 1/DP_n \qquad (2)$$

where $\overline{M}_n$ and DP_n, and $\overline{M}_w$ and DP_w are the number- and weight-average MW and degree of polymerization (DP), respectively. Under controlled conditions, nearly uniform polymers can be produced at sufficiently high MWs. The term 'living polymerization' is now related to synthetic polymers and represents controlled processes. This control, however, is still far from **real living** polymerizations that produce truly monodisperse long chain molecules such as proteins.[8] The achievement of this type of control requires the interfacing of polymer science with genetic engineering, a new revolution for the second millennium. Our perspective of the history of living polymerization was described recently.[5]

It has been predicted, based on theoretical considerations, that living carbocationic polymerization cannot be achieved due to the inherent instability of carbocations.[9] Living radical polymerization seemed even less possible. Living cationic and radical polymerizations are a reality today. Key to achieving living conditions is the utilization of "temporary deactivation" at the active centers:[4]

$$\underset{\text{inactive}}{P_n} \Longleftrightarrow \underset{\text{active}}{P_n^*}$$

$$P_n^* + M \Longrightarrow P_{n+1}^*$$

The active species can be free radicals or ionic species. It has been demonstrated by computer simulation that living conditions, i.e., steady polymerization rates demonstrated by linear semilogarithmic rate plots, together with linear $\overline{M}_n$ vs conversion plots and narrow MWD, can be achieved with the coexistence of species with different reactivities, provided the exchange between these species is fast enough.[4] The temporary deactivation process seems to protect the free radicals or ionic species from side reactions long enough for synthetic manipulation. It is understood that chain-breaking processes might be identified in polymerizations which are considered living today.[4,5] According to our pragmatic macromolecular engineering view, the real essence of living polymerization is the ability to control the process.[5] Except for block copolymer production, the uniformity of the polymer can be considered a disadvantage, since polydispersity improves the physical properties and/or processability of commodity polymers.[10] From an industrial point of view, it is also considered to be a disadvantage in living polymerizations that one initiator molecule produces only one polymer chain. However, the ability of living polymerization to produce new polymeric structures in a controlled manner may override these and other concerns. Anionic living polymerizations have long been commercialized, producing branched polybutadienes for high impact polystyrene production, styrene-isoprene-butadiene terpolymers and various functionalized rubbers for tire production, and styrenic block copolymers (recyclable rubbers).[10] Therefore, it is quite interesting that anionic polymerization is still viewed as a delicate experimental technique with limited capabilities.[6] In fact, ionic living polymerizations, including the relative newcomer, cationic living polymerization, are quite robust if handled with expertise. Ironically, large-scale commercial ionic polymerizations require less stringent conditions than laboratory procedures, due to the much smaller surface-to-volume ratios. Commercial examples of living cationic polymerizations include poly(vinyl ethers) used in liquid crystal technology,[11] polystyrene-polyisobutylene-polystyrene block copolymers and functionalized polyisobutylenes which have been test-marketed recently.[12] Our research efforts concentrate on living carbocationic polymerizations, so this process will be discussed in more detail.

Living Carbocationic Polymerization

Certain monomers such as isobutylene (IB) can only be polymerized cationically. The importance of this mechanism is demonstrated by various commercial processes.[13] Due to the high reactivity of carbocations, which tend to enter into irreversible termination and chain transfer reactions via b-proton expulsion, achievement of carbocationic living polymerization was considered to be impossible.[9] The discovery that reversible temporary deactivation "protects" the carbocations from entering into side reactions, provided the key to controlling carbocationic polymerizations and achieving living conditions. This deactivation is shown for a typical living carbocationic polymerization of isobutylene (IB):

$$\mathrm{TMPCl} + \mathrm{TiCl_4} \overset{K_i = K_1}{\Longleftrightarrow} \mathrm{TMP^+//A^-} \tag{3}$$

$$\mathrm{TMP^+//A^-} + \mathrm{M} \xrightarrow{k_i = k_p} \mathrm{P}_l^+\mathrm{//A^-} \tag{4}$$

$$\mathrm{P}_n\text{-}\mathrm{Cl} + \mathrm{TiCl_4} \overset{K_1}{\Longleftrightarrow} \mathrm{P}_n^+\mathrm{//A^-} \tag{5}$$

$$\mathrm{P}_n^+\mathrm{//A^-} + \mathrm{M} \xrightarrow{k_p} \mathrm{P}_{n+l}^+\mathrm{//A^-} \tag{6}$$

where A^- in general represents a counteranion, and 2-chloro-2,4,4-trimethylpentane (TMPCl) is an effective initiator. This system is used as a model for kinetic investigations, since TMPCl is essentially a polyisobutylene (PIB) dimer, therefore, $k_i \approx k_p$ and K_1 can be considered to be the same during initiation and propagation. Thus the overall (apparent) rate of polymerization, $k_{app} = K_1 \cdot k_p$, is comparable to the overall rate of initiation, which allows all the initiator molecules to start a chain in the early stages of the polymerization. This also gives a chance for all polymer chains to propagate with the same overall rate, leading to more uniform polymers, i.e., narrower MWDs. When k_i is not comparable to k_p, overall initiation rates faster than or equal to polymerization rates can be achieved by adjusting K_i relative to K_1, e.g., changing the experimental conditions; the solvent composition, the use of additives, etc. The key concept of "reversible termination" or "temporary deactivation" was obscured for a long time. Similar to the history of living anionic polymerization,[5] living cationic conditions had been achieved experimentally as early as 1974.[9,14] Some early examples were called "pseudocationic" or "quasiliving", then "truly living", but they displayed very similar characteristics.[5] Remarkably, the same key concept applies in living radical polymerizations. The real power of these systems is their ability to control the polymerization process in order to design and build new polymeric structures, allowing a pragmatic approach to the definition of "livingness" in carbocationic polymerization. The existence of the dynamic equilibrium between dormant covalent and active ionic species is now generally accepted. Ligand exchange and dynamic NMR studies[15–18] supported the evidence of the involvement of ionic species even in polymerizations that were thought to proceed by a "pseudocationic" or "insertion" mechanism. The narrowness of the MWD will depend on the dynamics of the equilibrium. The development of MWD in a living isobutylene polymerization with reversible deactivation and no detectable transfer was described as follows:[19]

$$DP_w/DP_n = 1 + l/DP_n \tag{7}$$

where run length, $l = (k_p/k_{-1})[\mathrm{M}]$, is the average number of monomer units incorporating in a productive ionization period. Equation (7) reduces to the Poisson distribution when $l = 1$ (see Equation (2)). The magnitude of l will define the narrowness of the MWD. At sufficiently high MW, $l = 25$ still yields $\overline{M}_w/\overline{M}_n < 1.1$.[19,20] Based on Equation (3), a further criterion for living carbocationic polymerizations with reversible deactivation can be defined as follows:[5]

$$\overline{M}_w - \overline{M}_n = \text{constant} \tag{8}$$

Thus the criterion of Poisson or very narrow MWD does not seem to be necessary in the definition of living polymerizations, because the Poisson distribution is a subcase of the general definition for $l = 1$. In fact, living carbocationic polymerization can be viewed as a process where the most probable distribution of monomer incorporation during an active ionization period is superimposed on a Poisson distribution of the repeating events of ionization periods. Depending on the lifetime of the active cationic species, the run length l can be $l \gg 1$, resulting in broader MWD. For instance, at $l = 50$, at $DP_n = 50$ the MWD will be $\overline{M}_w/\overline{M}_n = 2$. With increasing conversion, the MWD will get progressively narrower. It was shown by computer simulation that the coexistence of ion pairs and ions with identical reactivities but different lifetimes could lead to a bimodal distribution.[4] This is very important in light of the groundbreaking work of Mayr and coworkers who showed in model studies that the rate constants of electrophilic addition of benzhydryl cations, and corresponding ion pairs, to alkenes are identical.[21] Roth and Mayr[22] measured the rate constant of propagation for isobutylene to be in the diffusion range ($k_p = 6 \times 10^8\ \mathrm{L \cdot mol^{-1} \cdot s^{-1}}$) so propagation proceeds practically without activation energy, and entropy factors become very important.[23] This phenomenon is in line with the concept of "run length" discussed before, that is, that several monomer units will incorporate into the chain during each productive ionization period. It also indicates that the methods successfully used to mediate living carbocationic polymerizations (nucleophilic counteranions; added nucleophiles; added salts[4]) in fact may alter the dynamics of the equilibrium via entropy effects. The MW criteria may also be relaxed. It is possible that slow termination/transfer is operational in carbocationic polymerizations believed to be living today, and this might be the reason for not reaching very high MWs. This can be overcome by using multifunctional initiators, linking of shorter chains with crosslinking agents, or producing arborescent (random hyperbranched) polymers using an initiator carrying a polymerization-active functional group to reach high MWs. All three methods yielded polymers with $\overline{M}_n > 400\,000$ g/mol.[24–30]

Kinetic investigations showed that living isobutylene polymerization co-initiated by $\mathrm{TiCl_4}$ proceeds via ion pairs[19,31,32] and that the ionization equilibrium is strongly shifted towards covalent species (see Equation (6)). A similar mechanism was suggested for the living polymerization of isobutyl vinyl ether initiated by the monomer chloride/$ZnCl_2$ system. The following kinetic equations were developed for both systems.[31,33]

$$\ln([I]_0/[I]) = k_1 \times [LA]_0 \times t \tag{9}$$

$$\ln([M]_0/[M]) = k_p' \times [LA]_0 \times [I]_0 \times t' \tag{10}$$

where LA stands for Lewis acid, and $k_p' = K_1 \cdot k_p = (k_1/k_{-1}) \cdot k_p$. The reaction kinetics were studied in more detail in living isobutylene polymerizations. While the various systems investigated differ in the nature of initiator (I), additives (electron pair donors or proton traps) and solvents, the kinetic order with respect to initiator has been reported to be 1. The reaction order of the monomer was found to be 1 in most cases, but apparent zero order monomer dependence has also been reported.[17,34–38] The reaction order with respect to the Lewis acid has been debated. Most research groups reported second order dependency in $TiCl_4$-coinitiated systems, but first order dependence was also claimed under certain conditions.[31,39–41] The coexistence of monomeric and dimeric counterions was also postulated.[42] The role of certain additives is also debated.[4,39,42–56] While the effect of nonpolar medium and common ion salts was demonstrated to be shifting the ionic equilibria towards less dissociated species, the role of added nucleophiles and proton traps such as 2,5-di-*tert*-butylpyridine is still obscure. In the case of isobutylene polymerization, the effectiveness of these nucleophiles or electron pair donors was classified according to their Gutmann donor number;[36] defined as the molar enthalpy value of the interaction of the donor with the reference acceptor, $SbCl_5$.[57] The most effective nucleophiles such as *N*,*N*-dimethylacetamide or dimethyl sulfoxide have high Gutmann donor numbers. It was suggested that the role of additives is merely proton scavenging.[43,53] In fact, some additives were used as colorimetric indicators of effective proton scavenging.[58] At the same time, proton traps and donors were found to reduce the rate of isobutylene polymerization.[32,46,47,58] For isobutylene, the effectiveness of electron pair donors in preventing side reactions such as protic initiation, or electrophilic aromatic substitution and improving initiator efficiencies by reducing the overall propagation rate relative to initiation when aromatic initiators are used, were shown to increase with increasing Gutmann donor numbers.[36,59] The proton trap, 2,5-di-*tert*-butylpyridine, was found to cause proton elimination and subsequent chain coupling.[50,52]

The exact mechanisms and kinetics of various carbocationic polymerizations exhibiting living behavior remain debated. It is still controversial whether living carbocationic polymerization is a chemical or kinetic phenomenon.[31,33] All investigators, however, agree on the synthetic power of this method for the preparation of well-defined macromolecules. This technique was called "macromolecular engineering".[1] Both the term and the technique are widely used in the scientific community. Reaction order and polymerization rate information become important in macromolecular engineering, thus more research is needed in this area. Literature search revealed that publication activity in fundamental studies in cationic living polymerization peaked around 1993/1994 and has since been declining.[5] The emphasis shifted towards radical polymerizations exhibiting living character[4–6] and macromolecular engineering using living polymerization. Our research group has been concentrating on macromolecular engineering via carbocationic polymerization, and structure-property relationships of novel structures produced by carbocationic polymerization. We have developed the capabilities to produce polymers in sufficient quantity for meaningful mechanical and physical characterization (1 pound/batch). The following sections will discuss our latest results.

Results and Discussion

1. Polymerization

Our approach towards macromolecular engineering targeted a better understanding of the mechanism and kinetics of living carbocationic polymerizations. We have systematically been investigating several systems, including new initiators, and developed novel monitoring and characterization methods.

1.A) Real-Time Monitoring of Living Carbocationic Polymerizations

In the course of our investigations, we developed a novel fiber optic FTIR technique for the *real-time in-situ* monitoring of low temperature carbocationic polymerizations. The fiber optic probe can carry either an ATR (attenuated total reflectance) or a more sensitive TR (transmission) head, and is immersed into the reactor as shown in Figure 2.

The versatility of this system is apparent. This method has been used to monitor homogeneous living polymerizations as well as heterogeneous emulsion and suspension polymerizations, and gave insight into the mechanism and kinetics of initiation and propagation.[40,41,50–65]

1.B) New Initiators for Carbocationic Polymerization

We recently discovered that substituted epoxides can initiate the carbocationic polymerization of isobutylene and styrene. α-Methylstyrene epoxide (MSE), 2,4,4-trimethylpentyl epoxide-1,2 (TMPO-1), 2,4,4-trimethylpentyl epoxide-2,3 (TMPO-2), and hexaepoxysqualene (HES) were shown to initiate IB polymerization in conjunction with $TiCl_4$ (see formulae).[66–70]

A competitive reaction mechanism was proposed for initiation by epoxides, as shown in Figure 3 for MSE.

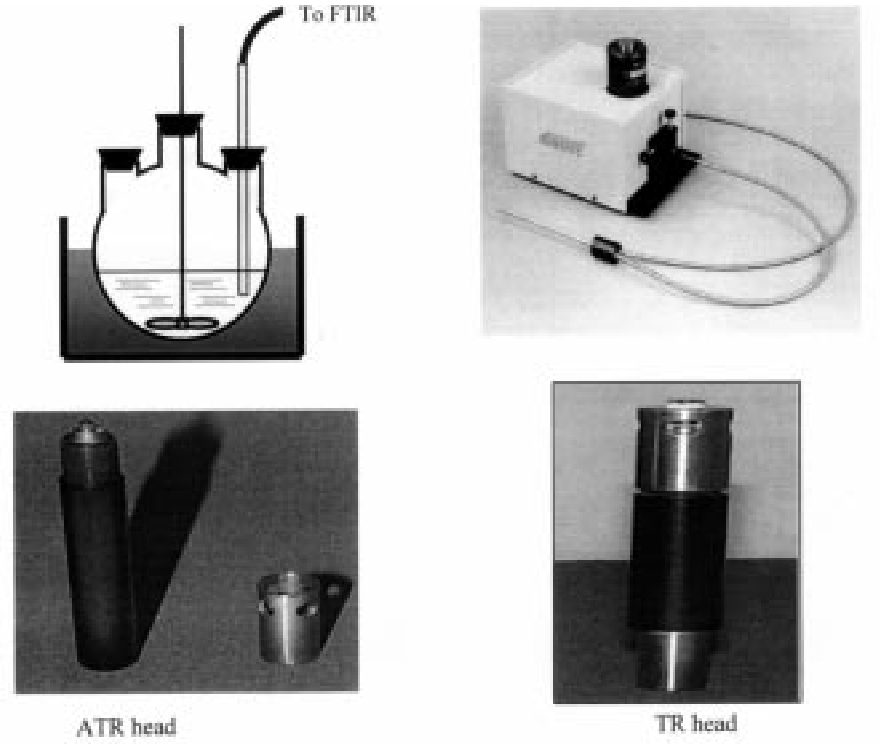
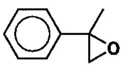
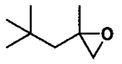


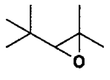
Figure 2. A real-time fiber optic mid-FTIR system for the *in situ real-time* monitoring of carbocationic polymerizations.



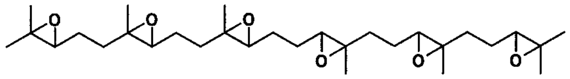
MSE



TMPO-1



TMPO-2



HES

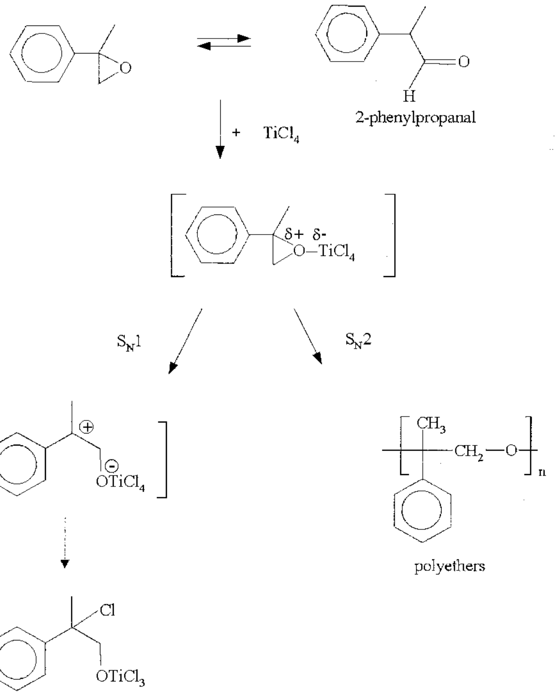


Figure 3. Proposed initiating mechanism of epoxides, shown for the MSE/$TiCl_4$ system.

The *tertiary* carbocation, or [I] forming by the S_N1 pathway, will initiate carbocationic polymerization, while the S_N2 pathway will produce polyethers, which are considered "side product" in the context of initiation. The latter may act as electron pair donor, which have been shown to have a positive influence on the polymerization. According to the proposed mechanism, initiator efficiency (I_{eff}) will be defined by the competition between the S_N1 and S_N2 reaction paths, which in turn will be influenced by the structure of the epoxide. For instance, MSE showed 40% I_{eff}, while TMPO-1 had less than 1% I_{eff}. *In-situ* FTIR monitoring gave further insight into the initiation step,[61] supporting the proposed initiating mechanism. Controlled initiation with external epoxides such as MSE would yield a *primary* hydroxyl head group and a *tert*-chloride end group. The presence of *tert*-chloride end groups was verified by NMR spectroscopy, while the presence of *primary* hydroxyl groups was inferred by model experiments.[68] Recently, we were able to verify that controlled initiation with MSE yielded one *primary* hydroxyl head group per molecule.[71] Multiple initiation by HES resulted in a star polymer with an average of 5.2 arms per molecule.[67] Epoxides are readily available or can be synthesized very easily, and are cost-efficient. Therefore they are attractive initiators for potential commercial living carbocationic polymerization processes. Our research group is presently involved with the investigation of various aspects of the new initiation process, and identifying the most effective epoxides.

1.C) Kinetics and Mechanism of Living Isobutylene Polymerizations

We have been investigating the kinetics of living isobutylene polymerizations, initiated by 2-chloro-2,4,4-trimethylpentane (TMPCl) in conjunction with $TiCl_4$ in methylcyclohexane (MeCHx)/methyl chloride (MeCl) or hexane (Hx)/MeCl 60/40 v/v at $-80\,°C$ in the presence of 2,6-di-*tert*-butylpyridine (D*t*BP) as a proton trap.[40,41,65] This is the model system for the living carbocationic polymerization of isobutylene, discussed in the *Introduction*. At TMPCl/$TiCl_4$ ratios higher than one, the reaction order in $TiCl_4$ was found to be close to 1. A comprehensive kinetic/mechanistic scheme was proposed, involving two competitive reaction pathways (Figure 4).[40]

The pathway on the left (Path A) is first order in [$TiCl_4$], and was found to dominate under $TiCl_4$ deficiency relative to $[I]_0$ as discussed above. The pathway on the right (Path B) is second order in [$TiCl_4$] and dominates when excess $TiCl_4$ relative to $[I]_0$ is used. Since both pathways proceed simultaneously, the experimental [$TiCl_4$] reaction order was measured to be 1.76. This value agrees with others published in the literature.[32,72] According to our present understanding[65,73] the initiation step is greatly affected by the first order pathway and very sensitive to solvent quality and monomer concentration (i.e., polarity), while the overall propagation is dominated by the second order pathway. Monomer concentration and temperature were found to have a profound effect on the polymerization. The apparent rate constant of polymerization, k_p' ($k_p' = K_{eq} \cdot k_p$, where K_{eq} is the equilibrium constant of the dormant-active equilibrium characteristic of living isobutylene polymerization, and k_p is the polymerization rate constant), increased exponentially with an increase of $[IB]_0$ or a decrease in temperature. More surprisingly, the kinetics of the polymerization appeared to be very sensitive to solvent impurities; different results were found when using solvents from two different providers and/or with and without further purification.[65] Our most recent investigations found similar competitive pathways for styrene polymerizations as well. The results will be published shortly.[74] Epoxides initiate only in the presence of excess $TiCl_4$, since cation formation from [I] requires more than equimolar amount of $TiCl_4$ relative to the epoxides. In MSE-initiated living isobutylene polymerization, a $TiCl_4$ order of 1.56 was found.[41] The fraction order indicates that following the initiation step, epoxy-initiated IB polymerizations will also proceed via a competitive mechanism, similar to that shown in Figure 4. The rate of initiation was fast relative to propagation; this can be rationalized by $k_i < k_p$ but $K_i \gg K_1$.

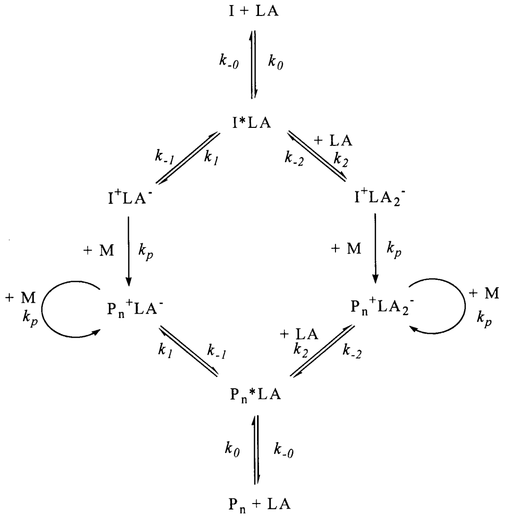


Figure 4. Kinetic/mechanistic scheme proposed for TMPCl/$TiCl_4$ initiated living IB polymerization.[40]

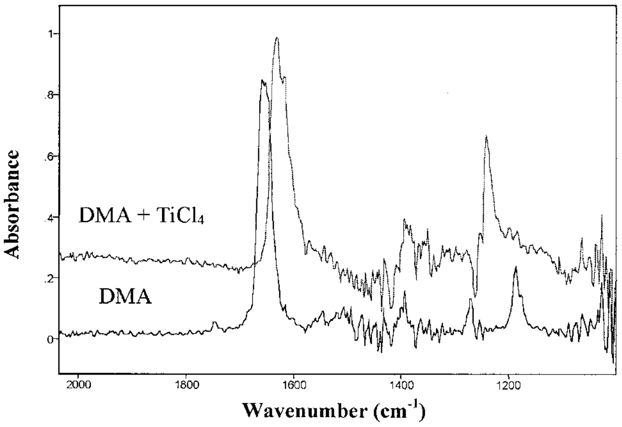


Figure 5. In-situ fiber optic FTIR monitoring of the complexation between DMA and $TiCl_4$. $[DMA]_0$ = 0.05 mol/L; $[TiCl_4]_0$ = 0.1 mol/L; [DtBP] = 0.01 mol/L; MeCHx/MeCl = 60/40 v/v; $T = -80\,°C$.

We have been investigating the effect of additives as well. The D*t*BP concentration did not seem to have an effect on the rate of polymerization under the conditions investigated.[65] Fiber-optic *real-time* FTIR monitoring demonstrated that *N*,*N*-dimethylacetamide (DMA), a strong electron pair donor, complexes with $TiCl_4$ under polymerization conditions as postulated by Storey.[32] Figure 5 contains FTIR spectra of DMA before and after the addition of $TiCl_4$. DMA has a strong carbonyl absorption at 1659 cm^{-1}, and another strong band at 1187 cm^{-1}, assigned to the amide groups. Addition of $TiCl_4$ to DMA in a 2:1 molar ratio shifted the 1659 cm^{-1} band to 1631 cm^{-1}. In contrast, the 1187 cm^{-1} band shifted to 1241 cm^{-1}. These shifts indicate that $TiCl_4$ complexes both on the carbonyl oxygen and the amide nitrogen.[75,76] Further investigations into the role of additives such as DMA in living carbocationic polymerizations using the *in situ* FTIR monitoring technique are in progress. Recent research data provided insight into the mechanism and kinetics of living carbocationic polymerizations and assisted us in designing and synthesizing novel polymeric structures. This work will be discussed next.

2. *Polymer Architectural Design and Synthesis*

The real power of living polymerization is the ability to control the process. This has allowed the synthesis of new polymeric structures such as star-branched polymers, grafts, arborescent (sometimes called hyperbranched) polymers, block copolymers, etc. New polymeric structures yield new and interesting properties, as demonstrated extensively by living anionic polymerization.[77] Cationic polymerization lags behind in the establishment of structure-property relationships and block copolymer morphology studies. In light of only a handful of studies in this area, extensive research is needed, especially for the industrially important polyisobutylene. Polyisobutylene-based elastomers such as butyl and halobutyl rubbers are the commercially most important polymers made by carbocationic polymerizations (butyl rubber is a copolymer of isobutylene with a small amount of isoprene, and halobutyl is its chlorinated or brominated version[9]). Our industrial collaboration is concentrating in this area.

2.A) Branched Polymers

Branched polymers have been in the forefront of research recently, due to some properties markedly differing from their linear counterparts. Branched polymers have lower solution and bulk viscosities and less shear sensitivity than linear polymers of the same MW. Interestingly, the branched nature of some commercial polymers came to light only recently, due to the development of modern detection methods such as laser light scattering or viscometry coupled with size exclusion chromatography (SEC). In traditional polymerization processes, there is little control on branching, in contrast to living polymerization where both the number of branches and their lengths can be controlled. The synthesis of branched polymers by living carbocationic polymerization does not have a long history. Some aspects have been reviewed.[5,78–81] The following is a report of our latest results in this area.

i) Star-Branched Polymers

Star-branched polymers can be made by the "arm first" or the "core first" methods, which were first developed for anionic systems.[82] In carbocationic isobutylene polymerization systems, the "arm first" method was used successfully for the synthesis of star-branched polyisobutylenes with 6–70 arms.[29,30,83–86] In this process, the monofunctional living polyisobutylene chains were reacted with bifunctional monomers such as divinyl- or diisopropylbenzene to form the crosslinked core. This method leads to "ill-defined" cores thus the number of the arms cannot be controlled precisely, and the reaction times were very long (10–100 h). The "core first" method is based on the usage of multifunctional initiators from which the star arms are grown. This method was successfully used for the synthesis of three- and four-arm star polyisobutylenes in non-living systems[87–89] and three- and six-arm star polyisobutylenes in living systems.[90,91] Recently the elegant synthesis of an eight-arm star polyisobutylene using a calixarene-based multifunctional initiator was reported.[92] We successfully synthesized high MW multi-arm-star polyisobutylenes by the "core first" method using multifunctional macroinitiators carrying *tert*-hydroxy functionalities prepared by the radical copolymerization of 4-(2-hydroxyisopropyl)styrene with styrene.[93,94] Star-branched polyisobutylenes with $\overline{M}_n$'s of about 400000 g/mol and average functionalities F = 8–73 were obtained in 30–60 min. The branched structure of the polymers was demonstrated by SEC analysis and selective core destruction. SEC with universal calibration using Mark-Houwink constants available for linear polymers (UCL) underestimates the MW of branched polymers, thus comparison of the MW measured by SEC-UCL and the absolute MW measured by multi-angle laser light scattering (MALLS) provides evidence for branching. For instance, a star with 23 arms and narrow distribution ($\overline{M}_w/\overline{M}_n$ = 1.2) had $\overline{M}_n$ = 267000 and 375000 g/mol by SEC-UCL and MALLS, respectively. The preparation of the macroinitiators is quite laborious and expensive. Following the discovery of epoxy initiation, hexaepoxysqualene (HES) was selected as a robust and cost effective multifunctional initiator. Polymerizations with HES/$TiCl_4$ produced star polyisobutylenes with MWs up to $\overline{M}_n$ = 415000 g/mol (351000 by UC).[68] End-capping the living

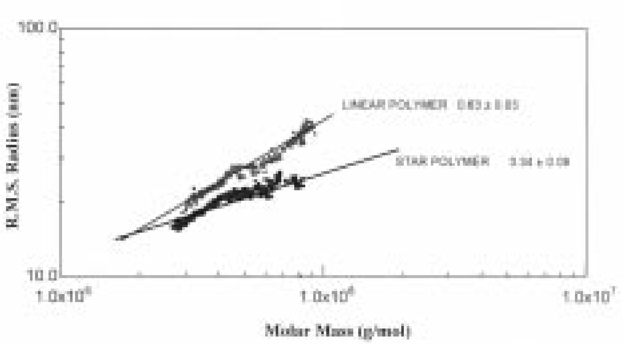


Figure 6. Plots of R.M.S. radius versus molar mass for star PIB and standard linear PS based on SEC analysis. [HES] = 0.00035 mol/L; $[DMA]_0$ = 0.007 mol/L; $[TiCl_4]_0$ = 0.15 mol/L; [D*t*BP] = 0.007 mol/L; [IB] = 2 mol/L; MeCHx/MeCl = 60/40 v/v; T = −80 °C; PIB $\overline{M}_n$ = 290000 g/mol; standard PS $\overline{M}_n$ = 400000 g/mol.

PIBs with diphenylethylene[95] yielded a polymer with 5.2 arms/molecule,[68] as indicated by NMR analysis. Additional evidence is the correlation between the size (radii) and MW of the molecules. Figure 6 shows the radii-MW plot for a representative HES-initiated polyisobutylene and a linear polystyrene. The slope of the line is 0.3, as expected for compact star polymers, in comparison with around 0.5–0.6 expected for linear polymers.[96]

The synthesis of star-branched polyisobutylenes using HES as a multifunctional initiator, along with structure-property relationship investigations, is in progress. An initial study of the viscoelastic properties of selected polymers has appeared recently.[97]

ii) Arborescent Polymers

Arborescent polymers belong to the class of dendritic polymers. Dendrimers have generated a lot of interest in recent years, due to their unusual properties.[98–100] In contrast to dendrimers, arborescent polymers have an irregular tree-like structure. We have used the term "hyperbranched" to describe polyisobutylenes with this kind of structure,[30, 97, 101] but now believe that "arborescent" is a better term.[102] These polymers are a relatively recent development and very little structure-property relationship data is available.[103] We have developed a commercially feasible route for the synthesis of arborescent polymers with very high MW. In this approach a small amount of *inimer,* a compound carrying both and ***ini****tiator* and a *mono****mer*** functionality (IM), is copolymerized with an olefin. Very high MW arborescent polyisobutylenes were successfully synthesized by this method using 4-(2-hydroxyisopropyl)styrene and 4-(2-methoxyisopropyl)-styrene as IM in a "one-pot" living-type polymerization system.[94, 101] The structure is shown in Figure 7.

The branching frequency can be calculated as follows:

$$BR = (\overline{M}_n/\overline{M}_{n,\text{theo}}) - 1$$

where $\overline{M}_{n,\text{theo}}$ would be the expected $\overline{M}_n$ if the IM acted as an initiator only. *BR* can be varied by the judicious selection of reaction conditions, and can be determined experimentally by selectively cleaving the aromatic junction points.[101] Table 1 shows very good agreement between the calculated and experimentally measured *BR*s on selected arborescent polyisobutylenes. These polymers showed very interesting properties. Figure 8 contains the stress-strain plots for selected samples, listed in Table 1, together with a commercial linear butyl sample (because of the very low isoprene content, this rubber can be considered as a linear PIB).

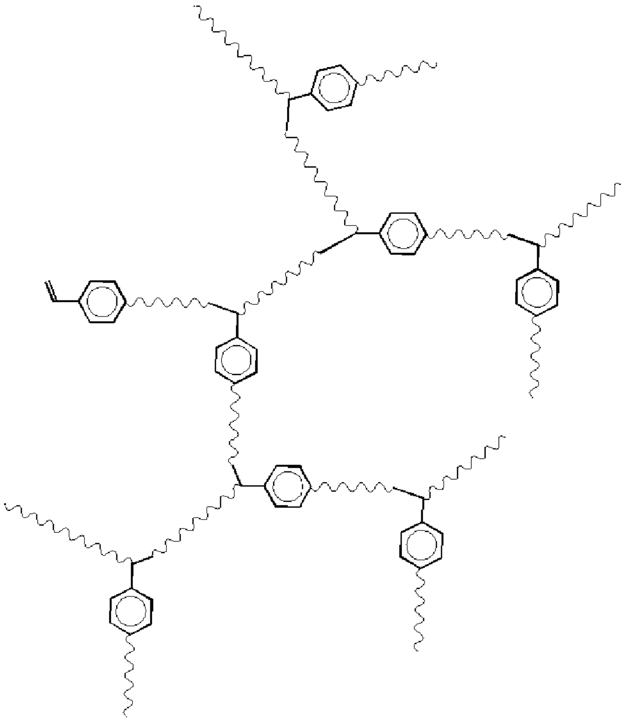


Figure 7. Structure of hyperbranched PIB synthesized by using inimer-type living IB polymerization.

Table 1. $\overline{M}_w$, MWD ($\overline{M}_w/\overline{M}_n$) and branching frequency (*BR*) of selected arborescent PIBs and a commercial linear sample.

Sample	$\overline{M}_w \times 10^3$ g/mol		$\overline{M}_w/\overline{M}_n$	Branching frequency	
	SEC-UCL	SEC-MALLS		Calc.	Exp.
PIB1	382	365	2.6	3.8	3
PIB2	556	1039	2.6	14	12
PIB3	390	790	1.3	42	44
PIB4	464	984	1.3	55	57
PIB5	286	681	1.2	40	33
PB301	652	630	2.1	–	–

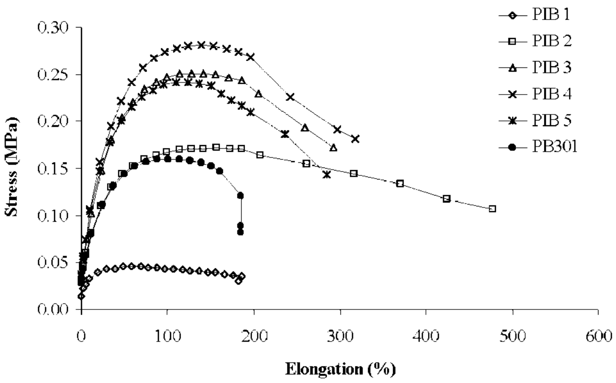


Figure 8. Stress-strain plots of hyperbranched PIBs in comparison with a commercial linear sample (see data in Table 1).

The $\overline{M}_w$ of PIB5 is similar to that of the linear sample (PB301), but its 100% modulus is considerably higher which would translate into improved "green strength" (modulus at 300% strain of the unblended polymer, an important property in tire building). Samples PIB3-5 all have narrow MWD; their moduli values scale with $\overline{M}_w$. PIB2 has a higher $\overline{M}_w$ and broader distribution than all the

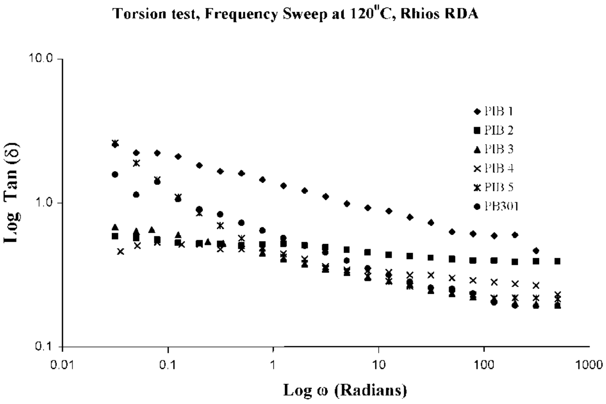


Figure 9. Dependence of the loss factor on shear rate in hyperbranched PIBs (see data in Table 1).

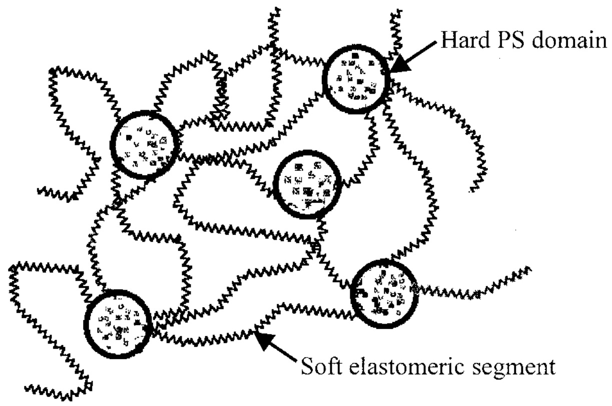


Figure 10. Phase structure of S-E-S block copolymers.

other samples, and displays an interesting balance of properties; a much higher elongation, higher moduli than the linear sample, and loss factor (tan *d*) values nearly independent of shear rate (see Figure 9). This behavior is similar to crosslinked polymers. The mechanical and viscoelastic characterization of these polymers are in progress.[104,105]

2.B) Block Copolymers

Block copolymers are a very important class of polymers because they give us a means to combine materials with different properties that may be incompatible by simple mixing. Since the block segments are covalently bonded, microphase separation occurs leading to various phase morphologies and interesting physical properties such as thermoplastic elastomeric (TPE) or amphiphilic behavior. TPEs behave like crosslinked rubbers, but can be processed like thermoplastics. The first block copolymers were made by sequential anionic living polymerization of styrene and dienes.[106] Most of these styrenic block copolymers have the general formula S-E-S, where S represents a hard amorphous polystyrene block and E represents a soft elastomeric block. Others have a branched structure with a general formula $(\text{S-E})_n\text{X}$, where X represents a multifunctional junction point. These block copolymers have a physically crosslinked elastomeric network structure, with the microphase separated hard phases serving as "crosslinking" or anchoring points (Figure 10).

The commercially available styrenic block copolymers are polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) or polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS). These block copolymers are available in various grades having different hardness and mechanical properties, depending on the ratio of polystyrene (PS) to polybutadiene (PB) or polyisoprene (PI) segments. At relatively low PS (≈15–40 wt.-%) content, these block copolymers behave like TPEs.[107,108] The advantages in processing flexibility, coupled with rubbery properties, make these materials attractive.[109,110] The unsaturated polydiene segments in SBS or SIS are often hydrogenated to yield ethylene-butylene (EB) and ethylene-propylene (EP) rubbery blocks, respectively, to improve their weathering and aging properties.

A new class of styrenic block copolymers with polyisobutylene (PIB) elastomer segments has been developed recently.[90,110–114] The goal was to develop novel block copolymers with aging and damping properties better than SBS or SIS. The synthesis of the first block copolymers with polyisobutylene rubbery segments and polystyrene or polystyrene derivative hard segments exhibiting thermoplastic elastomeric properties with good physical strength was reported by the Kennedy group.[110] Key to the synthesis of sufficiently uniform PIB was the use of electron pair donors. Sequential addition of styrene or styrene derivatives to bi- or tridirectionally growing living PIB-chains yielded linear or triarm-star branched block copolymers. A unique feature of the living carbocationic method was the ability to obtain copolymer hard segments, adjusting the T_g of the hard segment by the composition of the copolymer end block.[110] The profound influence of molecular architecture on the physical properties and their specific end-use property have made PIB-based block copolymers an attractive research area in recent years.[109,115]

Figure 11 shows the comparison of the stress-strain plots of a linear triblock and a three-arm star PS-PIB block copolymer with nearly identical PS content (≈40 wt.-%) and PIB arm length ($\overline{M}_n$ = 30 000 g/mol per arm). It is apparent that the three-arm star block copolymer shows higher modulus and lower elongation at break than the linear one, however, the tensile strength remains almost constant. The higher modulus of the 3-arm star block copolymer, compared to the linear one, is believed to be due to the permanent covalent junction point represented by the hub of the star within the elastomeric phase, which acts as an additional crosslinking junction point. Star block copolymers, therefore, would be more attractive than linear ones. Multiarm-stars would be even more

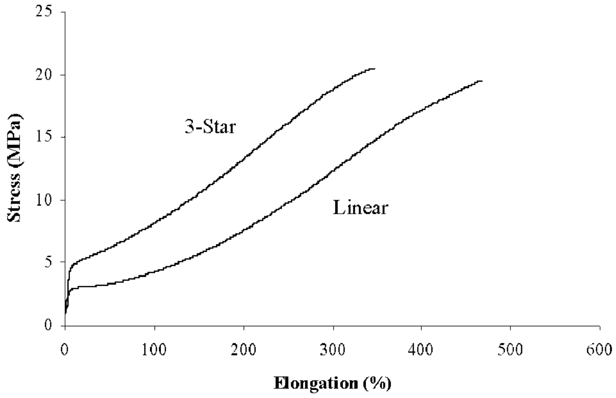


Figure 11. Stress-strain plots of 3-arm star and linear PS-PIB block copolymers.

preferred, due to their expected better shear stability. If one arm is sheared off a tri-arm star block, a linear block would be the result. In the case of multiarm stars, shearing off of some arms would still leave a star polymer. Eight-arm star block copolymers were made with calix[8]arene-based initiators (core first method).[116] Another approach was the "arm first" method, in which PS-PIB living diblocks were linked with divinylbenzene to make stars.[116] Disadvantages of the former are the expensive and not easily available initiator, and of the latter is the long reaction times and not well-defined structure. Our research group selected to use HES, a robust and cost effective multifunctional initiator to make star-branched PIB-based block copolymers.[96, 117] Figure 12 contains SEC traces of a living PIB chain before and after PS blocking. PIB is transparent to UV, thus blocking is demonstrated by the appearance of the intensive UV signal in the block.

The synthesis and characterization of branched PS-PIB block copolymers with various compositions and block lengths using HES as initiator are in progress. In this Feature Article, we would like to stress the techniques used to design and produce various structures by living carbocationic polymerization, which are available today.[118–122] Systematic study of structure-property relationships in cationic polymerization lags behind anionic polymerization. Hopefully more work will be done in this area.

3. Nanostructures Based on Block Copolymers

Nanostructured materials are a broad class of materials with microstructures modulated in zero to three dimensions on length scales less than 100 nm and the atoms are arranged in nanosized clusters, which become the constituent grains or building blocks of the material.[123–125] Conventional materials have grain sizes ranging from microns to several millimeters and contain several billion atoms each. Nanometer sized grains contain only about 900 atoms each. This smaller scale leads to a variety of confinement effects that dramatically change the properties of most materials, creating the opportunity for the re-engineering of existing products and the engineering of novel products to unprecedented performance levels. The material properties of nanostructured materials show remarkable improvement or deviation from the properties exhibited by coarser grained materials.[123, 124]

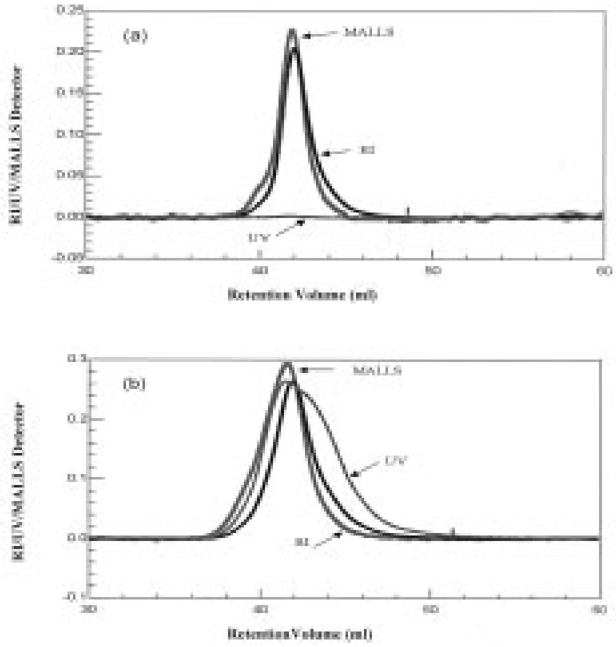


Figure 12. SEC traces of a PIB before (a) and PIB after blocking with PS (b) [HES] = 1 mmol/L; [$TiCl_4$] = 150 mmol/L; [IB] = 2 mol/L; [D*t*BP] = 7 mmol/L; $\overline{M}_n$ = 153 000 g/mol (PIB); $\overline{M}_w/\overline{M}_n$ = 1.17; $\overline{M}_n$ = 188 000 g/mol (Block); $\overline{M}_w/\overline{M}_n$ = 1.38; MeCyHx:MeCl = 60 : 40 v/v.

One unique feature of block copolymers is their ability to self-assemble into highly ordered microdomains or nanoscale morphologies whose characteristics can be easily controlled by changing the molecular weight, architecture or composition. Because of their ability to self-assemble into nanometer scale, they are classified as nanostructured materials.[126]

The phase morphologies of block copolymers prepared by anionic living polymerization have been studied in detail.[126–140] The microphase separation and the resultant molecular structure of the block copolymers can be controlled by varying the composition of the block copolymers, or by the segregation of phases via temperature or degree of polymerization. When the fraction of one component deviates from 50% (that is, when the system becomes increasingly asymmetric), transitions occur to structures that possess more interfacial curvature. Thus from a lamellar phase, the system goes through a hexagonal cylindrical phase to reach a body-centered cubic (bcc) spherical phase. The small differences in interfacial free energy between the different blocks tend to align the resulting microdomains. In the case of symmetric diblock

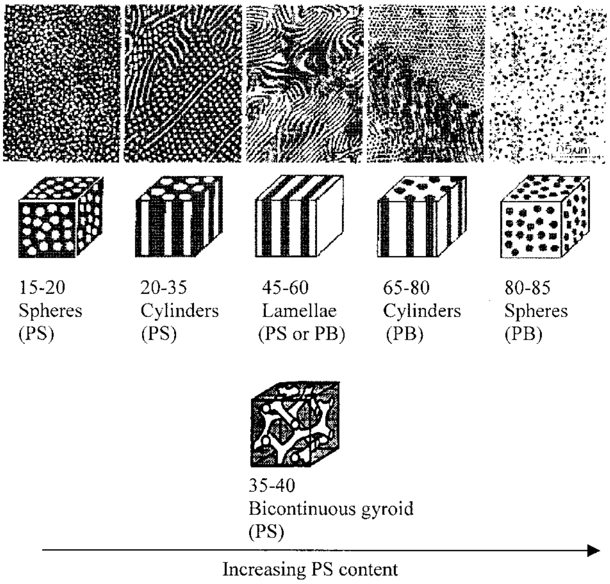


Figure 13. Phase morphology of SBS or SIS type block copolymers as a function of composition (in wt.-%).

copolymers, an effective alignment of the lamellae parallel to the plane of the film is observed. In addition, geometrical constraints have been found to play a decisive role in thin films whenever the film thickness is of the same order of magnitude as the characteristic equilibrium domain size.[127,128] Typical phase morphologies of SBS or SIS block copolymers are shown in Figure 13.[129,131]

In recent years, so-called complex phases, such as the bicontinuous gyroid, a phase of hexagonal packed cylinders and body centered cubic phase and perforated layer structures, have been identified for block copolymers.[129–133] In the intermediate segregation regime (when $xN \approx 15$–60, where N is the chain length and y the Flory interaction parameter between the two components), the gyroid phase is found between the lamellar and the cylindrical phases. Other 'perforated layer' structures have been reported, but seem to be metastable structures formed during transition to the gyroid structure.[131] There have been many misassignments of structures between the ordered bicontinuous double diamond morphology (OBDD, space group *Pn3m*), which is based on a tetrahedral arrangement of channels and gyroid, which has *Ia3d* symmetry and based on a tripod arrangement of channels.[134]

Ryan and Hamley have reviewed the morphology of SBS or SIS triblock copolymers with a PS content of about 15–40 wt.-%, in the melt and glassy states.[131] As the PS content increases, the morphology of the PS phase changes from spheres to cylinders, both dispersed in a continuous elastomeric phase. When the volume fractions of the elastomer and PS phases are about equal, the two form alternating lamellae. With a further increase in PS content, a continuous PS phase is formed in which either cylinders or spheres of the elastomer are dispersed in the PS matrix.[107,108,131] The morphologies of solution cast films depend on the nature of the solvent.[136] Good solvents for the PS segments favor the formation of a continuous PS phase. This yields products that are relatively stiff and inelastic. Conversely, good solvents for the elastomer segments favor the formation of a dispersed PS phase. The double gyroid structure appears in linear SIS triblock copolymer in the PS composition range of 32–36 wt.-%, independent of whether the minority components are the end blocks or the mid blocks.[135] Thus, both the A end blocks and the B mid block of an ABA triblock are capable of forming the interconnected double networks. Fetters and Thomas reported the ordered bicontinuous double diamond (OBDD) cubic morphology as a new equilibrium microdomain structure in star block copolymers of PS and PI with 8, 12, and 18 arms, for a PS volume fraction of 0.27.[137,138] Transmission electron microscopy (TEM) was performed on OsO_4-stained, cryo-ultramicrotomed PS-PI block copolymer specimens.

The morphology of PS-PIB block copolymers has scarcely been studied. Morphology study of a PS-PIB-PS triblock copolymer with 32 wt.-% PS by TEM showed both spherical and cylindrical PS domains (20-30 nm) dispersed in a continuous PIB matrix.[139] However, a PS-PIB-PS triblock copolymer with a lower PS content (<20 wt.-%) contained only spherical domains.[139] The morphology of cryo-ultramicrotomed samples of 800–1000 thickness were investigated by TEM, by staining the PS domains with RuO_4 after sectioning. Optimized synthesis conditions led to a very well defined phase morphology with PS cylinders aligned with their long axes parallel to each other in a hexagonal array.[90,140] Triblocks of poly(-*para*-chlorostyrene) and PIB, PpClS-PIB-PpClS, with 35 wt.-% hard segment, were found to display PpClS cylinders (40–70 nm long with 25–30 nm diameter), dispersed in a PIB matrix.[141] PαMeS-PIB-PαMeS triblocks with 20 wt.-% PαMeS showed spherical domains (15–20 nm), while at 30 wt.-% PαMeS formed cylinders. At 40 wt.-% and higher PαMeS content a lamellar morphology was observed with uniform thickness (30 nm).[140,142]

Our research group has been studying the phase morphologies of PS-PIB block copolymers. Solid-state NMR revealed a cylindrical morphology with $D = 10$–50 nm and $L = 26$–90 nm for linear and three-arm star blocks with PS = 13–31 wt.-%.[143] Thin films stained with RuO_4 were investigated with TEM, and a new bicontinuous gyroid morphology was observed for linear PS-PIB-PS triblock copolymers with 40 wt.-% PS content.[144] This was the first time this type of morphology had been observed for PS-PIB block copolymers.

Thus PIB-based block copolymers display various phase morphologies on a nanometer scale. The next sections will discuss the investigation of phase morphologies of various PS-PIB block copolymers by atomic force microscopy (AFM) in the tapping mode.

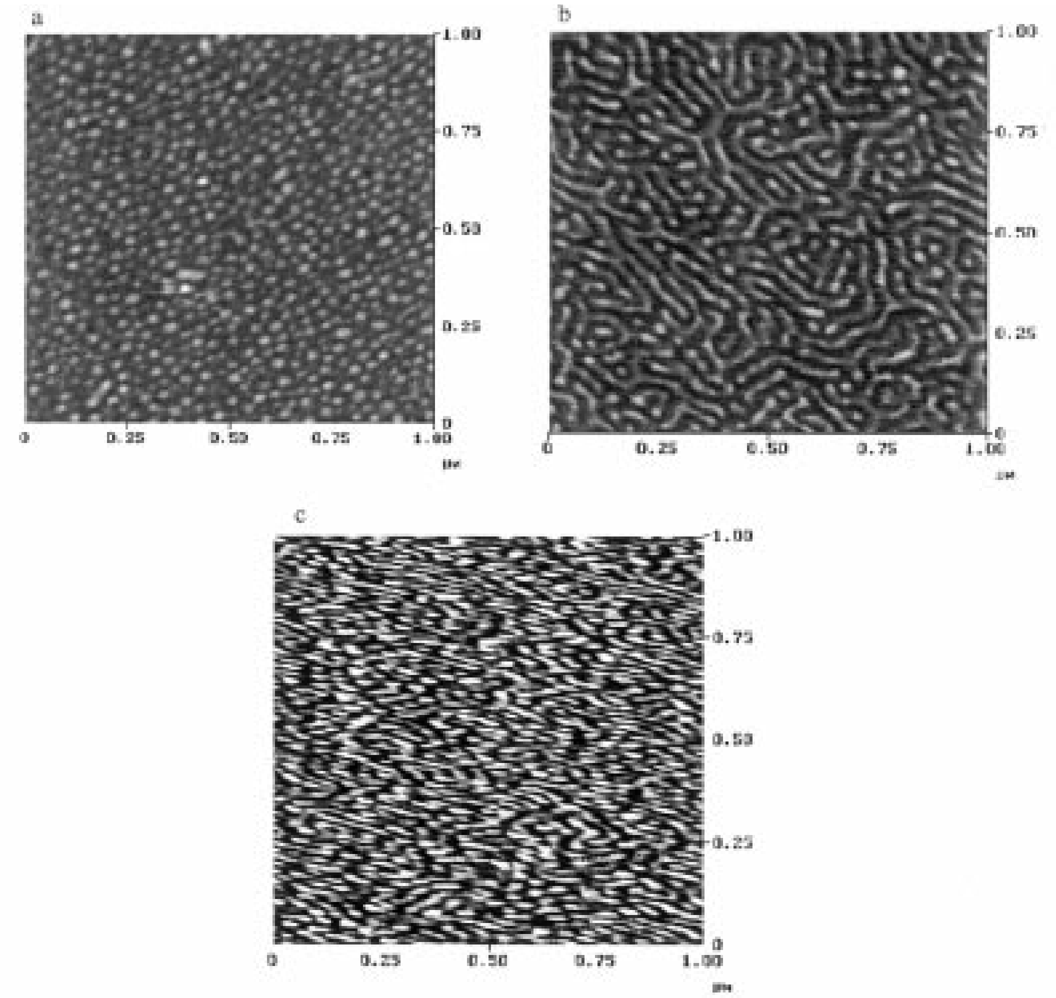


Figure 14. AFM images of the surface morphology of linear PS-PIB-PS triblock copolymers containing (a) 17.8, (b) 37.3 and (c) 40.3 wt.-% PS content before annealing.

3.A) Block Copolymer Synthesis

PS-PIB block copolymers were synthesized by living carbocationic polymerization with sequential monomer addition. Details of the synthetic procedures have been described elsewhere.[111, 112] Linear PS-PIB block copolymers with 17.8, 37.3 and 40.3 wt.-% PS content were produced in kg quantity and used in the morphological studies. The number average molecular weights of the PIB in the block copolymers were $\overline{M}_n$ = 42 800, 70 000 and 61 800 g/mol, respectively. The molecular weights and compositions of the polymers were determined by SEC and ^{1}H NMR as described.[144]

3.B) Thin Film Preparation and AFM

Thin films of the PS-PIB block copolymers were prepared by spin coating 3 wt.-% solutions in toluene onto silicon wafers by using a headway resist spinner at 6000 rpm for 30 s. The silicon wafers were cleaned with toluene, acetone and methanol in order to remove any grease or dust particles on the surface. The spin-coated films had a thickness of ≈150 nm. AFM was performed on these samples and on samples annealed at 115 °C for 25 h. AFM images were recorded with a Nanoscope III from Digital Instruments, operated in the tapping mode in air using microfabricated cantilevers with a spring constant of 30 $N \cdot m^{-1}$. For the analysis of the observed surface structures, the Nanoscope image processing software was employed. A lens-free AFM having a probe tip mounted on the end of a microfabricated cantilever was the instrument used.[145]

3.C) Nanostructure of PS-PIB Block Copolymers

Figure 14 shows the morphology of the PS-PIB block copolymers with 17.8, 37.3 and 40.3 wt.-% PS content. For the block copolymer with 17.8 wt.-% PS content, spherical PS domains of 25–35 nm diameter are dispersed in the continuous PIB phase. The block copolymer with 37.3 wt.-% PS content showed a morphology in

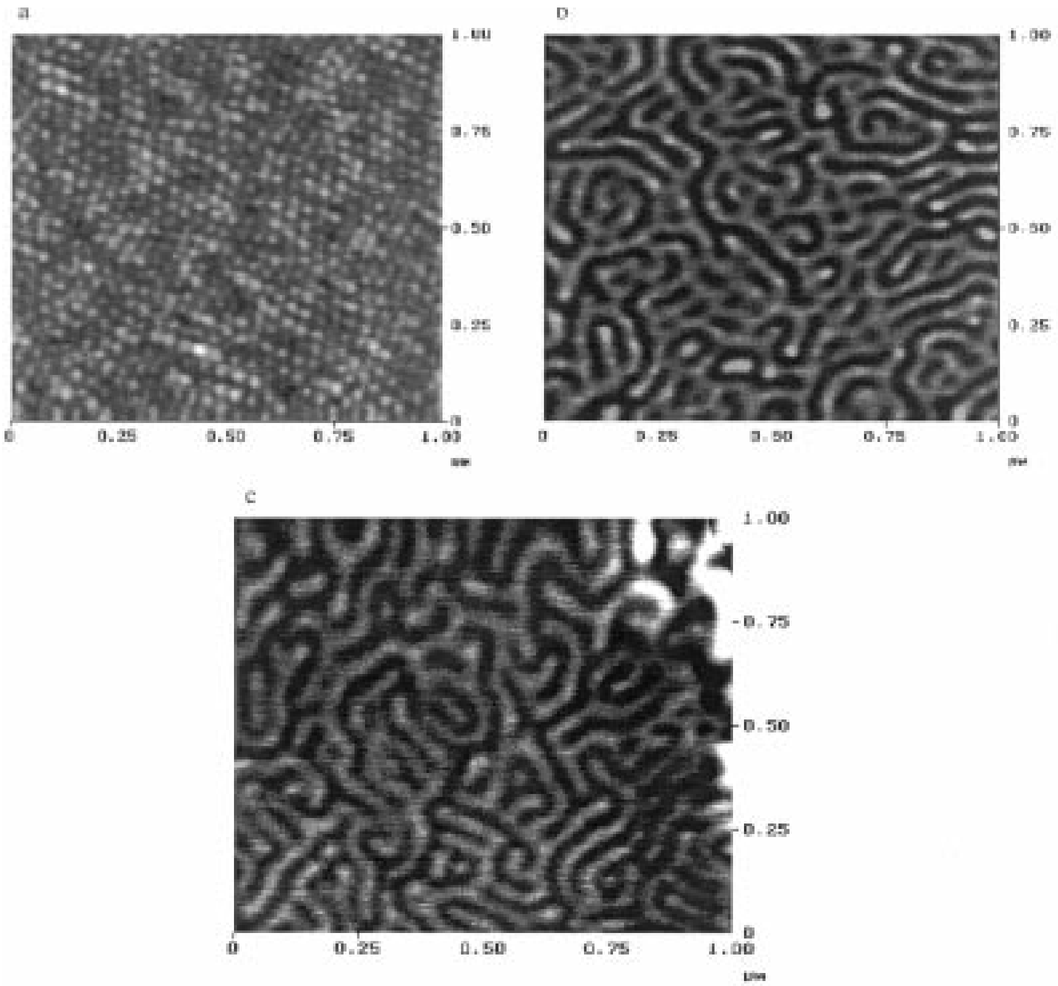


Figure 15. AFM images of the surface morphology of linear PS-PIB-PS triblock copolymers containing (a) 17.8, (b) 37.3 and (c) 40.3 wt.-% PS content after annealing at 115 °C for 25 h.

which PS forms a combination of cylinders and lamellae with a PS domain size of 30–36 nm. However, at 40.3 wt.-% PS content, the morphology changes from cylinders to an interpenetrating network structure or a gyroid bicontinuous morphology (i.e. a combination of hexagonal-packed cylinders and spheres), in which PS forms cylinders with 40-50 nm and spheres with 50–70 nm diameter. This morphology is similar to that observed for PS-PI diblock copolymers.[130,131] Figure 15 shows the effect of annealing (115 °C, 25 h) on the morphology of the same block copolymers. It is evident that after annealing, the block copolymers show a more stable and ordered morphology. The temperature of 115 °C is above the glass-transition temperature of both the PIB and PS blocks, so that the polymer segments can relax and rearrange into a position of a more ordered structure. It is also apparent that there is an increase in PS domain size after annealing. For example, the domain size of the block copolymer containing 37.3 wt.-% increases from 30–36 nm to 50–60 nm after annealing. The disappearance of the gyroid morphology in the block copolymer with 40.3 wt.-% PS content after annealing indicates that this morphology is not thermally stable.

This self-assembling behavior of PS-PIB block copolymers lends itself to the preparation of PS or PIB nanoparticles or nanostructures by selectively destroying one or the other phase in the film. PS can be selectively destroyed with a mixture of trifluoroacetic acid and 30% aqueous hydrogen peroxide, which leaves the PIB intact.[116] This method was used to destroy aromatic PS linkages in star-branched and hyperbranched PS-PIB block copolymers.[101,116] It was applied to an annealed (at 115 °C for 25 h) linear PS-PS-PIB triblock copolymer thin film containing 37.3 wt.-% PS. Selective destruction of the PS cylinders, dispersed in the PIB matrix, created nanosize holes in the PIB. The size and shape of the holes can be changed, by changing the phase morphology of the block copolymers. This opens up an interesting area of application for these blocks.

In summary, this Feature Article presented an overview of our recent developments in living carbocationic polymerization and the research philosophy of our group, rooted in interdisciplinary research. In addition to the areas discussed here, we are presently exploring the use of PIB-based materials for biomedical applications, with very promising results that will be published shortly.

Acknowledgement: Many thanks to *Cindy Simmons*, B.Sc., for editing the manuscript. Financial support by the *Bayer/NSERC Industrial Research Chair in Elastomer technology*, *NSERC*, *MMO* and *UWO* is greatly appreciated.

Received: January 31, 2001
Revised: July 20, 2001

[1] B. Ivan, J. P. Kennedy, "*Designed Polymers by Carbocationic Macromolecular Engineering*; *Theory and Practice*", Hanser Publishers, Munich 1991.
[2] O. W. Webster, *Science* **1994**, *251*, 887.
[3] J. M. J. Frechet, *Science* **1994**, *263*, 1710.
[4] K. Matyjaszewski, M. Sawamoto, *Plast. Eng. (N. Y.)* **1996**, *35*, 265.
[5] J. E. Puskas, G. Kaszas, *Prog. Polym. Sci.* **2000**, *25*, 403.
[6] E. E. Malmstrom, C. J. Hawker, *Macromol. Chem. Phys.* **1998**, *199*, 923.
[7] M. Szwarc, *Nature* **1956**, *178*, 1168.
[8] T. Morrison, R. N. Boyd, "*Organic Chemistry*", 6th ed., Prentice Hall, Englewood Cliffs, New Jersey 1992.
[9] J. E. Puskas, G. Wilson, J. Duffy, "Synthesis of Butyl Rubber by Cationic Polymerization", in: *Ullmann's Encyclopaedia of Industrial Chemistry*, Vol. A23, Wily-VCH, New York 1998, Ch. 3, p. 51.
[10] D. C. Pepper, *J. Polym. Sci., Polym. Symp.* **1975**, *50*, 51.
[11] V. Percec, D. Tomazos, *Adv. Mater.* **1992**, *4*, 548.
[12] J. P. Kennedy, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2285.
[13] R. J. Pazur, H.-H. Greve, *NATO Sci. Ser. E, Appl. Sci.* **1999**, *359*, 13; J. E. Puskas et al., Eds.; Kluwer Academic Publishers, Dordrecht 1999.
[14] D. C. Pepper, *Makromol. Chem.* **1974**, *175*, 1077.
[15] K. Matyjaszewski, C. H. Lin, A. Bon, J. S. Xiang, *Macromol. Symp.* **1994**, *85*, 65.
[16] M. Kamigaito, Y. Maeda, M. Sawamoto, T. Higashimura, *Macromolecules* **1993**, *26*, 1643.
[17] G. Kaszas, J. Puskas, J. P. Kennedy, *Makromol. Chem., Macromol. Symp.* **1988**, *13*, 473.
[18] M. Zsuga, T. Kelen, J. Borbely, *Polym. Bull. (Berlin)* **1991**, *26*, 417.
[19] J. E. Puskas, G. Kaszas, M. Litt, *Macromolecules* **1991**, *24*, 5278.
[20] G. Kaszas, J. E. Puskas, J. P. Kennedy, *Polym. Bull. (Berlin)* **1987**, *18*, 123.
[21] H. Mayr, *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1371.
[22] M. Roth, H. Mayr, *Macromolecules* **1996**, *29*, 6104.
[23] H. Mayr, "*Ionic Polymerization and Related Processes*", *NATO Sci. Ser. E, Appl. Sci.* **1999**, *359*, 99; J. E. Puskas et al., Eds., Kluwer Academic Publishers, Netherlands 1999.
[24] J. E. Puskas, W. E. Pattern, M. G. Lanzendorfer, D. Jamieson, L. O. Al-Rais, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39(1)*, 325.
[25] J. E. Puskas, C. J. Wilds, *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 85.
[26] H. Deng, S. Kanaoka, M. Sawamoto, T. Higashimura, *Macromolecules* **1996**, *29*, 1772.
[27] R. F. Storey, K. A. Shoemake, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35(2)*, 578.
[28] S. Kanaoka, M. Sawamoto, T. Higashimura, J. Won, C. Pan, T. P. Lodge, M. Fujiwara, D. M. Hedstrand, D. A. Tomalia, *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 527.
[29] T. M. Marsalko, I. Majoros, J. P. Kennedy, *Polym. Bull. (Berlin)* **1993**, *31*, 665.
[30] J. E. Puskas, M. Grasmüller, *Macromol. Symp.* **1998**, *132*, 117.
[31] G. Kaszas, J. E. Puskas, *Polym. React. Eng.* **1994**, *2*, 251.
[32] R. F. Storey, K. R. Choate, Jr., *Macromolecules* **1997**, *30*, 4799.
[33] M. Kamigaito, K. Yamaoka, M. Sawamoto, T. Higashimura, *Macromolecules* **1992**, *25*, 6400.
[34] M. Zsuga, T. Kelen, L. Balogh, I. Majoros, *Polym. Bull. (Berlin)* **1992**, *29*, 127.
[35] T. Kelen, M. Zsuga, L. Balogh, I. Majoros, G. Deak, *Makromol. Chem., Macromol. Symp.* **1993**, *67*, 325.
[36] G. Kaszas, J. E. Puskas, J. P. Kennedy, *J. Macromol. Sci.* **1989**, *A26*, 1099.
[37] M. Zsuga, J. P. Kennedy, *Polym. Bull. (Berlin)* **1989**, *21*, 5.
[38] M. Roth, M. Patz, H. Freter, H. Mayr, *Macromolecules* **1997**, *30*, 722.
[39] J. P. Kennedy, I. Majoros, A. Nagy, *Adv. Polym. Sci.* **1994**, *112*, 1.
[40] J. E. Puskas, M. G. Lanzendörfer, *Macromolecules* **1998**, *31*, 8684.
[41] J. E. Puskas, M. G. Lanzendörfer, H. Peng, A. Michel, L. B. Brister, C. Paulo, "*Ionic Polymerization and Related Processes*", *NATO Sci. Ser. E, Appl. Sci.* **1999**, *359*, 143; J. E. Puskas et al., Eds., Kluwer Academic Publishers, Netherlands 1999.
[42] S. Hadjikyriacou, R. Faust, *Macromolecules* **1995**, *28*, 7893.
[43] M. Gyor, H.-C. Wang, R. Faust, *J. Macromol. Sci., Chem.* **1992**, *A129*, 639.
[44] R. F. Storey, K. Choate, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35(2)*, 506.
[45] R. F. Storey, K. Choate, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36(1)*, 193.
[46] P. Sigwalt, *Makromol. Chem., Macromol. Symp.* **1991**, *47*, 179.
[47] S. Penczek, *Makromol. Chem. Rapid Commun.* **1992**, *13*, 147.
[48] T. Pernecker, J. P. Kennedy, *Polym. Bull. (Berlin)* **1992**, 29, 15.
[49] S. Keki, Gy. Deak, M. Zsuga, *Muanyag Gumi* **1997**, *34*, 295.
[50] D. Held, B. Ivan, A. H. E. Muller, F. De Jong, T. Graafland, *ACS Symp. Ser.* **1997**, *665*, 63.
[51] V. Bennevault, F. Peruch, A. Deffieux, *Macromol. Chem. Phys.* **1996**, *197*, 2603.
[52] D. Held, B. Ivan, A. H. E. Müller, F. Jong, T. Graafland, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37(1)*, 333.
[53] Zs. Fodor, R. Faust, *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 1985.
[54] K. Matyjaszewski, *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 107.
[55] C.-H. Lin, K. Matyjaszewski, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31(1)*, 599.
[56] Y. Tsunogae, J. P. Kennedy, *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 403.

[57] V. Gutmann, "*Donor-Acceptor Approach to Molecular Interactions*", Plenum Press, New York 1978.

[58] R. F. Storey, Choate, Kim R., Jr., *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 1195.

[59] G. Kaszas, W. G. Hager, J. E. Puskas, J. P. Kennedy, *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 421.

[60] J. E. Puskas, A. J. Michel, L. B. Brister, *Kautsch. Gummi Kunstst.* **2000**, *53*, 1.

[61] A. J. Michel, J. E. Puskas, L. B. Brister, *Macromolecules* **2000**, *33*, 4634.

[62] M. Hoffman, J. E. Puskas, K. Weiss, *Polym. Mater. Sci. Eng.* **2000**, *83*, 440.

[63] A. Michel, L. B. Brister, J. E. Puskas, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40(1)*, 214.

[64] J. E. Puskas, M. G. Lanzendörfer, W. E. Pattern, *Polym. Bull. (Berlin)* **1998**, *40*, 55.

[65] C. Paulo, J. E. Puskas, S. Angepat, *Macromolecules* **2000**, *33*, 3518.

[66] US Patent 2,268,446 (2001), University of Western Ontario, inv.: J. E. Puskas.

[67] J. E. Puskas, L. B. Brister, A. J. Michel, M. G. Lanzendörfer, D. Jamieson, W. G. Pattern, *J. Polym. Sci.* **2000**, *38*, 444.

[68] J. E. Puskas, A. J. Michel, *Macromol. Symp.* **2000**, *161*, 141.

[69] L. B. Brister, J. E. Puskas, E. Tzaras, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40(1)*, 141.

[70] J. E. Puskas, W. E. Pattern, P. M. Wetmore, A. Krukonis, *Polym. Mater. Sci. Eng.* **1999**, *82*, 42.

[71] J. Song, J. Bodis, J. E. Puskas, *J. Polym. Sci.*, submitted.

[72] R. F. Storey, B. J. Chisolm, L. B. Brister, *Macromolecules* **1995**, *28*, 4055.

[73] J. E. Puskas, H. Peng, *Polym. React. Eng.* **1999**, *7*, 553.

[74] W. Luo, J. E. Puskas, unpublished data.

[75] J. Dabrowski, M. Ktcka, *J. Mol. Struct.* **1972**, *12*, 179.

[76] M. Krombholz, J. E. Puskas, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2001**, *41(1)*, 337.

[77] H. L. Hsieh, R. P. Quirk, "*Anionic Polymerization: Principles and Practical Applications*", Marcel Dekker, New York 1996.

[78] M. K. Mishra, *Macromol. Symp.* **1996**, *107*, 243.

[79] S. Ingrisch, O. Nuyken, M. K. Mishra, *Plast. Eng. (N.Y.)* **1999**, *53*, 77.

[80] M. Sawamoto, S. Kanaoka, T. Higashimura, in: "*Hyper-Struct. Mol. I: [Int. Forum]*", H. Sasabe, Ed., Gordon & Breach, Amsterdam 1999, p. 43–61.

[81] B. Charleux, R. Faust, *Adv. Polym. Sci.* **1998**, *142*, 1.

[82] Y. Gnanou, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1996**, *C36(1)*, 77.

[83] T. M. Marsalko, I. Majoros, J. P. Kennedy, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35(2)*, 504.

[84] R. F. Storey, K. A. Shoemake, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35(2)*, 578.

[85] R. F. Storey, K. A. Shoemake, B. J. Chisolm, *J. Polym. Sci., Polym Chem.* **1996**, *34*, 2003.

[86] L. Wang, S. T. McKenna, R. Faust, *Macromolecules* **1995**, *28*, 4681.

[87] J. P. Kennedy, L. R. Ross, J. E. Lackey, O. Nuyken, *Polym. Bull. (Berlin)* **1981**, *4*, 67.

[88] K. J. Huang, M. Zsuga, J. P. Kennedy, *Polym. Bull. (Berlin)* **1988**, *19*, 43.

[89] G. Kaszas, J. E. Puskas, J. P. Kennedy, C. C. Chen, *Polym. Bull. (Berlin)* **1988**, *20*, 413.

[90] R. F. Storey, B. J. Chisholm, K. R. Choate, *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 969.

[91] E. Cloutet, J.-L. Fillaut, Y. Gnanou, D. Astruc, *Chem. Commun.* **1996**, 2047.

[92] S. Jacob, I. Majoros, J. P. Kennedy, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38(1)*, 208.

[93] J. E. Puskas, C. J. Wilds, *J. Polym. Sci.* **1998**, *36*, 85.

[94] J. E. Puskas, M. Grasmuller, *Macromol. Symp.* **1998**, *132*, 117.

[95] S. Hadjikyriacou, R. Faust, *Macromolecules* **1995**, *28*, 7893.

[96] K. Yongmoon, J. E. Puskas, "*ACS Meeting, Rubber Division*", Cincinnati, October 17–20, 2000.

[97] P. G. Santangelo, C. M. Roland, J. E. Puskas, *Macromolecules* **1999**, *32*, 1972.

[98] J. M. Fréchet, *Science* **1994**, *263*, 170.

[99] B. I. Voit, *Acta Polym.* **1995**, *46*, 87.

[100] D. A. Tomalia, *Macromol. Symp.* **1996**, *101*, 243.

[101] C. Paulo, J. E. Puskas, *Macromolecules* **2001**, *34*, 734.

[102] M. Gauthier, M. Möller, *Macromolecules* **1991**, *24*, 4548.

[103] M. Gauthier, "*Ionic Polymerization and Related Processes*", *NATO Sci. Ser. E, Appl. Sci.* **1999**, *359*, 239; J. E. Puskas et al., Eds., Kluwer Academic Publishers, Dordrecht 1999.

[104] C. G. Robertson, C. M. Roland, *J. Rheol.* **2001**, *45*, 759.

[105] V. Altstadt, C. Paulo, J. E. Puskas, in preparation.

[106] B. M. Walker, "*Handbook of Thermoplastic Elastomers*", Van Nostrand Reinhold, New York 1979.

[107] G. Holden, N. R. Legge, in: "*Thermoplastic Elastomers–A Comprehensive Review*", G. Holden, N. R. Legge, R. Quirk, H. E. Schroeder, Eds., Hanser Publishers, Munich 1996.

[108] R. P. Quirk, M. Morton, in: "*Thermoplastic Elastomers–A Comprehensive Review*", G. Holden, N. R. Legge, R. Quirk, H. E. Schroeder, Eds., Hanser Publishers, Munich 1996.

[109] G. Holden, N. R. Legge, R. P. Quirk, H. E. Schroeder, Eds., "*Thermoplastic Elastomers – A Comprehensive Review*", Hanser Publishers, Munich 1996.

[110] U.S. 4,946,899 (1990), University of Akron, invs.: J. P. Kennedy, J. E. Puskas, G. Kaszas, W. G. Hager.

[111] G. Kaszas, J. E. Puskas, J. P. Kennedy, W. G. Hager, *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 427.

[112] G. Kaszas, *Polym. Mater. Sci. Eng.* **1992**, *67*, 325.

[113] J. E. Puskas, G. Kaszas, J. P. Kennedy, W. G. Hager, *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 41.

[114] Zs. Fodor, R. Faust, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*, 176.

[115] J. E. Puskas, G. Kaszas, *Rubber Chem. Technol.* **1996**, *69*, 462.

[116] S. Jacob, J. P. Kennedy, *Adv. Polym. Sci.* **1999**, *146*, 1.

[117] J. E. Puskas, W. Pattern, P. M. Wetmore, V. Krukonis, *Rubber Chem. Technol.* **1998**, *72*, 559.

[118] P. Sigwalt, *Makromol. Chem., Macromol. Symp.* **1991**, *47*, 179.

[119] J. E. Puskas, G. Kaszas, *Rubber Chem. Technol.* **1996**, *69*, 462.

[120] R. Faust, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40(2)*, 960.

[121] P. Rempp, E. Franta, *Macromol. Symp.* **1995**, *91*, 51.

[122] P. Rempp, E. Franta, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34(2)*, 658.

[123] J. H. Fendler, Ed., "*Nanoparticles and Nanostructured Films: Preparation, Characterization and Applications*", Wiley-VCH, New York 1998.

[124] R. W. Siegel, E. Hu, M. C. Roco, Eds., "*Nanostructure Science and Technology*", Kluwer Academic Publishers, Dordrecht 1999.

[125] A. N. Goldstein, "*Handbook of Nanophase Materials*", Marcel Dekker Inc., New York 1997.

[126] I. W. Hamley, "*The Physics of Block Copolymers*", Oxford University Press, Oxford 1998.

[127] L. H. Radzilowski, B. L. Carvalho, E. L. Thomas, *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 3081.

[128] M. Konrad, A. Knoll, G. Krausch, R. Magerie, *Macromolecules* **2000**, *33*, 5518.

[129] A. K. Khandpur, S. Foerster, F. S. Bates, *Macromolecules* **1995**, *28*, 8796.

[130] A. K. Khandpur, C. W. Macosko, F. S. Bates, *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 247.

[131] A. J. Ryan, I. W. Hamely, in: "*The Physics of Glassy Polymers*", R. N. Haward, R. J. Young, Eds., Chapman and Hall, London 1997.

[132] S. Forster, A. K. Khandpur, A. K. Zhao, *Macromolecules* **1994**, *27*, 6922.

[133] F. S. Bates, J. H. Rosedale, G. H. Friedrickson, *J. Chem. Phys.* **1990**, *92*, 6255.

[134] D. A. Hajduk, P. E. Harper, S. M. Grunner, *Macromolecules* **1995**, *28*, 2570.

[135] A. Augeropoulos, B. J. Dair, N. Hadjichristidis, E. L. Thomas, *Macromolecules* **1997**, *30*, 5634.

[136] J. F. Beecher, L. Marker, R. D. Bradford, S. L. Aggarwal, *J. Polym. Sci.* **1969**, *26*, 117.

[137] D. B. Alward, D. J. Kinning, E. L. Thomas, L. J. Fetters, *Macromolecules* **1986**, *19*, 215.

[138] E. L. Thomas, D. B. Alward, D. J. Kinning, *Macromolecules* **1986**, *19*, 2197.

[139] M. Gyor, Zs. Fodor, H.-C. Wang, R. Faust, *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 2055.

[140] D. Li, R. Faust, *Macromolecules* **1995**, *28*, 4893.

[141] J. P. Kennedy, J. Kurian, *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 3725.

[142] D. Li, R. Faust, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*, 100.

[143] C. Neagu, J. E. Puskas, M. A. Shing, A. Natansohn, *Macromolecules* **2000**, *33*, 5976.

[144] S. S. Lawrence, D. M. Shinozaki, J. E. Puskas, M. Gerchcovich, U. Myler, G. Kaszas, "*ACS Meeting, Rubber Division*", Cincinnati, October 17–20, 2000.

[145] B. D. Ratner, V. V. Tsukruk, Eds., "*Scanning Probe Microscopy of Polymers*", *ACS Symp. Ser.* **1998**, *694*; American Chemical Society, Washington, DC 1998.