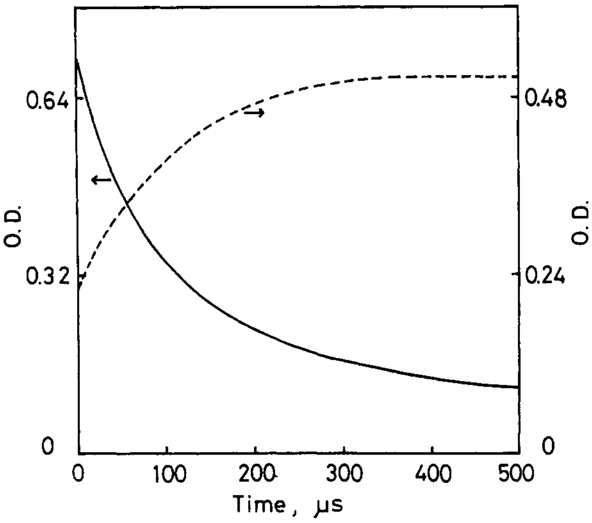

Figure 2. Decay of PVB anions (solid line) and the growth of PVPy anions (dashed line) in the MTHF–THF mixture containing 0.6 M PVB and 0.2 M PVPy after pulse irradiation at 130 K.

Table I
Rate Constants for Electron-Transfer Reactions in the MTHF–THF (1:1 Mixture) Solvents[a]

reaction	k, L mol^{-1} s^{-1} 130 K	k, L mol^{-1} s^{-1} 140 K
$Ph_2^- + Py \rightarrow Ph_2 + Py^-$	3.1×10^7	8.1×10^7
$PVB^- + Py \rightarrow PVB + Py^-$	7.2×10^6	1.5×10^7
$Ph_2^- + PVPy \rightarrow Ph_2 + PVPy^-$	1.0×10^6	2.5×10^6
$PVB^- + PVPy \rightarrow PVB + PVPy^-$	2.8×10^4	8.9×10^4

[a] Ph_2, Py, PVB, and PVPy represent biphenyl, pyrene, poly(4-vinylbiphenyl), and poly(1-vinylpyrene), respectively.

M represents MTHF or THF. Though reactions 2 and 3 are competitive processes for electron capture, PVB captures electrons more efficiently than PVPy immediately after pulse irradiation under our experimental conditions. This is shown in Figures 1 and 2. Then, $PVPy^-$ is formed by an electron-transfer reaction from PVB^- to PVPy. The decay rate of PVB anions by the electron-transfer reaction is represented by the following equation

$$-d[PVB^-]/dt = k[PVPy][PVB^-] \qquad (5)$$

where k is a decay rate constant. Since the concentration of PVPy, [PVPy], is sufficiently high compared to the concentration of PVB anions, $[PVB^-]$, and consequently [PVPy] is approximately constant, the decay of PVB anions can be regarded as a pseudo-first-order process. In fact, the decay of the PVB anions shown in Figure 2 can be represented by a first-order kinetic plot. Thus, the rate constant, k, for the electron-transfer reaction from PVB anions to PVPy molecules was obtained as 2.8×10^4 L mol^{-1} s^{-1} at 130 K. Similar kinetic treatments were operative for other electron-transfer reactions in the MTHF–THF–Ph_2–PVPy, MTHF–THF–PVB–Py, and MTHF–THF–Ph_2Py systems.

The rate constants obtained for all the systems studied in the present work are summarized in Table I. The electron-transfer rates from biphenyl anions to pyrene molecules are about as thousand times as large as those from PVB anions to PVPy molecules at 130 and 140 K. The rate for the electron-transfer reaction decreases with decreasing temperature and is probably controlled by a diffusion process. The much larger electron-transfer rate for the $Ph_2^- + Py$ reaction than that for the $PVB^- + PVPy$ reaction corresponds to the large diffusion coefficient for biphenyl anions and pyrene molecules as compared with that for PVB anions and PVPy polymers.

Since, the radius of gyration of PVB polymer coils is 107 Å in MTHF,[3] the critical concentration of the polymer coil overlap is estimated as 0.3 M. In the MTHF–THF–PVB–PVPy system, the concentration of PVB used is 0.6 M, which is higher than the critical concentration. Thus it appears that the electron-transfer reaction from PVB anions to PVPy polymers is caused by the diffusion of polymer chains. The rate constant, k, for a bimolecular diffusion-controlled reaction of spherical particles is represented by the following Stokes–Einstein equation

$$k = 4\pi RD \qquad (6)$$

where R is the radius of the reaction sphere and D is the sum of the diffusion coefficients of two reacting particles. In the electron-transfer reaction of the polymer system, the reaction takes place between biphenyl anions and pyrene molecules hanging to polymer chains. Thus, R is regarded as the sum of the radii of biphenyl and pyrene molecules and is taken to be 7 Å. D equals $D_{PVB} + D_{PVPy}$, where D_{PVB} and D_{PVPy} are the diffusion coefficients of PVB and PVPy polymer chain, respectively. Thus the values of D can be obtained from the experimental value of k for the electron-transfer reaction, and they were estimated as 5.3×10^{-11} cm^2 s^{-1} at 130 K and 1.7×10^{-10} cm^2 s^{-1} at 140 K. It appears that the rate of the electron transfer in the semidilute region of polymer solution is closely related to the diffusional motion of polymer chains. Since the optical absorption of the anions in this system is very strong, the electron-transfer reaction can be used in the future as a probe of diffusional motion of polymer in the glassy state.

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Registry No. PVB, 25232-08-0; PVPy, 25120-43-8; MTHF, 96-47-9; THF, 109-99-9.

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Anionic Synthesis of Isotactic Polystyrene

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Introduction

The synthesis of isotactic polystyrene (iPS) is usually accomplished using some form of coordination chemistry such as Ziegler–Natta catalysis. Early experiments by

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Table I
Polymerization of Styrene in Hexane at −30 °C

sample	tBuOLi/BuLi	% conv isotactic	M_n isotactic	T_g, °C	T_m, °C	% cryst
PSO	0	0				
iPS3	1	13	110 000	102	213	16
iPS4	1	20	42 000	99	214	15
iPS5	10	1	140 000	104	205	10
iPS6	10	3	122 000	100	211	22

Kern,[1] however, showed that isotactic polystyrene could also be obtained from butyllithium-initiated (BuLi) anionic polymerization at very low temperatures (<−30 °C), and subsequent work suggested that association of lithium organic compounds was responsible for the observed tacticity.[2] Worsfold and Bywater[3] later indicated that small amounts of water were essential for the isotactic placement to occur; they proposed that water molecules react with the BuLi initiator to form LiOH, which would then interact with the living end of the polystyrene chain. They also conducted experiments using lithium isobutoxide, lithium methoxide and lithium carbonate as associating agents, but in these cases no isotactic material was obtained. Kawamura et al.[4] gave a different explanation of the role of water, stating that at low temperatures water molecules do not react with the initiator but rather associate to form a complex such as $Li^+(H_2O)_n$. This would then coordinate with the polystyryllithium chain ends and enhance isotactic placement, very much like a Ziegler–Natta system.

Due to the unknown chemistry and the lack of control involved with the use of water in anionic polymerizations, we set out to find a stable compound that might associate with living polystyryllithium to give isotactic placement of the repeat units. Our motivations were based on the desire to produce isotactic polystyrene samples with some control over molecular weight and to provide a simple synthetic pathway for the production of block copolymers containing at least one iPS sequence. Guided by the earlier work cited above, we have employed lithium *tert*-butoxide in the anionic polymerization of polystyrene and, as described below, we have successfully and reproducibly obtained highly isotactic polystyrene.

Experimental Section

A middle 80% fraction of hexane solvent was initially vacuum distilled onto calcium hydride, stirred overnight, and then distilled a second time and held over a sodium dispersion. Styrene monomer was washed with 10% NaOH solution followed by distilled water, dried over calcium hydride, and then kept over dibutylmagnesium, where yellow was used as indication of purity. Both solvent and monomer were vacuum distilled into a 250-mL glass reactor, which had been cleaned with HF and flamed prior to use, and subsequently placed under argon (99.999% ultrahigh-purity Matheson gas purified further by passing over 4A molecular sieves followed by a deoxifying BASF copper-based catalyst column). The monomer/solvent mixture (1:1 by volume) was initially broght to 0 °C using an external isopropanol/Neslab cryogenic immersion cooler bath. *n*-BuLi initiator (Aldrich) was injected and the whole system brought to −30 °C. Stirring was achieved using an agitator driven by an external ACE Model B air stirrer. Lithium *tert*-butoxide was added in hexane solution (Table I) prior to the initiator or in some cases simultaneously with the initiator via an *n*-BuLi solution partially neutralized with *tert*-butyl alcohol.[5] The polymerizations were terminated after 2–5 days by either the addition of methanol or an end-functionalizing agent. The polymerization product, which in most cases corresponded to about 50% conversion of monomer, was then subjected to refluxing with methyl ethyl ketone (MEK) in a Soxhlet extractor for several days to separate soluble atactic polystyrene from the insoluble isotactic product. ^{13}C NMR spectra were provided by the Department of Chemistry Spectroscopy Laboratory at MIT using a Bruker ^{13}C NMR at 67.89 MHz at room temperature. Sample NMR tubes were prepared by dissolving iPS samples in $CDCl_3$ (~3% v/v) and heating to 50 °C to enhance solubility. Upon cooling to room temperature, some of the dissolved polymer precipitated into suspension. The NMR spectra were expanded in the range of 140–150 ppm, where three main peaks for polystyrene can be identified: at 146.8 ppm for isotactic, 146.0 ppm for atactic, and 145.6 ppm for syndiotactic material.[4] The polymers were also characterized using a Perkin-Elmer DSC-4 differential scanning calorimeter and Waters Model 100A GPC. Solutions for the latter were prepared in toluene or xylene heated to 100 °C in concentrations of ≈5 g/L and subsequently cooled to room temperature. Prior to injection, the solutions were filtered twice using 0.5-μm PTFE membrane filters.

Results and Discussion

Preliminary experiments were carried out in small-scale test tube reactors (total volume of reactants ≈25 mL) using tBuOLi/BuLi ratios varying from 1:2 to 2:1. Yields were estimated to range from 20 to 30% isotactic material. Tacticity of the insoluble product was confirmed by observing the ^{13}C NMR peaks in the 140–150 ppm range. The sharp peak at 146.8 ppm, in Figure 1 for example, indicates highly isotactic material, while the soluble product of the MEK reflux presents a much broader peak, as shown in Figure 2. For modifier to initiator ratios in the range of 1:2 to 2:1, there was no noticeable change in the yield; however, at much higher values of this ratio, a very apparent decrease in the yield of iPS was observed, as summarized in the results of four larger scale polymerizations (volume of reactants ≈ 200 mL) presented in Table I. PSO is presented as a control experiment where no tBuOLi was added to the polymerization; no isotactic polystyrene product was obtained after polymerizing for 2 days.

Molecular weights were determined using GPC in either toluene or xylene. Due to the unknown kinetics of the low-temperature polymerization of styrene in the presence of tBuOLi, molecular weights could not be targeted based on monomer to initiator ratio as done conventionally with anionic polymerizations. However, some degree of control was achieved by varying initiator concentrations and polymerization times; in this way molecular weights were obtained ranging from 42 000 for iPS4 (polymerization time ≈ 2 days) to 1 200 000 for some of the small-scale test tube reactions (polymerization time ≈ 5 days). The GPC traces displayed broad peaks, with polydispersities ranging from 1.5 to as high as 5.0 for the larger molecular weight samples. This is in part attributed to the use of hexane as the low-temperature solvent. The choice of hexane was motivated by its nonpolar nature, necessary for isotactic placement, and by its advantage over toluene regarding the absence of transfer reactions. It is, however, a poor solvent for atactic polystyrene and a nonsolvent for the isotactic product. Though the initial reaction mixture (1:1 solvent/monomer) provides a good environment for polymer dissolution, as the reaction progresses the polymer chains begin to precipitate out of solution, adding to the observed polydispersity.

DSC revealed T_g's of 99–102 °C and melting temperatures at 205–215 °C. In some instances a second less

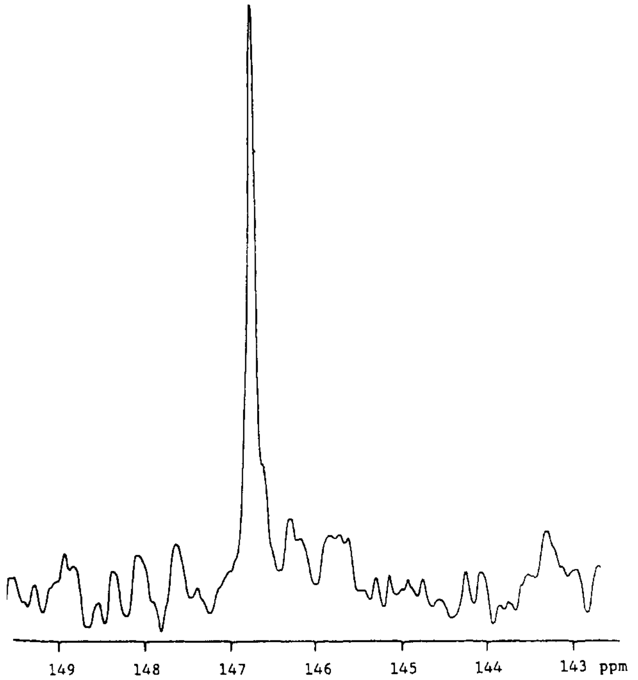

Figure 1. ^{13}C NMR spectrum of the MEK insoluble fraction of iPS6.

pronounced melting peak was observed around 180 °C; this is attributed to the melting of imperfect crystalline regions in the sample. Crystallinity for our samples varied between 10 and 25% and is here defined as

$$\% \text{ crystallinity} = \frac{\Delta H_f}{\Delta H_f^\circ} \times 100$$

where $\Delta H_f^\circ = 20.65$ cal/g for a pure crystalline sample.[6]

Although the anionic polymerization of isotactic polystyrene is achieved using the tBuOLi modifier, the mechanism involved in the isotactic placement of styrene is not altogether clear. Roovers and Bywater conducted studies on the effects of tBuOLi on the initiation and propagation rates in the room-temperature anionic polymerization of styrene in benzene.[5] They found that the addition of tBuOLi causes the initiation rate to change from $^1/_6$ order with respect to BuLi to $^1/_2$ order, possibly due to disruption of the hexameric alkyls by the alkoxide. The propagation rate was still found to be $^1/_2$ order with respect to the polystyryl anion as expected in anionic synthesis, but reaction rates were greatly reduced up to ratios of tBuOLi/BuLi of unity. Roovers and Bywater then proposed that the polymerization could proceed with the polystyryl ion existing in association with the alkoxide in dimeric form: $(\text{PstLi/tBuOLi})_2 \Leftrightarrow 2(\text{PstLi/tBuOLi})$. Their experiments were conducted in benzene at 30 °C, and no mention was made to the presence of any insoluble product that would indicate the synthesis of isotactic material. We have found that increasing the ratio of alkoxide to alkyl does not appear to enhance the amount of recovered product; nothing can be said at this point regarding the level of association of the two compounds in our reaction.

From our results it is clear that the essential conditions for the synthesis of isotactic polystyrene are low temperatures (in the range of −30 °C), nonpolar solvents, and the presence of an associating agent. The alkoxide, in an associated form with the growing polystyryl ion, could present enough steric hindrance to induce isotactic placement of incoming monomer units. For the insoluble fractions obtained in our low-temperature polymerizations, the ^{13}C NMR spectra we obtained displayed a pronounced isotactic peak with a significant absence of an atactic signal; this suggests that once a chain begins to polymerize isotactically, it continues to add units in the same manner, rather than shift back and forth from the associated to nonassociated dimeric polystyryl form as is the case at a higher temperature. Thus at low temperatures we envision a rather static mixture consisting of associated complexes, resulting in the formation of the iPS fraction of the total product, and unassociated anions, yielding the atactic material.

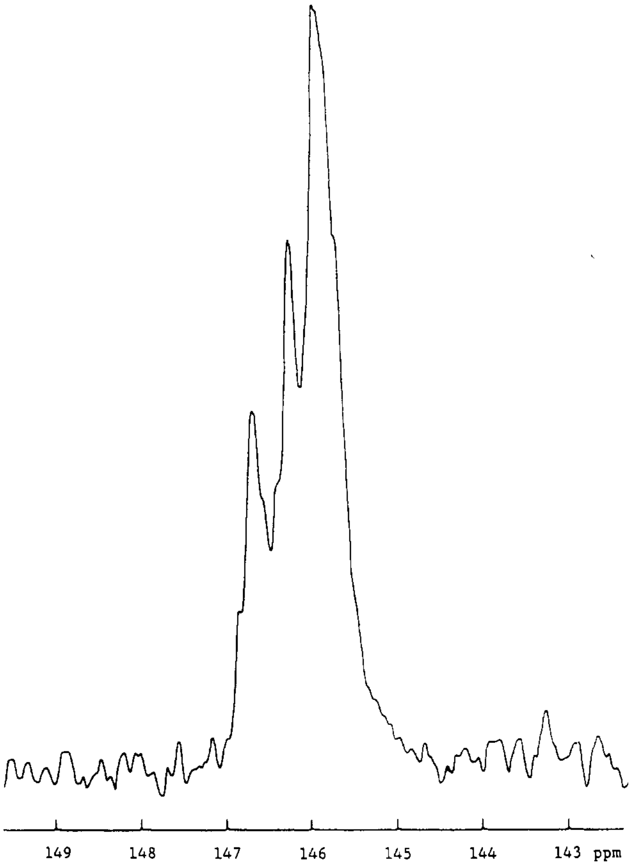

Figure 2. ^{13}C NMR spectrum of the MEK soluble fraction of iPS6.

There are several advantages to the method of anionic synthesis of isotactic polystyrene reported here over other methods. While for Ziegler–Natta systems the overall yields of isotactic product are much larger (>90%), there is very little control of molecular weight or polydispersity (6–9 range). This new anionic polymer synthesis route results in lower polydispersities and allows, through a combination of the polymerization time and the amount of initiator used, better control of the molecular weight of the final product than other methods.

As mentioned initially, one of the most attractive aspects of this synthesis procedure is that it provides a pathway for subsequent block copolymer preparation. The "living" character of the isotactic chains has been confirmed in several ways. We have observed that molecular weight increases with conversion in all our reactions. Also, the isotactic polystyryl anions have been successfully end-functionalized using various reaction conditions and reagents that have been employed[7] for living atactic polystyrene chains. Finally, we have been successful in carrying out sequential anionic polymerizations of isotactic polystyrene/polybutadiene block copolymers. Details of the synthesis and characterization of block copolymers containing isotactic polystyrene will be presented in a forthcoming communication.

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Communications to the Editor

Bicontinuous Microfoams by Water-Induced Phase Separation in Poly(vinyl methyl ether)-*cross*-Polystyrene Semiinterpenetrating Networks

Introduction. Semiinterpenetrating (semi-IPN's) and interpenetrating (IPN's) polymer networks based on miscible polymer blends are receiving increasing attention.[1-7] Major points of interest are influences of cross-linking of one or both components on the phase diagram[1-5] and also the dynamics of phase separation. Another point is related to the orientational coupling between the two components in such a multicomponent material.[3] Cross-linking of one of the components allows the study of segmental orientation up to large deformations in uniaxial elongation. In addition, cross-linking provides a simple means to study the mechanical behavior in the glass-transition region over the whole composition range.[7] Other features of miscible semi-IPN's include the investigation of the relaxation of the free chains as a function of cross-link density and molecular weight of the free chain.

In the present communication we report the formation of bicontinuous microfoams starting from PVME-*cross*-PS semi-IPN's. Microfoam materials can show unconventional morphologies. The most recent work in the field has been developed by the groups of Keller[8] and Berghmans[9] by preparing glassy microfoams from PS solutions.

PVME-*cross*-PS semi-IPN's are prepared by reacting poly(styrene-*co*-maleic acid) copolymer P(S-*co*-MA) (about 4.8 mol % of MA units) with hexamethylenediamine (HMDA) in solution in the presence of PVME. A more detailed description of the synthesis is given elsewhere.[3,7] The synthesis of semi-IPN's starting from polymeric precursors rather than using cross-linking polymerization of styrene and divinylbenzene[2,10] has two major advantages. S/DVB polymerization is known to result in heterogeneous networks; the formation of graft copolymer by radical abstraction of the tertiary hydrogen cannot be excluded. In addition, phase separation occurs at rather low levels of cross-linking.[2,6,10]

Experimental Section. Semi-IPN's of varying composition (0–90 wt % PVME) and cross-link density (1–4 mol % HMDA with respect to styrene repeating units) were prepared. Usually films of 0.1–0.3 mm thickness were prepared. After careful drying the samples were stored in a desiccator prior to use.

Swelling and Extraction. The swelling experiments in water were performed at 25 °C over a period of 4–5 mo, until no changes in the sample weight were detectable. Water was frequently exchanged to enhance the extraction rate by an osmotic pressure gradient.

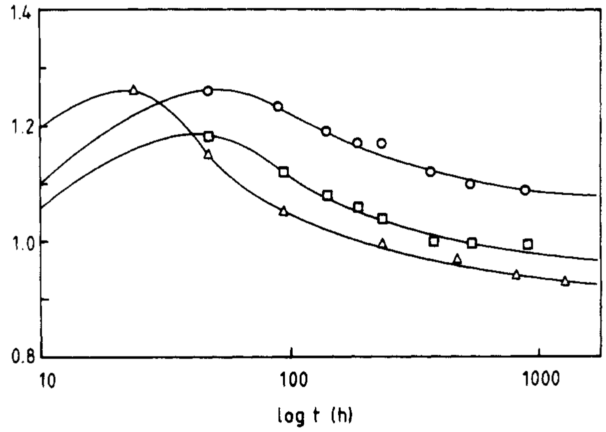

Figure 1. Change of the mass of PVME-*cross*-PS semi-IPN's with time upon swelling in water (T = 25 °C). Cross-link density: 4 mol % HMDA. The different symbols are related to different sample compositions. wt % PVME: ○, 60; △, 70; □, 80.

Electron Microscopy. The extracted samples were imbedded in EPON 812; ultrathin sections were obtained using a Reichert–Jung ultramicrotome (Ultracut E). A Zeiss 902 electron microscope, which allows element specific image analysis,[11] was used for the morphological studies. Both elastic bright field and element specific images from inelastically scattered electrons were made to cross-check the structural information.

Results. Homogeneous, single-phase networks are obtained at low levels of cross-linking (1 and 2 mol % of crosslinker).[7] Two glass transitions are observed for networks with a higher degree of cross-linking (3 and 4 mol %).[12] This clearly demonstrates the significant influence of cross-linking on the phase behavior. A more detailed study of these phenomena will be given elsewhere.[12]

Water easily penetrates into the PVME-*cross*-PS semi-IPN's due to the hydrophilicity of PVME and the low glass transition (despite for materials with a high PS content). The transparent semi-IPN's become opaque, indicating phase separation.

The overall process to be considered upon immersing the semi-IPN's in water includes swelling, phase separation (or further phase separation in the higher cross-linked samples), and extraction of free PVME chains.

While the observed turbidity clearly proves water-in-

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