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Synthesis and Characterization of Isotactic Polystyrene/Polybutadiene Block Copolymers

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ABSTRACT: Diblock copolymers of isotactic polystyrene and 1,4-polybutadiene were successfully synthesized by two methods: (a) sequential anionic synthesis of the isotactic polystyrene followed by the polybutadiene block and (b) end functionalization and coupling of the two homopolymers. The polybutadiene blocks were prepared by anionic polymerization, with a resulting microstructure of approximately 90% 1,4 and 10% 1,2 addition. The preparation of the isotactic polystyrene block involved a novel anionic polymerization technique using a nonpolar solvent, low temperatures, and the addition of *tert*-BuOLi to induce stereospecific placement.[1] The polymers were fully characterized by GPC, ^{1}H and ^{13}C NMR, and DSC to determine molecular weights, tacticity, and thermal transitions. Wide-angle X-ray scattering was used to determine the crystallinity of the iPS regions of the heterogeneous materials. The blocklike structure of the copolymers was supported by the results of transmission electron microscopy (TEM), which revealed morphological order and length scales typical of microphase-separated block copolymers.

Introduction

There has been increased interest in our laboratory in block copolymer systems where one or more of the block segments can crystallize, such as in the case of isotactic polypropylene/polybutadiene,[2] isotactic polypropylene/isotactic polystyrene,[3] atactic polystyrene/poly(ethylene-*co*-butylene),[4] and nylon 6/poly(dimethylsiloxane).[5] These studies have attempted to develop an understanding of how the extra dimension of crystallinity can affect the microphase-separated morphology and therefore the properties of the block copolymer. The present paper focuses on the synthesis and characterization of semicrystalline diblock copolymers of isotactic polystyrene/amorphous polybutadiene. We intend to examine the effectiveness of these diblock copolymers as emulsifying and toughening agents for isotactic polystyrene/polybutadiene homopolymer blends; results of mechanical property studies of these systems will appear in a forthcoming publication.

Various synthesis pathways were considered for the semicrystalline iPS/PB diblock copolymers. The amorphous polybutadiene segments were prepared by traditional anionic polymerization techniques, with *n*-BuLi as the anionic initiator in the nonpolar solvent hexane. This procedure resulted in well-defined living PB blocks, which can be easily incorporated into a diblock copolymer preparation scheme. The synthesis of isotactic polystyrene was a more complex problem, as stereospecific growth is required to obtain the isotactic microstructure necessary for the material to crystallize. The use of a Ziegler–Natta catalytic system for the iPS block was rejected due to the high chain termination inherent in this kind of polymerization chemistry; while of little consequence when preparing semicrystalline homopolymer, terminated chains are of no further use in the subsequent preparation of a diblock copolymer. We also considered and rejected the possibility of employing some form of transformation reaction as described in the literature[6,7] and previously employed in our laboratory.[2] A novel method for the anionic synthesis of isotactic polystyrene was investigated instead; the details of this polymerization have already been described in a previous paper.[1] By using *tert*-BuOLi as an associating agent in the *n*-BuLi initiated polymerization of styrene at low temperatures, isotactic placement of the monomer is achieved in reasonable yields with the significant advantage that the chains retain the living end characteristic of anionic synthesis.

Semicrystalline iPS/PB diblocks were prepared by following one or two procedures: (1) sequential polymerization of the butadiene and styrene monomers or (2) termination of the individual homopolymers with specific end functionalizers, followed by a coupling reaction to produce a well-defined block copolymer structure.

Experimental Section

Reagents and Apparatus. All reagent purifications and subsequent syntheses were conducted by using a high vacuum/inert gas setup. Vacuums of better than 10^{-5} Torr were achieved by means of a roughing pump and oil diffusion pump connected to a mannifold equipped with Teflon/O-ring valves. The argon gas (>99.999% ultrahigh-purity Matheson Gas) passed through a 4-Å molecular sieve column followed by a deoxifying BASF copper-based catalyst column before use in flushing reactors and in maintaining an inert-gas blanket for all polymerizations.

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 an indication of purity. The butadiene monomer was washed with 10% NaOH solution, collected over calcium hydride at −78 °C, and then vacuum distilled through a series of flasks coated with fresh sodium mirrors before being placed in the freezer. This monomer was likewise stored with appropriate amounts of Bu_2Mg to ensure purity. A middle fraction of hexane solvent was initially vacuum distilled onto calcium hydride, stirred overnight, distilled a second time, and finally stored over a sodium dispersion. The initiator for our anionic polymerizations was *n*-BuLi, 1.6 or 2.5 M in hexanes as acquired by Aldrich Chemical Co.; the molarity of these solutions was checked by titrating with *sec*-butanol in xylene. The *tert*-BuOLi was either acquired from Aldrich as a powder and dissolved in hexane prior to addition to the reactor or prepared directly in specific ratios of *tert*-BuOLi/BuLi as described in the literature.[8]

Carbon dioxide gas for the polybutadiene end-capping reaction was purchased from Matheson as bone dry CO_2. The polystyrene chains were aminated by using *N*-benzylidene(trimethylsilyl)imine as an end-functionalizing agent.[9] This compound was prepared following the procedure of Krüger, Rochow, and Wannagat.[10]

Sequential Synthesis. For this approach, living polybutadiene was used to initiate the polymerization of styrene. The butadiene monomer and hexane solvent were vacuum distilled directly into a reactor flask that had been previously cleaned with hydrofluoric acid and flamed dried under vacuum. The

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Table I
Polymerization Conditions in Hexane

sample	block	polym temp, °C	initiator	end-capping agent
S41/B11	PB	50	*n*-BuLi	CO_2
(coupled)	iPS	−30	*n*-BuLi/*tert*-BuOLi	$C_5H_6CHNSi(CH_3)_3$
S15/B4.5	PB[a]	50	*n*-BuLi	not terminated
(sequential)	iPS	−30	PB[a]/*tert*-BuOLi	MeOH
S30/B13	PB[a]	50	*n*-BuLi	not terminated
(sequential)	iPS	−30	PB[a]/*tert*-BuOLi	MeOH
S100B52	PB	50	*n*-BuLi	CO_2
(coupled)	iPS	−30	*n*-BuLi/*tert*-BuOLi	$C_5H_6CHNSi(CH_3)_3$

[a] Indicate living polybutadiene used in sequential block polymerization.

Table II
Diblock Characterization

	S41/B11	S15/B4.5	S30/B13	S100/B52
wt % iPS	79	77	70	66
wt % PB	21	23	30	34
M_n^{iPS}	41 000	15 000	30 000	100 000
M_n^{PB}	11 000	4500	13 000	52 000
T_m^{iPS}, °C	210–216	204–210	205–210	213
T_g^{iPS}, °C	97	92	92	89
T_g^{PB}, °C	−91		−92	−88
% cryst[a]	11–20	7–11	3–7	20

[a] Based on DSC measurements and taken on a polybutadiene-free basis.

mixture was stirred continuously at 0 °C to reduce butadiene monomer pressure. After injection of *n*-BuLi initiator, the temperature was raised to 50 °C and the reaction allowed to proceed to completion as calculated by available kinetic data.[11] The second reactor consisted of a 500-mL flask set up with a central shaft to accommodate an external stirrer. Styrene monomer and hexane solvent were introduced into this flask via vacuum distillation from their respective storage flasks. A *tert*-BuOLi (0.77 M) solution was added in an approximate 1:1 ratio with the living polybutadiene initiator. The temperature of this styrene reactor was lowered to 0 °C by an isopropyl alcohol bath equipped with a Neslab cryogenic cooler offset by an immersion heater. The previously prepared living polybutadiene was then transferred into this reactor through a cannula using argon overpressure, and the final polymerization temperature was set at −25 °C. The reaction was allowed to proceed for approximately 2–4 days, after which it was terminated by the addition of a few milliliters of degassed methanol.

Coupling Reaction. The procedures for the synthesis of the individual homopolymers to be used in the coupling reaction are similar to those stated in the previous section; the polymerization of styrene was, however, initiated directly by *n*-BuLi in the presence of *tert*-BuOLi. In both cases, the reaction was not terminated with degassed methanol but rather by the addition of a specific end-functionalizing agent. For the polybutadiene living homopolymer bone dry carbon dioxide gas was bubbled directly into the reactor so as to terminate the chains with a carboxylic acid end group; tetrahyrofuran was added prior to this in order to prevent coupling reactions.[12] End functionalization was checked by titrating with a 0.01 M KOH solution to the phenolphthalein end point.[13]

For polystyrene, *N*-benzylidene(trimethylsilyl)imine was the chosen end functionalizer and was added directly to the polymerization reactor in stoichiometric excess.[9] The polymer was then recovered in methanol, dried, dissolved in xylene at elevated temperatures in order to force the isotactic polystyrene into solution (≈100 °C), and finally hydrolyzed with dilute acid solution (pH 3–5 using HCl in a 75% hydrocarbon/25% water v/v solvent) in order to cleave the silyl group, thereby resulting in an amine-terminated polymer.[14] The product was refluxed in methyl ethyl ketone using a Soxhlet extractor, with the insoluble portion recovered as the desired isotactic polymer.[1] Titrations to determine percent end functionalization were conducted by using perchloric acid in glacial acetic acid to the potentiometric or crystal violet indicator end point.[15]

The condensation reaction to couple the blocks was conducted in dry toluene under inert argon atmosphere conditions to minimize polybutadiene oxidation. A stoichiometric excess of the polybutadiene–COOH end-capped homopolymer was used to shift the condensation equilibrium toward complete diblock formation. 1-Hydroxybenzotriazole and dicyclohexylcarbodiimide were also added to aid in the coupling reaction.[16] A summary of the polymerization conditions for several diblocks is given in Table I.

Measurements. Molecular weights for our samples were determined by gel permeation chromatography (GPC) on either a 510 or a 100A Waters GPC equipped with 10^3-, 10^4-, and 10^5-Å columns with toluene as the solvent phase. Samples for differential scanning calorimetry were dissolved in toluene, precipitated in methanol, vacuum dried at 80 °C, and pressed into aluminum pans for analysis on a Perkin-Elmer DSC4. ^1H and ^{13}C NMR scans were provided by the Department of Chemistry Spectroscopy Laboratory at MIT. Thin samples were prepared by either static casting from toluene solutions at 50 °C or by molding in a Carver press at 260 °C into thin films in the range of 0.2–1.0 mm. Various thermal histories were applied to the films using a high-temperature VWR 1410D vacuum oven. After staining the material using 1% OsO_4 or 0.5% RuO_4 solutions, thin sections were ultramicrotomed on a LKB Ultratome II and were collected on 200-mesh copper specimen grids and examined with a Phillips 300 TEM. Wide-angle X-ray scattering data were collected by a Rigaku Denki rotating-anode X-ray source and Rigaku pole figure detection hardware. Characterization results for our diblock copolymers are presented in Table II.

Results and Discussion

It is important to establish unequivocably the blocklike nature of the final recovered material. Extensive characterization is required in order to satisfactorily distinguish the block copolymer from a simple blend of two or more homopolymers. The sequential synthesis method we have employed starts off with a well-characterized polybutadiene block which provides the only available site for the styrene monomer to grow, while for the coupling method the two-block nature of the final copolymer material is inherent to the coupling reaction itself. While these techniques then preclude some alternating or random copolymerization, they do not address the possibility of a blend. The sequential synthesis product includes atactic diblock and prematurely terminated polybutadiene chains, while the coupling product may in principle contain a mixture of the diblock and both of the uncoupled homopolymers. Removing the semicrystalline iPS/PB copolymer from these polymerization byproducts is also a major consideration.

Characterization of the sequential block copolymers involved some estimation of the molecular weight of the isotactic polystyrene segment. Since the iPS blocks were grown directly from living polybutadiene chains, they could not be separately characterized as in the analogue coupling case. An aliquot of the living polybutadiene was extracted and characterized by GPC prior to the addition of the styrene monomer. After complete polymerization, the reaction product was washed several times with MEK to extract any atactic copolymer formed as well as any prematurely terminated homopolymer polybutadiene chains. The final composition of the cleaned-up copolymer was determined through ^1H NMR: the ratio of the styrene aromatic proton peaks (≈7.0 ppm) to those of the polybutadiene (≈4.5–5.0 ppm) and the known M_n of the original PB segment were sufficient to calculate an approximate M_n for the isotactic polystyrene block. In this way, S15/B4.5 was determined to have a M_n^{iPS} of 15 000, while the corresponding value for the S30/B13 block was calculated as 30 000.

For the coupling reaction scheme, the end-functionalized homopolymers were extensively characterized prior

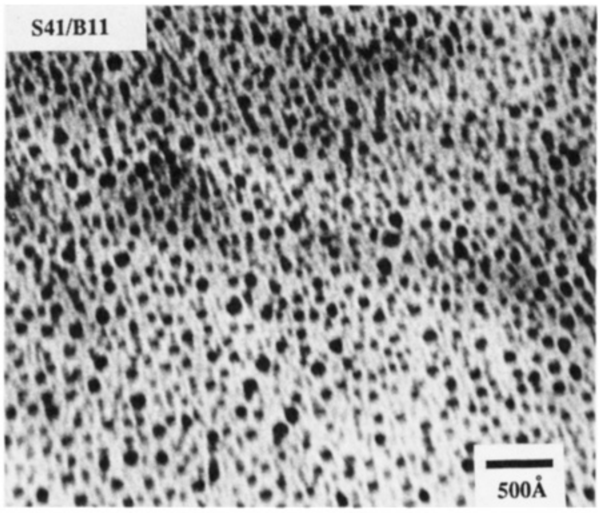


Figure 1. TEM micrograph of S41/B11, molded at 260 °C and quenched to ambient temperature.

to being incorporated into the diblock. The ^{1}H NMR spectra of the polybutadiene blocks were consistent with the expected ≈90% 1,4 and ≈10% 1,2 microstructure typical of anionic synthesis of butadiene in a nonpolar solvent. GPC analysis of the PB blocks used in the S41/B11 and S100/B52 coupling reactions yielded number-average molecular weights of approximately 11 000 and 52 000, respectively. The iPS homopolymer was extracted in refluxing methyl ethyl ketone until the ^{13}C NMR spectra showed a sharp peak at ≈146.8 ppm, indicating >95% isotactic content.[1,17] GPC provided a M_n^{iPS} value of approximately 42 000 for the iPS homopolymer used in the S41/B11 coupling reaction.

After coupling, excess amorphous PB is easily removed by washing the reaction product several times in hexane. The separation of any uncoupled iPS homopolymer from the final diblock copolymer cannot be as easily achieved. The overall iPS homopolymer and diblock content left after PB extraction may, however, be deduced from the GPC homopolymer data and the ratio of iPS to PB peaks obtained from ^{1}H NMR spectra; for S41/B11 this ratio approached that expected for complete coupling and was taken as an indication of successful (>95% yield) diblock copolymer formation. In the case of the S100/B52 coupling reaction, the original hexane-washed product contained a significant amount of unreacted iPS homopolymer, which had to be removed through several fractionation steps. The final recovered diblock product was analyzed through ^{1}H NMR and characterized as having a M_n^{iPS} value of approximately 100 000. The fractionation procedure resulted in a final yield of 39%.

DSC provided some further insight regarding the block-like nature of the copolymers. Three of the four diblocks displayed two glass transition temperatures in the range of +95 to ±90 °C for T_g^{iPS} and T_g^{PB}, respectively. Though this indicates the presence of heterogeneity in the materials, it does not necessarily substantiate the claim of diblock copolymer formation, as multiple glass transition temperature could apply to a blend as well. Granger and co-workers have measured a depressed T_g^{PS} of approximately 90 °C for the atactic polystyrene segment of heterogenous PS/PB block copolymers.[18] Our isotactic polystyrene T_g values appear to follow this trend. The sequential S15/B4.5 material differed from the other copolymers in that, while a transition at 92 °C for T_g^{iPS} was observed, no clear indication of a T_g^{PB} in the lower temperature range could be identified. Instead, a very distinct transition is observed at approximately 65 °C, which corresponds roughly to the weighted average of the glass transition temperatures for the two individual homopolymers. These results suggest that some fraction of this particular copolymer is homogeneous, while another fraction is heterogeneous due possibly to partial crystallization occurring in solution. The semicrystalline regions will contain some uncrystallized glassy iPS, which is responsible for the transition at 92 °C.

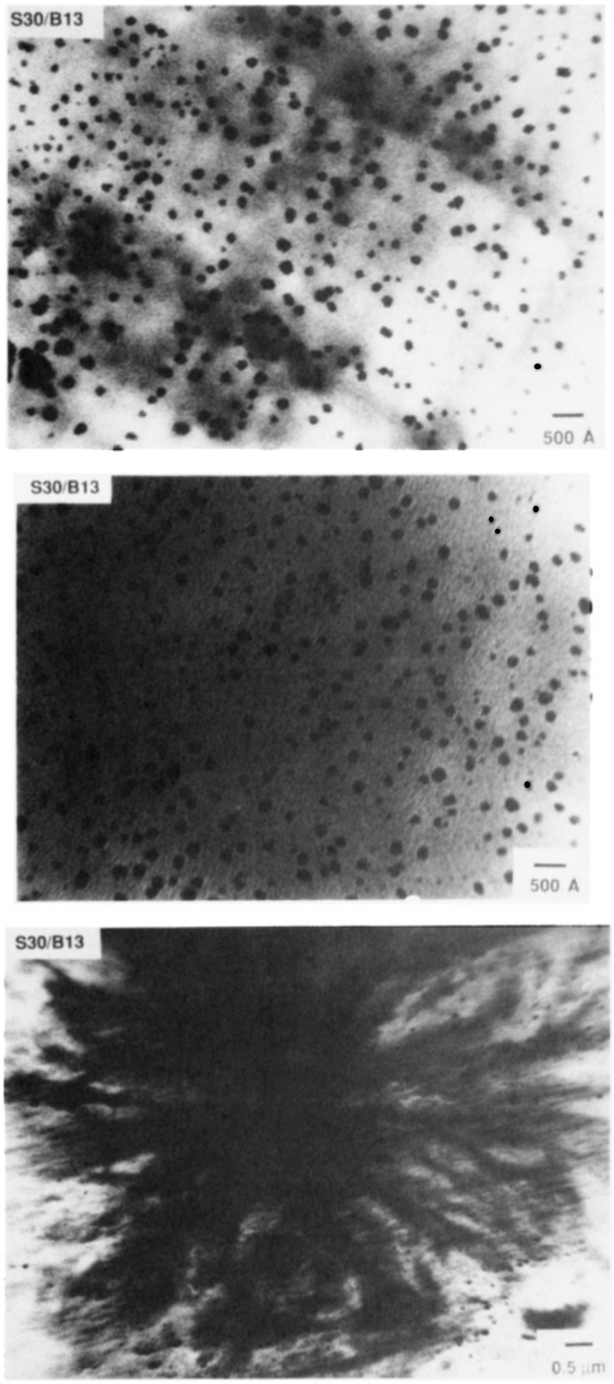


Figure 2. TEM micrographs of S30/B13 (a, top) molded at 260 °C and quenched and (b and c, middle and bottom, respectively) annealed at 175 °C for several hours.

Transmission electron microscopy (TEM) provided direct and conclusive visual evidence for the diblock nature of the synthesized materials. Due to the restriction imposed by the chemical linkage between the two blocks, the scale of morphological heterogeneity of diblock copolymers is limited to the nanometer scale characteristic of microphase-separated materials. Figure 1 shows the

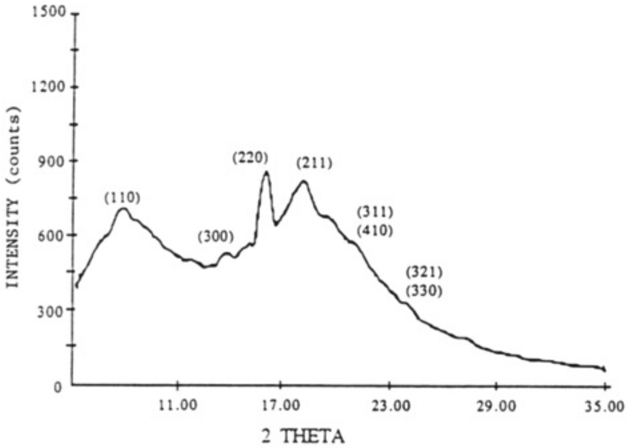
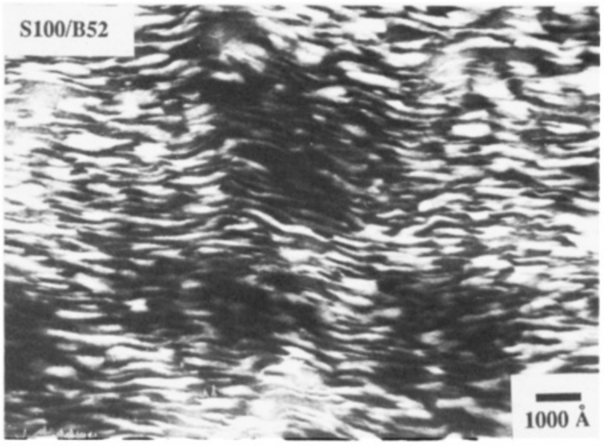


Figure 3. WAXS diffraction pattern for S30/B13 molded at 260 °C and subsequently annealed at 175 °C for several hours.



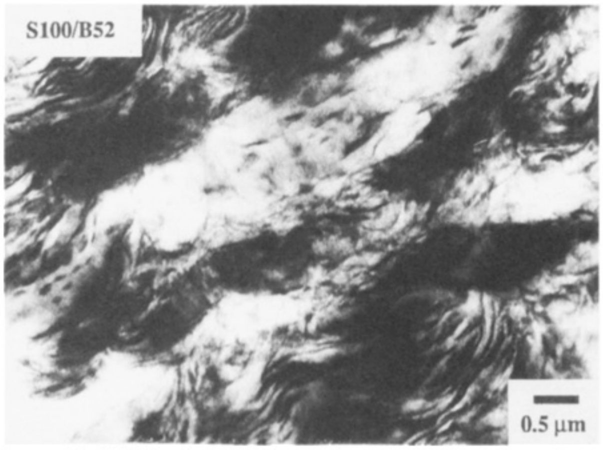


Figure 4. TEM micrographs of S100/B52 (a, top) molded at 260 °C and quenched and (b, bottom) annealed at 175 °C for several hours.

morphology observed for S41/B11, compression molded and quenched in liquid nitrogen so as to minimize the effects of crystallization. A fine distribution of small dark spherical polybutadiene domains (OsO_4 stained) averaging a few hundred angstroms in diameter appears to be uniformly distributed throughout the polystyrene matrix. For the case of an incompatible homopolymer blend, this regularity and scale of phase separation could not be achieved using the simple molding procedure we have employed.

Further examination of the morphologies of these materials focused on the competition between crystallization and microphase separation.[4,5] Figure 2a represents S30/B13 molded at 250 °C and quenched in liquid nitrogen, while parts b and c of Figure 2 show the same sample after several hours at the optimum crystallization temperature[19] of 175 °C. The spherical morphology observed in the amorphous sample (Figure 2a) persists in the crystallized material (Figure 2b) for which evidence of spherulites can be seen at lower magnification (Figure 2c). The presence of crystallinity is confirmed by the WAXS scans shown in Figure 3. The crystallized sample shows the typical pattern for a partially crystallized unoriented isotactic polystyrene homopolymer.[20] As in the case of other semicrystalline block copolymers,[5] when the formation of spherulitic crystalline texture occurs in the presence of the microphase-separated morphology, the former engulfs the latter but does not destroy or disrupt the nanoscale structure.

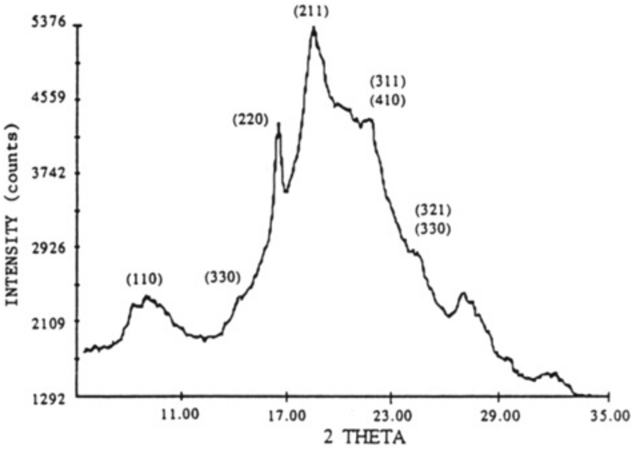
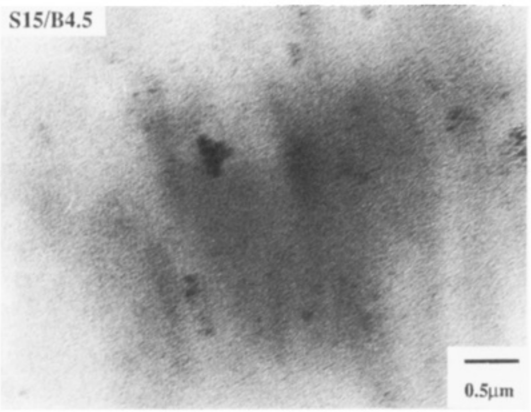


Figure 5. WAXS diffraction pattern for S100/B52 molded at 260 °C and subsequently annealed at 175 °C for several hours.



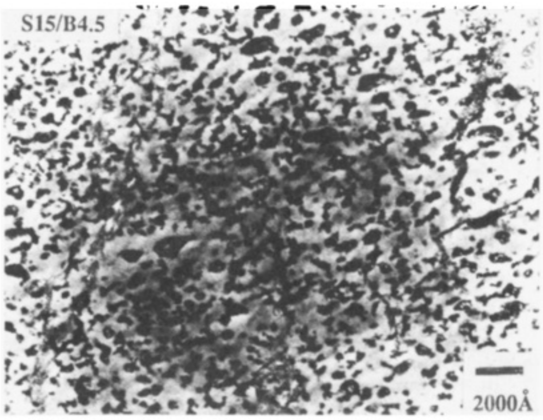


Figure 6. TEM micrographs of S15/B4.5 (a, top) molded at 260 °C and quenched and (b, bottom) annealed at 175 °C for several hours.

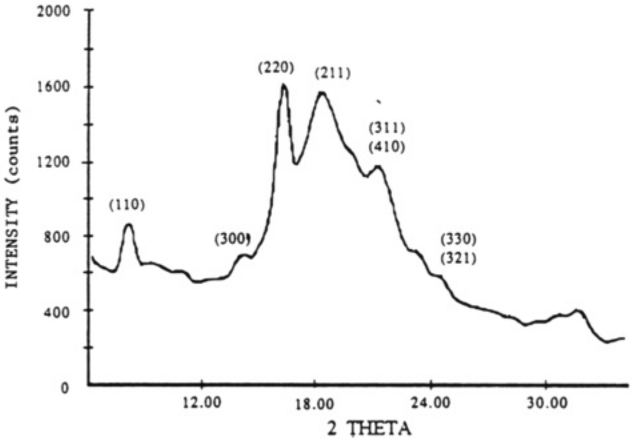


Figure 7. WAXS diffraction pattern for S15/B4.5 molded at 260 °C and subsequently annealed at 175 °C for several hours.

Similar behavior is observed for the S100/B52 semicrystalline diblock copolymer. In this case the phase separation takes the form of cylinders of polybutadiene imbedded in the isotactic polystyrene matrix as shown in Figure 4a for a sample molded at approximately 260 °C and quenched to ambient temperature. The same sample is shown in Figure 4b after several hours at 175 °C. The cylindrical morphology still permeates the entire sample, though there is some distortion of the ordered PB domains in the presence of crystallinity in the iPS matrix. The presence of crystallinity is again supported by WAXS (Figure 5).

For the S15/B4.5 copolymer the low molecular weights of both segments suggest a homogeneous material at room temperature as indicated earlier in the DSC data and confirmed by the featureless TEM micrograph of Figure 6a. With the onset of crystallization, the rubber is excluded from the crystalline lamellae into separate domains as shown in Figure 6b; the observed morphology does not show typical regularity of size and shape expected for diblock copolymers. Evidently, for S15/B4.5, crystallization occurs prior to any microphase separation, and the morphology observed in Figure 6b reflects this fact. The presence of crystallinity is confirmed through the WAXS scan of Figure 7.

This crystallization-driven microphase separation is not necessarily limited to the specific case of low molecular weight diblocks but can also occur with the higher molecular weight copolymers that have been subjected to different processing conditions. This can be clearly illustrated by examining the TEM micrographs of Figure 8 for the S15/B4.5, S30/B13, and S100/B52 semicrystalline diblock materials static cast from toluene solution at approximately 50 °C. Crystallization once again precedes phase separation for the lower molecular weight copolymer as observed in Figure 8a, with an exclusion of the rubber from the growing crystalline fronts that are clearly highlighted by the RuO_4 staining. The same behavior is noted for the larger diblocks (parts b and c of Figure 8), where the onset of crystallization results in either complete suppression or considerable disruption of the expected equilibrium microphase-separated structure.

These results can be interpreted through a simplified phase diagram such as those described in refs 4 and 5. A diblock sample molded above both the microphase separation temperature (T_{MST}) and the melting point T_m eliminates any effects of crystallinity or phase separation. As the temperature is decreased, microphase separation is achieved at T_{MST} prior to crystallization, which then occurs at $T_m < T_{MST}$. This is the case for both the S30/B13 and S100/B52 diblocks shown in Figures 2 and 4. When the same materials are instead dissolved in toluene and static cast at 50 °C, crystallization is observed, and this effectively suppresses any later microphase separation that might be expected at lower solvent content; in this way a morphology reminiscent of that observed for the S15/B4.5 sample in Figure 6b is produced. These results indicate the need for understanding the level of interaction between thermodynamically controlled and kinetically restricted processes that can combine to define a final morphology in semicrystalline block copolymers. Clearly the profile of properties exhibited by such materials will be dictated by the particular path-dependent morphology that exists in a given specimen.

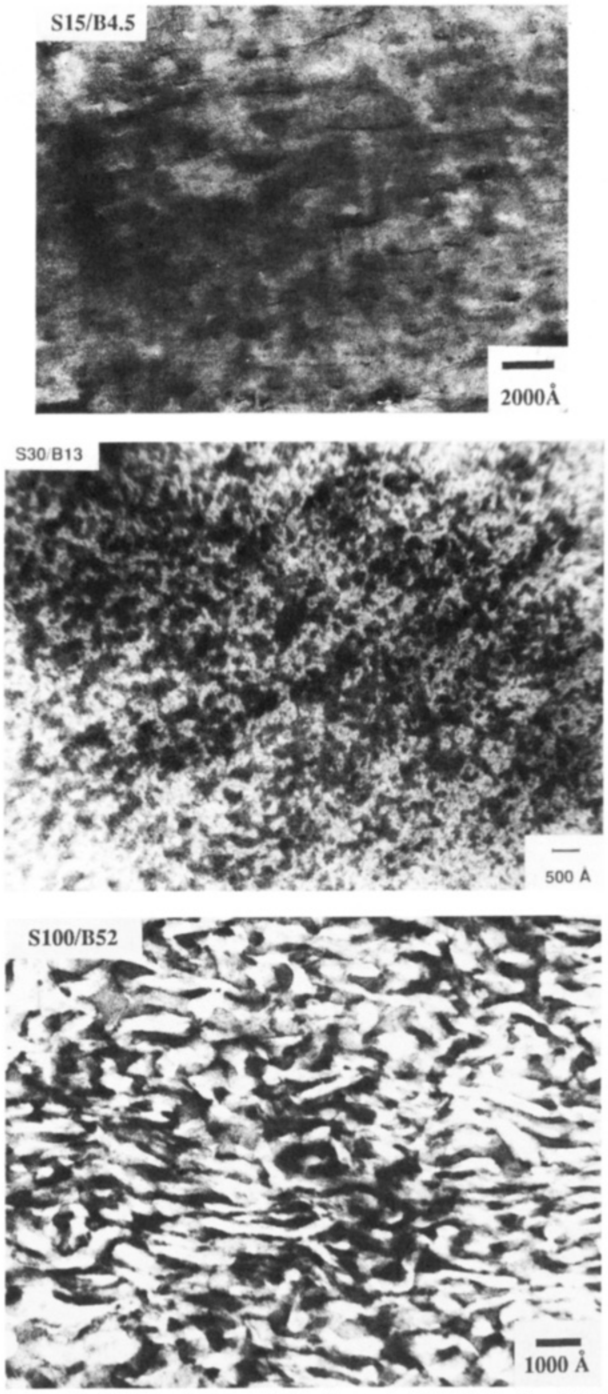


Figure 8. TEM micrographs for (a, top) S15/B4.5, (b, middle) S30/B13, and (c, bottom) S100/B52 static cast from toluene at 50 °C.

Conclusions

By employment of a novel anionic polymerization technique for the semicrystalline isotactic polystyrene segment, diblock copolymers of iPS/PB have been successfully prepared. The sequential synthesis of the two monomers or the coupling reaction of two end-capped homopolymers provided materials with well-defined diblock structures. The ratio of isotactic polystyrene to polybutadiene in these copolymers resulted in various microphase-separated morphologies, all at a scale typical of diblock copolymers. Path-dependent morphologies were observed, indicating that crystallization can occur prior to or after microphase separation, resulting in materials with significantly different final morphologies.

In the case of the amorphous PS/PB analogue system, diblocks have been found to act as emulsifiers for the incompatible homopolymers. The extent to which our iPS/PB diblocks can produce the same emulsification effect in the presence of isotactic polystyrene crystallinity will be the focus of a forthcoming paper.

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Registry No. (PS)(PB) (block copolymer), 106107-54-4; CO_2, 124-38-9; *tert*-BuOLi, 1907-33-1; *N*-benzylidene(trimethylsilyl)imine, 17599-61-0.