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Effect of Selective Perfluoroalkylation on the Segregation Strength of Polystyrene−1,2-Polybutadiene Block Copolymers

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ABSTRACT: A series of partially fluorinated ($C_6F_{13}H$-modified) polystyrene-*b*-1,2-polybutadiene (PS-*b*-1,2-PB) copolymers were prepared by the reaction of a model PS-*b*-1,2-PB copolymer with *n*-$C_6F_{13}I$ followed by substitution of hydrogen for the iodine by hydrogenolysis. The morphologies and domain spacings of the ordered samples at 120 and 195 °C were determined as a function of $C_6F_{13}H$ modification extent using small-angle X-ray scattering (SAXS). From the domain spacings an effective interaction parameter (χ_{eff}) between the PS and partially $C_6F_{13}H$-modified 1,2-PB blocks was estimated. The χ_{eff} at 120 °C increases significantly with fluorination, from ca. 0.05 (0 mol % $C_6F_{13}H$ modification) to ca. 0.75 (80 mol % $C_6F_{13}H$ modification). The order−disorder transition temperature (T_{ODT}) for a partially $C_6F_{13}H$-modified PS-*b*-1,2-PB (25 mol %) was determined to be 186 ± 3 °C, using rheology and static birefringence. From self-consistent mean-field theory χ_{eff} for this block copolymer is estimated to be 0.16 at T_{ODT}, which agrees well with the value of 0.21 estimated from the domain spacing. These estimated interaction parameters demonstrate that a selective perfluoroalkylation approach can strongly enhance the incompatibility of PS-*b*-1,2-PB copolymers and is a powerful method for examining large regions of the block copolymer phase diagram with a single precursor molecule.

Introduction

The selective modification of block copolymers provides a means to continuously tune the interaction strength between the blocks and affect the self-assembly of the resultant materials, thus providing a powerful method for investigation of phase behavior. This is particularly true when the modification leads to a significant change in the magnitude of the segment−segment interaction, since large spans of segregation strength can be systematically studied using one parent material. Fluorination of model block copolymers is one such modification. Several examples of selective polymer modifications, including fluorinations, employ polystyrene−polydiene block copolymers as the starting materials due to the potential reactivity of the polydiene double bonds and the relatively inert nature of polystyrene (e.g., polydiene chlorination,[1] epoxidation,[2] and hydrogenation[3]). The incorporation of fluorine yields polymer materials with low surface energies,[4] enhanced solubility in supercritical CO_2,[5] and low refractive indices and dielectric constants.[6] Because of their low cohesive energy densities, highly fluorinated polymers are also strongly incompatible with both nonpolar and polar polymers such as polyolefins and polyethers, respectively.[7] Therefore, mild, selective, and quantitative fluorinations are important tools to introduce desired properties into polymeric materials and to systematically increase the incompatibility between the two blocks in a block copolymer to a substantial degree. Recent work suggests that block copolymers might exhibit novel self-assembly behavior in bulk[8] and solution[9] when the incompatibility between the blocks is sufficiently large. Our research focus has been on the post-polymerization fluorination of polydienes and the extension of the above methods to selective block copolymer modification with these goals in mind.[10]

We previously reported a new method for the selective and quantitative functionalization of polydienes with difluorocarbene (CF_2),[11] applied this selective modification to polystyrene-*b*-polyisoprene (PS-*b*-PI) copolymers, and systematically investigated the effect of CF_2 modification on the block copolymer interaction strengths.[12] Interestingly, in this case the incorporation of fluorine *increased* the cohesive energy density of the material, due to the polarity of the resulting difluorocyclopropane unit. In a subsequent effort, we developed a mild route to highly fluorinated model polymers via the modification of polydienes using perfluoroalkyl iodides (R_fI).[13] In this paper we assess the effect of perfluoroalkylation on the PS-*b*-(1,2-polybutadiene) (1,2-PB) copolymer interaction strength.

Experimental Section

Materials and Molecular Characterization. Detailed descriptions of the preparation of the model block polymer precursor, reaction with perfluorohexyl iodide ($C_6F_{13}I$), and hydrogenolysis of the resulting $C_6F_{13}I$-modified block polymers can be found in the previous paper.[13] Briefly, the precursor was synthesized by sequential living anionic polymerization in cyclohexane, using *sec*-butyllithium as the initiator. The perfluoralkyl groups were incorporated into the polydiene block by a free radical process, initiated by triethylborane in the presence of air, and conducted at room temperature in a 1:1 mixture of hexanes and 1,1,2-trichlorotrifluoroethane. The iodine atoms incorporated into the chain were removed by hydrogenolysis in a mixture of α,α,α-trifluorotoluene ($PhCF_3$, BTF), methanol, and KOH, using Pd on $CaCO_3$ as the catalyst at 70 °C under ca. 500 psi of H_2 for 109 h, conditions identical to those reported previously.[13] The PS-*b*-1,2-PB:$C_6F_{13}H$ copolymers were precipitated in methanol with 0.1 wt % 2,6-di-*tert*-butyl-4-methylphenol (BHT), which can minimize thermal degradation during subsequent morphological characterization at elevated temperatures without significant effects on the morphologies.[14] All the block polymers were characterized by

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nuclear magnetic resonance (NMR) spectroscopy and size exclusion chromatography (SEC). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian 300 VXR or a Varian 500 VI spectrometer. A Hewlett-Packard 1100 series liquid chromatography system equipped with a Hewlett-Packard 1047A refractive index (RI) detector and three Jordi Gel columns of 500, 10^3, and 10^4 Å porosities was calibrated using polystyrene standards (Polymer Laboratories). The block copolymer precursor was also characterized by a second SEC system equipped with a Wyatt OPTILAB RI detector, a Wyatt multiangle light scattering detector (MALS), and three Phenogel (Phenomenex) columns of 10^3, 10^4, and 10^5 Å porosities.

Morphological Characterization. The morphological characterization by small-angle X-ray scattering (SAXS) was performed at the University of Minnesota on a home-built beamline. Two-dimensional diffraction images were recorded using a Siemens area detector located at the end of an evacuated flight tube and corrected for detector response before analysis. The two-dimensional images were azimuthally integrated and reduced to the one-dimensional form of scattered intensity vs scattering wavevector, $q = 4\pi\lambda^{-1}\sin(\theta/2)$, where θ is the scattering angle. All the rheological measurements were performed on a Rheometrics ARES rheometer. The parallel plate geometry was used throughout, with a plate diameter of 25 mm and gap height of 0.8–1.4 mm. The temperature of the sample chamber was controlled by a nitrogen convection oven. The dynamic storage (G') and loss (G'') moduli were recorded as a function of temperature. For the static birefringence measurements polymers were pressed in a 1 mm thick aluminum ring, sandwiched by two Teflon sheets using a hot press. The annealed sample was then sandwiched between two polished glass disks and sealed with a high-temperature silicone sealant (General Electric). The sealed sample cell was placed into a sample holder and heated to a temperature above the T_g of both blocks using an electrically heated copper block. A vertically polarized laser beam from a 5 mW HeNe laser passed through the sample cell. The transmitted beam passed through a horizontal polarizer and was converted to a voltage signal by a photodiode detector. The transmitted depolarized light intensity was recorded as a function of temperature.

Results and Discussion

We prepared and characterized a series of partially fluorinated ($C_6F_{13}H$-modified) PS-*b*-1,2-PB copolymers by the reaction of a model PS-*b*-1,2-PB copolymer with *n*-$C_6F_{13}I$ followed by substitution of hydrogen for the iodine by hydrogenolysis.[15] As described in detail in the previous paper,[13] the addition of $C_6F_{13}I$ to the pendant double bonds in the 1,2-PB block preferentially yields the cyclization product over the open-chain addition, and predominant five-member ring formation along the polymer backbone was observed (Figure 1). Using this method, the PS-*b*-1,2-PB copolymers were modified to different extents by controlling both the molar ratios of the reagents (i.e., $C_6F_{13}I$ and Et_3B) and the reaction times, using similar procedures to those described previously (Table 1).[13] All these partially $C_6F_{13}I$-modified block copolymers exhibited PDIs less than 1.1 (SEC), indicating that there was no significant chain scission and/or coupling during the $C_6F_{13}I$ modification. In the ^{1}H NMR spectrum of the 25 mol % fluorinated PS-*b*-1,2-PB copolymer, we observed resonances at 4.4 and 3.1 ppm corresponding to the iodomethylene and iodomethyl protons in the open-chain adduct and cyclized product, respectively, and estimated that 3% of the double bonds formed open-chain adducts and 22% of the double bonds were cyclized. Since the extent of open-chain addition is modest, exclusive cyclization (Figure 1) was assumed at different extents of $C_6F_{13}I$ modification in subsequent calculations. Because the $C_6F_{13}I$ modification of a 1,2-PB block occurs homogeneously in a solution, we also assume the fluorination occurs randomly along the backbone.

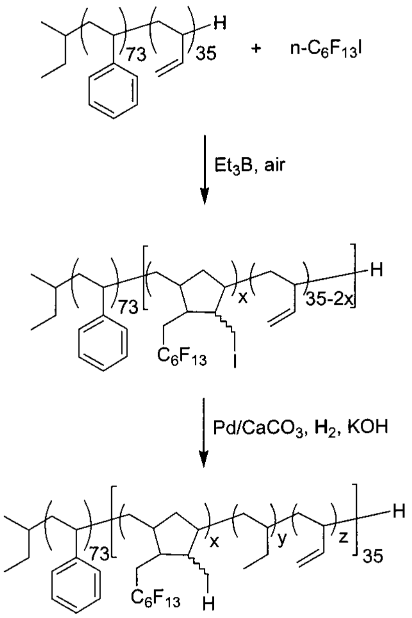

Figure 1. Reaction scheme for the selective addition of *n*-$C_6F_{13}I$ to the 1,2-PB block of a PS-*b*-1,2-PB copolymer and the subsequent hydrogenolysis.

The partially $C_6F_{13}I$-modified PS-*b*-1,2-PB materials with different extents of modification were subjected to hydrogenolysis conditions ($Pd/CaCO_3$, KOH, H_2).[13] Disappearance of resonances at 4.4 and 3.1 ppm in the ^{1}H NMR spectra of the reaction products suggests the complete removal of iodine. We also examined the extent of hydrogenolysis by elemental analysis. As reported in our previous paper, the iodine mass composition of a highly $C_6F_{13}I$-modified PS-*b*-1,2-PB copolymer after the hydrolysis was 569 ppm, equivalent to an extent of hydrogenolysis of 99.7%.[13] A $C_6F_{13}I$-modified PS-*b*-1,2-PB copolymer (35 mol %) after hydrolysis was scrutinized for the iodine mass composition, which was found to be 0.40%, corresponding to a hydrogenolysis extent of 96%. Further NMR analysis showed a significant fraction of double bonds (25% to 51%) remained after the hydrogenolysis (Table 1). For instance, in entry 1 of Table 1, the $C_6F_{13}I$ modification consumed 25% of the double bonds, and under the hydrogenolysis conditions the iodine was replaced by hydrogen and 24% of the double bonds were saturated. Therefore, 51% of the double bonds remained after the hydrogenolysis. In entry 4, there is actually an increase in the number of double bonds after the hydrogenolysis. We suspect that new double bonds were formed through the elimination of HI during the hydrogenolysis.[16] For the following analysis we will treat the fluorinated butadiene segments of the $C_6F_{13}H$-modified block copolymers as random copolymers of 1,2-PB and the corresponding cyclized (i.e., $C_6F_{13}H$-modified) repeat units described above. While the presence of saturated butadiene units is variable (Table 1), the difference in the interaction parameters between PS/1,2-PB and PS/hydrogenated 1,2-PB is minimal[17] and should not significantly affect our subsequent extraction of all pairwise interaction parameters relevant to this system. Characterization by SEC of the $C_6F_{13}H$-modified block copolymers was unsuccessful due to suspected aggregation of the block copolymers in solution.[18]

Table 1. Fluorination and Hydrogenolysis of a PS-*b*-1,2-PB Copolymer SB(8,2)[15]

entry	$[C_6F_{13}I]_0/[C{=}C]_0$	$[Et_3B]_0/[C{=}C]_0$	reaction time (h)[a]	C=C conversion (%)	product M_n (kg/mol)[b]	product PDI[b]	C=C remaining after hydrogenolysis (%)
1	0.25	0.125	3.5	25	10.9	1.04	51
2	0.25	0.125	6	35	11.2	1.05	44
3	0.5	0.25	3	63	12.1	1.06	25
4	1	0.5	20	80	11.5	1.07	35

[a] The reactions were run under an air flow of 3 cm^3/min in a 1/1 mixed solvent of α,α,α-trifluorotoluene ($PhCF_3$, BTF) and hexanes. [b] Measured by SEC system with PS standards calibration.

Table 2. Molecular and Morphological Characteristics of $C_6F_{13}H$-Modified SB(8,2)

entry	mol % $C_6F_{13}H$	vol % $C_6F_{13}H$	sample code	morphology[a]	D (Å)[c] 120 °C, 195 °C	f_{PS}[b]	N[d]	χ_{eff} at 120 °C, 195 °C	T_{ODT} (°C)[e]
1	0	0	SB(8,2)F00	DIS		0.78	94	0.05, 0.04	
2	25	40	SB(8,2)F25	HEX	127, 122	0.74	99	0.27, N/A	186 ± 3
3	35	52	SB(8,2)F35	HEX	131, 129	0.72	101	0.30. 0.27	
4	63	77	SB(8,2)F63	LAM	155, 151	0.68	107	0.66, 0.56	
5	80	89	SB(8,2)F80	LAM	162, 158	0.66	111	0.75, 0.65	

[a] DIS = disordered; HEX = hexagonally packed cylinders; LAM = lamellar. The morphologies were determined by the SAXS measurements at 120 and 195 °C, except that SB(8,2)F25 was disordered at 195 °C. [b] Volume fractions of PS calculated from the mol % $C_6F_{13}H$ modification using $\rho(PS) = 1.04$ g/cm^3, $\rho(1,2\text{-PB}) = 0.90$ g/cm^3, and $\rho(1,2\text{-PB}:C_6F_{13}H) = 1.80$ g/cm^3. [c] D-spacings were obtained by analysis of the principal peak from the 1-D SAXS data. These data have been confirmed through appropriate equilibration studies. [d] The degree of polymerization (using the PS repeat unit as the reference volume) calculated from the M_n of the precursor, $C_6F_{13}H$ modification extent, and the densities listed above. [e] By both rheology and static birefringence measurements (see Experimental Section).

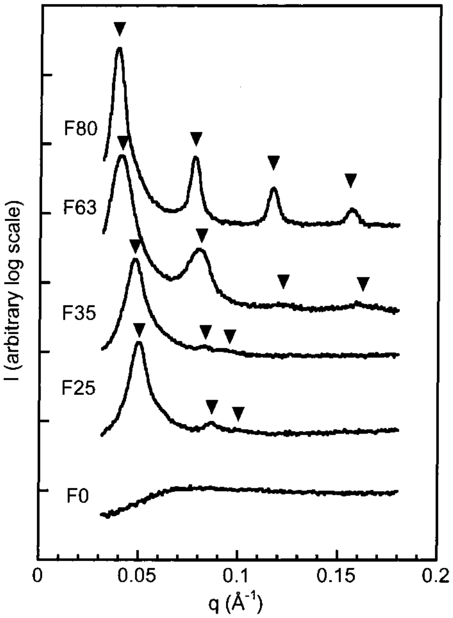

Figure 2. One-dimensional SAXS profiles at 120 °C of SB-(8,2)Fzz with different degrees of $C_6F_{13}H$ modification. The triangles correspond to $q/q^* = 1, 2, 3$, and 4 for F63 and F80 and to $q/q^* = 1, \sqrt{3}$, and $\sqrt{4}$ for F25 and F35. The data were shifted vertically for clarity.

Figure 2 shows the one-dimensional SAXS scattering profiles obtained at 120 °C for a series of PS-*b*-1,2-PB copolymers with 0−80 mol % of $C_6F_{13}H$ modification, synthesized from a PS-*b*-1,2-PB copolymer precursor with a PS block of 8 kg/mol and a 1,2-PB block of 2 kg/mol, SB(8,2).[15] When the extent of $C_6F_{13}H$ modification was zero, no sharp peaks were observed, indicating that the block copolymer precursor is disordered at 120 °C, as expected. Upon increasing to 25 and 35 mol % modification [SB(8,2)F25 and SB(8,2)F35, respectively], we clearly observed sharp principal peaks (at q^*) and higher-order reflections at $\sqrt{3}q^*$ and $\sqrt{4}q^*$, consistent with a hexagonally packed cylinder structure. Upon further $C_6F_{13}H$ modification [SB(8,2)F63 and SB(8,2)-F80], the ratios of the peak positions to the primary peak were 1:2:3:4, consistent with a lamellar morphology. Similar SAXS profiles were observed at 195 °C, except that a broader principal peak and no higher-order reflections were observed for SB(8,2)F25 at 195 °C, suggesting that this sample was disordered. The domain spacings (D) of these block copolymers at 120 and 195 °C were calculated via eq 1 (Table 2); they increased significantly with level of fluorination.[19]

$$D = \frac{2\pi}{q^*} \tag{1}$$

We also examined the order−disorder transition (ODT) of SB(8,2)F25 using two independent methods. The ODT is signaled by a sharp drop of the dynamic storage modulus (G') at a sufficiently low frequency, upon increasing the temperature slowly.[20] The rheological measurement was taken at a frequency of 1 rad/s, a strain of 1%, and a heating rate of 1 °C/min. We located the T_{ODT} of SB(8,2)F25 at 188 °C. Another established method to locate T_{ODT} of block copolymers is static birefringence.[14] A sharp drop in the transmitted depolarized light intensity can be observed when a lamellar or cylindrical block copolymer disorders. Using this method with a heating rate of 1 °C/min, we determined T_{ODT} for SB(8,2)F25 to be 184 °C, in satisfactory agreement with the rheology measurement.

The main object of this study is to obtain reasonable estimates of the interaction strength in this system, which can be quantified by the interaction parameter (χ). This can be done both from the dependence of D on modification extent and from the value of T_{ODT} for any particular sample. The domain spacing is determined by the balance between the unfavorable interfacial energy and the entropic penalty due to the stretching of the polymer coils.[21] Semenov pointed out that the characteristic period (D) for all three "classical" block copolymer microstructures (spheres, cylinders, and lamellae) obeys the following scaling:[22]

$$D \sim aN^{2/3}\chi^{1/6} \tag{2}$$

where a is the average statistical segment length of the block copolymer and N is the overall degree of polymerization. The exact result for the domain spacing in a lamellar structure is

$$D = 1.10 a N^{2/3} \chi^{1/6} \tag{3}$$

Equation 3 is strictly applicable to lamellar structures in the strong-segregation regime ($\chi N \geq 100$) but nevertheless should provide a reasonable and internally consistent estimate of χ for ordered lamellar and cylindrical block copolymers at a variety of segregation strengths. For example, Matsen and Bates calculated D using self-consistent mean-field theory without the traditional approximations and compared the results with eq 3.[23] The results differ by approximately 20% when $\chi N = 10$ and by only 1% when χN increases to 100. Furthermore, D does not change by more than a few percent upon traversing the cylinder/lamellae boundary.

Since the increase in the domain spacing can be influenced by three different parameters (eq 3), we need to examine the effect of fluorination on a and N in order to extract χ from D. The appropriate degree of polymerization, N, is based on a PS repeat unit reference volume. As an example of the changes in N upon modification, in the sample with the highest level of $C_6F_{13}H$ modification [SB(8,2)F80] N increased by only 18% from the precursor, SB(8,2) (entry 5 in Table 2). The average statistical segment length for a PS-*b*-1,2-PB copolymer (a_{SB}) in eq 3 can be written as

$$a_{SB} = \left(\frac{f_{PS}}{{a_S}^2} + \frac{1 - f_{PS}}{{a_B}^2} \right)^{-1/2} \tag{4}$$

where f_{PS} is the volume fraction of the PS block.[12] Using eq 4, we calculated a_{SB} for the PS-*b*-1,2-PB copolymer precursor to be 6.7 Å with the literature values of $a_{PS} = 6.7$ Å and $a_{1,2-PB} = 6.8$ Å (using the PS repeat unit as the reference volume and $\rho_{1,2-PB} = 0.90$ g/cm^3 and $\rho_{PS} = 1.04$ g/cm^3 to adjust $a_{1,2-PB}$).[17,24] We neglect the temperature dependence of the statistical segment length, since it is usually weak.[25] The $C_6F_{13}H$ modification may affect the statistical segment length of the 1,2-PB block; however, we did not explicitly measure the statistical segment length of the modified polybutadiene. For simplicity, we assume the effect of $C_6F_{13}H$ modification on the statistical segment length of the 1,2-PB block to be negligible for the estimation of an effective interaction parameter, χ_{eff}, between the PS block and the PB/$C_6F_{13}H$-modified PB block. Using the calculated N (Table 2) and a values, eq 3 was inverted to generate χ_{eff} at different extents of $C_6F_{13}H$ modification (Table 2). Clearly, χ_{eff} increases substantially with fluorination.[26]

Figure 3 illustrates the change in χ_{eff} as a function of the extent of $C_6F_{13}H$ modification. In an effort to understand this behavior, we adapted a binary interaction model that describes the phase behavior for polymer blends composed of a homopolymer and a statistical copolymer.[27-29] The effective interaction parameter in such a three-component system can be expressed in terms of the three pairwise interaction parameters and the composition of the statistical coblock:

$$\chi_{eff} = \chi_{SFB} x + \chi_{SB}(1 - x) - \chi_{BFB} x(1 - x) \tag{5}$$

where χ_{SFB}, χ_{SB}, and χ_{BFB} are the pairwise interaction parameters among the polystyrene (S), fully $C_6F_{13}H$-modified 1,2-polybutadiene (FB), and 1,2-polybutadiene (B) segments, respectively, and x is the extent of $C_6F_{13}H$ modification of the 1,2-PB block (on a volume basis). Equation 5 is thus quadratic in x and fits the experimental χ_{eff} data well (Figure 3). The resulting values of the pairwise interaction parameters at 120 and 195 °C can be extracted from these fits and are given in Table 3. The most important result in Table 3 is the strong increase in χ brought about by fluorination. The styrene–butadiene χ, ca. 0.05, has a typical value for common styrenic copolymers, whereas the styrene–fluorinated butadiene χ value is a factor of 20 larger.

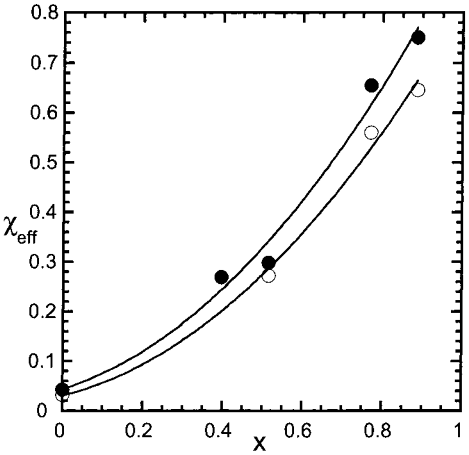

Figure 3. Dependence of the calculated χ_{eff} from eq 3 at 120 °C (solid circles) and 195 °C (open circles) on the $C_6F_{13}H$ modification extent (x) on a volume basis. The solid curves are the best-fit quadratic curves ($y = ax^2 + bx + c$).

Table 3. Pairwise Interaction Parameters and Their Temperature Dependences (Eq 6)

	SFB	BFB	SB
χ (120 °C)	0.94	0.66	0.05
χ (195 °C)	0.81	0.60	0.04
α	319	147	32
β	0.13	0.29	−0.030

The temperature dependence of χ can generally be written as follows:[21]

$$\chi = \frac{\alpha}{T} + \beta \tag{6}$$

where α and β are enthalpic and excess entropic coefficients, respectively. The pairwise interaction parameters at 120 and 195 °C are therefore sufficient to estimate χ_{eff} at any given temperature and fluorination extent (Table 3). Equation 5 is at best approximate, as pointed out by Freed and co-workers, particularly in the case where the excess entropic coefficient β plays a significant role.[30] In this instance α, however, is rather large, and given that the main object is to extract an estimate of the various interaction parameters and their evolution with extent of reaction, eq 5 should be adequate.

The main result from use of the binary interaction model to fit χ_{eff} is the relative magnitude of the pairwise interaction parameters: $\chi_{SFB} > \chi_{BFB} \gg \chi_{SB}$. This result is analogous to that reported by Hashimoto and coworkers[3b] for a partially hydrogenated PS-*b*-PI system. They observed a monotonic increase in χ_{eff} as the PI block in a PS-*b*-PI copolymer was selectively hydrogenated, and χ_{eff} increases about 3-fold upon complete PI hydrogenation. However, χ_{eff} increases to a much greater

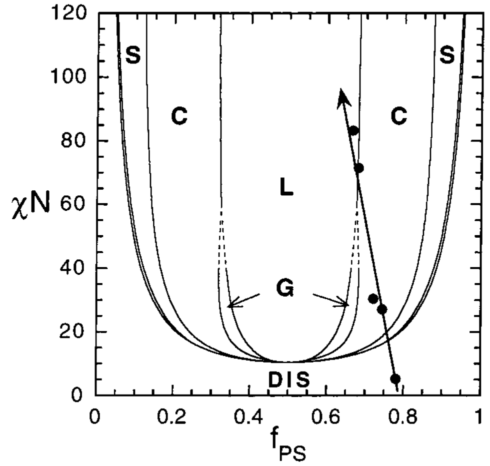

Figure 4. Schematic illustration of the effect of fluorination on the incompatibility shown in the theoretical phase diagram calculated by Matsen and Bates (ref 23). The data (at 120 °C) are represented by solid circles, and the arrow serves as a guide to the eye.

extent in these fluorinated materials, by a factor of 15 at 80% modification. This result also implies that the cohesive energy density or the solubility parameter of fluorinated butadiene is much smaller than that of styrene. As a simple check of this conclusion, we recall the solubilities of the fluorinated 1,2-PB reported previously.[13] The $C_6F_{13}I$-modified 1,2-PB homopolymers are only soluble in fluorinated solvents, CFC-113 and BTF ($PhCF_3$), and in THF at low concentrations. Furthermore, the $C_6F_{13}H$-modified 1,2-PB homopolymers were insoluble in all solvents tested, at both ambient and elevated temperatures. Although qualitative, this analysis is consistent with the conclusion that the $C_6F_{13}H$ modification of 1,2-PB decreases the cohesive energy density significantly.

Finally, we can also estimate χ_{eff} from the location of the order−disorder transition (ODT). Using self-consistent mean-field theory, Matsen and Bates located the ODT at $\chi N = 16$ for a diblock copolymer with $f = 0.74$.[23] Thus, χ_{eff} for SB(8,2)F25 at T_{ODT} is 0.16 using the N value given in Table 2. (This result may underestimate χ_{eff}, since fluctuation effects will tend to shift the actual ODT to a higher value of χN,[31] but this level of sophistication in the analysis is not warranted here.) Using the values in Table 3 extracted from the domain spacing measurements, we estimate χ_{eff} at 25 mol % fluorination and 186 °C to be 0.21. Thus, the χ_{eff} for SB(8,2)F25 from the two independent experiments and analyses agree quite well.

Figure 4 locates the experimental points according to the χN (at 120 °C) and f values (Table 2) of the partially $C_6F_{13}H$-modified PS-*b*-1,2-PB copolymers on the theoretical phase diagram obtained by Matsen and Bates.[23] The experimentally observed morphologies agree well with the theoretical predictions. As the $C_6F_{13}H$ modification extent increases, f_{PS} decreases from 0.78 in SB(8,2) to 0.66 in SB(8,2)F80, and the calculated segregation strength (χN) increases significantly (from 5 to 83). Therefore, the sequential observation of the disordered state, hexagonally packed cylinder structure, and lamellar morphology at different extents of $C_6F_{13}H$ modification is anticipated, as illustrated in Figure 4. This figure also serves to underscore the power of chemical modification as a means to traverse large regions of the phase diagram with one series of molecules. A factor of 15 in degree of segregation is much larger than could be obtained by varying just temperature (typically, temperature gives access to a change in χ of about 2). Although a similar range could be achieved by synthesizing a series of different polymers with varying N and constant f, it would be a much more laborious task.

Summary

We have characterized a set of partially $C_6F_{13}H$-modified PS-*b*-1,2-PB copolymers prepared by the reaction of a model PS-*b*-1,2-PB copolymer with n-$C_6F_{13}I$ and subsequent hydrogenolysis. For partially $C_6F_{13}H$-modified PS-*b*-1,2-PB copolymers, we determined the morphologies and domain spacings at different levels of $C_6F_{13}H$ modification by SAXS at 120 and 195 °C. The χ_{eff} between the PS and partially $C_6F_{13}H$-modified 1,2-PB blocks at different extents of $C_6F_{13}H$ modifications was estimated. At 120 °C, χ_{eff} increases significantly from about 0.05 at 0 mol % $C_6F_{13}H$ modification to about 0.75 at 80 mol % $C_6F_{13}H$ modification. This dependence of χ_{eff} on the $C_6F_{13}H$ modification extent is rationalized semiquantitatively using a binary interaction model. This analysis also yields estimates of the three pairwise interaction parameters at 120 and 195 °C, which were utilized further to extract the temperature dependences of the three pairwise interaction parameters. As a result, one can estimate χ_{eff} at any given fluorination extent and temperature. We also determined the T_{ODT} for SB(8,2)F25 by rheology and static birefringence and estimated χ_{eff} to be 0.16 at T_{ODT}, which agreed well with the value (0.21) estimated from the domain spacing measurements. This paper illustrates how chemical modification of block copolymers using these fluorinated reagents is a particularly powerful method for not only producing novel materials but also mapping large regions of the block copolymer phase diagram using one parent block copolymer.

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(15) The preparation of the PS-*b*-1,2-PB copolymer precursor was previously described (ref 13). The molecular characterization of the block copolymer precursor was performed by NMR spectroscopy and SEC. From the peak integrations in the ^{1}H NMR spectrum, the weight fraction of the PS was determined to be 0.8, and the 1,2-content of the PB block to be higher than 99%. The M_n of the block copolymer precursor was found using SEC with a Wyatt multiangle light scattering (MALS) detector. The dn/dc of PS and 1,2-PB in THF at 40 °C and 633 nm wavelength were 0.192 mL/g (Miller, L. M.S. Thesis, University of Minnesota, Minneapolis, 1998) and 0.130 mL/g (Rosedale, J. Ph.D. Thesis, University of Minnesota, Minneapolis, 1993), respectively. The refractive index increment for a copolymer was calculated using $v = v_A w_A + v_B w_B$, where w_i and v_i are the weight fraction and refractive index increment of component i, respectively (Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 4th ed.; John Wiley & Sons: New York, 1999). The SEC analysis yielded $M_n = 9.5$ kg/mol and PDI = 1.01, which agreed well with the results previously reported using an SEC system calibrated by PS standards. Thus, we calculated the M_n of the PS and 1,2-PB blocks to be 7.6 and 1.9 kg/mol, respectively.

(16) In an attempt to saturate the remaining double bonds, a PS-*b*-1,2-PB:$C_6F_{13}H$ sample with 35 mol % fluorination was subject to heterogeneous catalytic hydrogenation conditions with Pd/$CaCO_3$ as the catalyst in cyclohexane under 500 psi of H_2. However, no further saturation was observed after the reaction, which might be explained by the fact that the remaining double bonds were inside micellar cores and unable to adsorb onto the catalyst surface. See: Rosedale, J. H.; Bates, F. S. *J. Am. Chem. Soc.* **1988**, *110*, 3542.

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(19) We also prepared block copolymers with 93 and 98 mol % $C_6F_{13}H$ modification and characterized their morphologies using SAXS. These high levels of $C_6F_{13}H$ modification are due to open chain addition of the perfluoroalkyl iodides to pendant double bonds. We observed that *D decreased* at these levels of $C_6F_{13}H$ modification. The origin of this decrease is not known at this time but warrants further investigation.

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