Synthesis, Characterization, and Interaction Strengths of Difluorocarbene-Modified Polystyrene−Polyisoprene Block Copolymers

Yu Ren, Timothy P. Lodge,* and Marc A. Hillmyer*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455-0431

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ABSTRACT: The effect of difluorocarbene (CF_2) modification on the self-assembly of polystyrene-*b*-polyisoprene (PS-*b*-PI) copolymers was investigated. We prepared a set of fully CF_2-modified PS-*b*-PI copolymers (PS-*b*-FPI) with different molecular weights (8−13 kg/mol) and located their order−disorder transition temperatures (T_{ODT}) by rheology and static birefringence. Using both mean-field and fluctuation theory, we determined the temperature dependence of the interaction parameter between the styrene and CF_2-modified isoprene segments (χ_{SFI}). Two series of polystyrene-*b*-(partially CF_2-modified polyisoprene) (PS-*b*-(FPI-*s*-PI)) materials with different levels of CF_2 modification were also prepared from the reaction between difluorocarbene and two nearly symmetric PS-*b*-PI precursors with molecular weights of 18 and 61 kg/mol, respectively. A lamellar morphology was established for all of the PS-*b*-(FPI-*s*-PI) copolymers below the T_{ODT} by small-angle X-ray scattering (SAXS) and rheology. The effective interaction parameter (χ_{eff}) between the PS and FPI-*s*-PI blocks, calculated from the domain spacing determined by SAXS, passes through a minimum before increasing smoothly by a factor of 4 upon complete CF_2 modification. Using the binary interaction model originally developed for homopolymer/copolymer blends, we were able to understand the dependence of the χ_{eff} on the CF_2-modification extent in a quantitative manner and extracted the three pairwise interaction parameters. Rheology and static birefringence were also used to locate the T_{ODT} for the lower molecular weight PS-*b*-(FPI-*s*-PI) series. The T_{ODT} was found to behave in a manner similar to the χ_{eff}: a decrease was observed at initial CF_2 modification, and a sharp increase was observed upon further CF_2 modification.

Introduction

The covalent connection of two chemically distinct polymer chains leads to the formation of a simple AB diblock copolymer. To minimize unfavorable segment−segment interactions and chain deformations, these hybrid materials will self-assemble into ordered morphologies with compositional heterogeneities on a nanometer length scale.[1] The principal domain spacing and ordered state symmetry depend on the molecular weight and composition of the block copolymer. Fundamental studies on the dynamics[2] and thermodynamics[3] of block copolymers have been reviewed, and contemporary theories have been able to explain block copolymer phase behavior to a large degree.[4] Many of the experimental studies have relied on the preparation of block copolymers with well-defined block lengths and narrow molecular weight distributions. These model block copolymers are typically prepared by living or controlled polymerizations through sequential addition of monomers.

The three parameters that are most important for the control of block copolymer phase behavior are the overall number-average degree of polymerization (N), the volume fraction of component i (f_i), and the Flory−Huggins segment−segment interaction parameter (χ). In a typical block copolymer synthesis, both N and f_i can be easily controlled over a large range. On the other hand, χ is determined by the selection of the monomers, and the range over which χ can be tuned depends on the temperature dependence of χ for that particular system. Because the combination parameter χN dictates the degree of segregation in a given block copolymer, through changes in N and χ one can tune the state of a block copolymer melt from strongly segregated ($\chi N \gg 10$) to disordered ($\chi N < 10$). Many model block copolymer systems encompassing a relatively wide range of χ have been studied over the past decade.[5]

The selective modification of block copolymers is a way to systematically tune the thermodynamics between the two segments of a block copolymer. Changing the chemical nature of one or both of the component blocks can change χ and may have dramatic effects on the self-assembly of the resultant material. There have been various block copolymer modification schemes described in the literature. Because of their ease of synthesis and availability, modification of the polydiene block in polystyrene−polydiene block copolymers has received much attention. For example, chlorination,[6] fluorination,[7] epoxidation,[8] and hydrogenation[9] of the polydienes in polydiene-containing block copolymers have been reported. Detailed studies on the effect of modification on the block copolymer thermodynamics have only been done on the hydrogenated derivatives.[9]

Our synthetic focus has been on the postpolymerization modification of polydienes using reagents containing atomic fluorine. The incorporation of fluorine into polymers can lead to materials with interesting properties, such as low surface energies,[10] solubility in supercritical CO_2,[11] and resistance to harsh chemical environments. Recently, we reported the mild, selective, and quantitative functionalization of polydienes by difluorocarbene (CF_2).[12] The insertion of CF_2 into polydienes significantly altered the physical properties of the materials, such as the solubilities and glass-transition temperatures. We also provided one example of the selective modification of a polystyrene−polyisoprene block copolymer.[12] Since then, we have prepared

* To whom correspondence should be addressed. E-mail: lodge@chem.umn.edu and hillmyer@chem.umn.edu.

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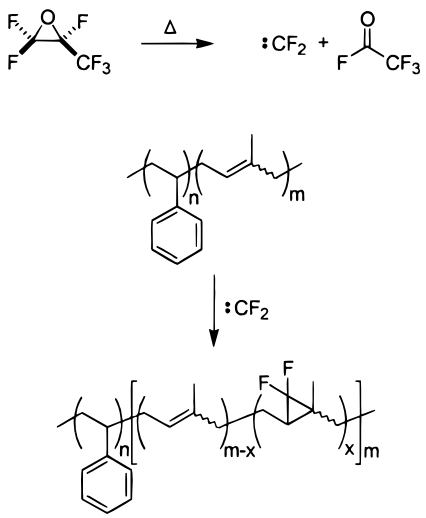


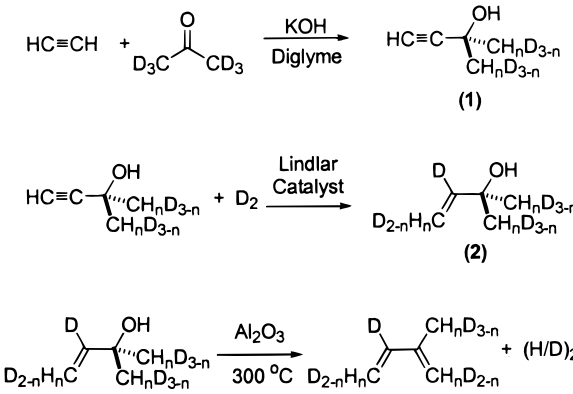
Figure 1. Thermolysis of HFPO to generate difluorocarbene (CF_2) and the use of CF_2 to selectively modify the PI block in a PS-*b*-PI diblock copolymer.

and characterized a wide array of CF_2-modified polystyrene−polyisoprene diblock copolymers. Figure 1 shows the modification scheme we employed. In this paper, we report on the effect of CF_2 modification on the block copolymer thermodynamics.

Experimental Section

Materials. All chemicals were used without further purification except as noted. Styrene (Aldrich) was stirred over CaH_2 for about 12 h and distilled into a flask containing dibutylmagnesium (Aldrich). The styrene was stirred over dibutylmagnesium for 5 h at room temperature and then distilled into a flame-dried buret. Isoprene (Aldrich) was purified by two successive distillations from *n*-butyllithium stirred at 0 °C for 1 h and was then distilled into a flame-dried buret. The concentration of *sec*-butyllithium (Aldrich) was determined by the Gillman double-titration method prior to use.[13] Cyclohexane (Aldrich) was purified by passage through an activated alumina column (LaRoche) to remove protic impurities and through a supported copper catalyst (Engelhard) to remove trace oxygen, using a home-built solvent purification system.[14] The solvent system was connected to a flame-dried air-free flask by a Cajon connection to allow anhydrous/anaerobic collection of the purified solvent.

Synthesis of Partially-Deuterated Isoprene. Perdeuterated isoprene was previously synthesized from acetone-d_6 and acetylene-d_2 by Craig and co-workers using the Favorskiĭ−Bergmann route.[15] We adopted a similar approach, utilizing KOH and C_2H_2 instead of KOD and C_2D_2. Potassium hydroxide (>85%, Aldrich), 82.22 g (1.32 mol), and diglyme (200 mL) were added to a three-neck flask equipped with a condenser and magnetic stir bar. The mixture was heated to 160 °C under N_2 atmosphere, stirred vigorously to dissolve KOH, and then cooled to 0 °C using an ice−water bath. Approximately 60 g (2.3 mol) of acetylene (Praxair) was bubbled through the KOH slurry over 2 h, and 43.52 g (0.68 mol) of acetone-d_6 (Cambridge Isotope Laboratories) was added into the flask dropwise over 2 h at 0 °C. The reaction mixture thickened after storing at −20 °C for 12 h. Deionized water (101 g, 5.6 mol) was added to the reaction mixture, and sulfuric acid (9 M, 80 mL) was added to neutralize the mixture. The neutralized mixture was filtered and distilled using a vacuum-jacketed Vigreux (20 cm high) distillation head. The azeotrope of partially deuterated 2-methyl-3-butyn-2-ol (**1**) and H_2O was collected at 85−99 °C. The distillate was saturated with NaCl (previously baked at 90 °C) and separated into two phases. The organic layer was separated using a separatory funnel, and diethyl ether (3 × 10 mL) was used to wash the aqueous layer. The combined organic phase was dried over $MgSO_4$ and distilled again using a 13 cm high Vigreux column. A fraction of **1** was collected between 101 and 103 °C (33.01 g, 0.38 mol, 56%).



1 (33.01 g, 0.38 mol) was added to a high-pressure reactor with 1.65 g of Lindlar catalyst (Strem). The reactor was pressurized with deuterium gas (Cambridge Isotope Laboratories), and the deuteration proceeded until the resonance corresponding to the alkynyl proton ($\delta = 2.44$ ppm) was absent from the ^{1}H NMR spectrum. Partially deuterated 2-methyl-3-buten-2-ol (**2**) (30.87 g, 0.343 mol) was recovered after filtering the reaction mixture, and the isolation yield was 90% for the deuteration. The dehydration was carried on a home-built alumina column. A 12 in. long stainless steel tube with an OD of $^3/_4$ in. was filled with activated Al_2O_3 (LaRoche) and then was heated to 300 °C. **2** (30.87 g) was dropped into the column under a N_2 flow over 2 h. The bottom of the Al_2O_3 column was connected to a two-neck flask immersed in a dry ice bath. The N_2 flow exiting from the two-neck flask passed through a liquid N_2 cold trap before a bubbler. The dehydration products were collected and separated into ice and organic liquid. The crude deuterated isoprene weighed 22.02 g (0.305 mol), and the isolation yield for the dehydration was 89%. Combined batches of crude partially deuterated isoprene (34.59 g, 0.480 mol) were refluxed with 2.55 g (0.11 mol) of sodium for 30 min. Polymerization-grade partially deuterated isoprene (27.52 g, 0.382 mol) was collected at 31−34.2 °C. The monomer was characterized by ^{1}H and ^{2}H NMR spectroscopy and GC-MS (Finnigan Mat 95) equipped with a chemical ionization source using NH_3 as the carrier gas. The mass spectrum of the deuterated monomer shows a series of $(M + 18)^+$ molecular ion peaks, indicating that the product contained a mixture of monomers with different numbers of deuterons. The average number of deuterons per isoprene was calculated to be 4.24. We suspect that the deuterium distribution arises primarily during the first step of the synthesis, due to exchange between the deuterons in acetone-d_6 and the protons in H_2O (the KOH contains 10−15% H_2O).

Synthesis of Polystyrene-*block*-Polyisoprene (PSPI). In this study, six PSPI diblock copolymers with different molecular weights were synthesized by sequential living anionic polymerization.[16] The polymerizations were performed in purified cyclohexane using *sec*-butyllithium as the initiator. The preparation of a representative copolymer (entry 2 in Table 1) is described below. A 2 L round-bottom flask equipped with five internal ACE-THREDS ports was heated to 250 °C under 10 mTorr for 12 h to remove any adsorbed H_2O. After being cooled, purified cyclohexane (≈1 L) was added to the flask, followed by the injection of a calculated amount of *sec*-butyllithium solution (1.28 M in cyclohexane, 3.06 mL, 3.93 mmol). The purified styrene (39.33 g, 0.378 mol) was added to the flask and stirred at 45 °C for 4 h to achieve complete polymerization.[17] The purified isoprene (32.46 g, 0.477 mol) was added and allowed to polymerize for another 4 h. The living chains were terminated by the injection of excess degassed methanol. The polymer was precipitated by pouring the solution slowly into a 2:1 (v/v) mixture of 2-propanol and methanol and subsequently dried at room temperature and <100 mTorr for 48 h. Size exclusion chromatography (SEC)

Table 1. Molecular Characteristics of PSPI Diblock Copolymers

entry	10^3 M_n[a]	PDI[a]	10^3 M_n[b]	10^3 M_n[c]	10^3 M_n[d]	sample code[e]	f_{PS}[f]
1	61	1.05				PSPI(34, 27)	0.518
2	18	1.01			18	PSPI(10, 8)	0.518
3	9.7	1.04	10.2	10	9.2	PSPI(5.5, 4.5)	0.517
4	7.5	1.04	8.0	7.8	8.2	PSPI(4.2, 3.6)	0.502
5	7.2	1.01	7.3	7.2	7.0	PSPI(4.1, 3.1)	0.531
6	6.4	1.01	6.7	6.6	6.8	PSPI(3.8, 2.8)	0.541
7	6.1	1.03	6.4	6.2	7.0	PSPI(3.2, 3.0)	0.477

[a] Measured by the SEC system equipped with Wyatt MALS detectors (see Experimental Section). [b] Determined by end group analysis from the ^{1}H NMR spectra. [c] Average M_n of the SEC and NMR results. [d] Calculated by the reaction stoichiometry. [e] See description of sample code in text. Molecular weights of blocks calculated from the average M_n for entries 3−7, from the M_n (SEC/LS) for entries 1−2, and the mass percentage determined from ^{1}H NMR spectra. [f] Volume fractions calculated from ^{1}H NMR spectra using room temperature densities.

analysis with light scattering detection gave $M_w/M_n = 1.01$ and $M_n = 18.3$ kg/mol, which agreed very well with the targeted molecular weight ($M_n = 18.3$ kg/mol) calculated from the reaction stoichiometry. The isolation yield was 70.57 g (98%). All block copolymers were stored at −20 °C.

Reaction with Difluorocarbene. The fluorinations were performed in cyclohexane using hexafluoropropylene oxide (HFPO) as the difluorocarbene source. A specific example (entry 15 in Table 2) of the general method is reported here. PS-*b*-PI (1.487 g, with a PS block of 10.1 kg/mol and PI block of 8.2 kg/mol, 9.82 mmol of olefinic sites), 2,6-di-*tert*-butyl-4-methylphenol (0.106 g, 0.481 mmol), and a magnetic stir bar were added to a high-pressure reactor. In an inert atmosphere drybox, purified cyclohexane (≈70 mL) was added to the reactor and the reactor was sealed. The reactor was removed from the drybox, and a known amount of hexafluoropropylene oxide (5.2 g, 31 mmol) was charged into the reactor. The reactor was heated to 185 °C for 16 h and cooled to ambient temperature. The gas inside the reactor was discharged by bubbling through an aqueous NaOH solution. The solution inside the reactor was filtered,[18] concentrated on a rotary evaporator, and precipitated in a 2:1 mixture of 2-propanol and methanol. The precipitated polymer was collected and dried at room temperature and <100 mTorr for 12 h. The isolated yield was 1.810 g (92%).

Characterization. All of the block copolymers were characterized by nuclear magnetic resonance (NMR) spectroscopy and size exclusion chromatography (SEC). ^{1}H, ^{2}H, and ^{19}F NMR spectra were recorded on a Varian 300 VXR spectrometer. The NMR samples were prepared by dissolving approximately 30 mg of polymer in 750 μL of deuterated chloroform (Cambridge Isotope Laboratories). Hexafluorobenzene (Aldrich) was added to the solutions as the internal standard ($\delta = -162.9$ ppm) for the ^{19}F NMR spectra.[19] Two different SEC systems were used in this study. 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 columns and RI detector were maintained at 40 °C. The second system includes 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. The columns were at ambient temperature, and the RI detector was set at 40 °C. The refractive index increments (d*n*/d*c*) for PS, PI, and FPI in THF at 40 °C and 633 nm wavelength were determined to be 0.192, 0.124, and 0.040 mL/g, respectively, using the Wyatt RI detector in an off-line mode. The refractive index increment for a copolymer was calculated using $\nu = w_A\nu_A + w_B\nu_B + w_C\nu_C$, where w_i and ν_i are the weight fraction and refractive index increment of component i, respectively.[20] The SEC measurements were performed at a flow rate of 1 mL/min, and tetrahydrofuran (THF) was used as the mobile phase in both systems.

Preparation of Small-Angle Neutron Scattering (SANS) Cells. A partially deuterated polyisoprene (dPI) ($M_w = 60$ kg/mol, PDI = 1.04; SEC/LS, i.e., SEC with the multiangle light scattering detector) was obtained by the anionic polymerization of the partially deuterated isoprene monomer. This material was modified using the protocol described above to yield a partially deuterated fluorinated polyisoprene (dFPI) with $M_w = 111$ kg/mol and PDI = 1.12 by SEC/LS. A hydrogeneous polyisoprene (hPI) with a similar molecular weight was also synthesized ($M_w = 63$ kg/mol, PDI = 1.04; SEC/LS) and modified ($M_w = 111$ kg/mol, PDI = 1.13; SEC/LS). hPI, dPI, hFPI, and dFPI were characterized by ^{1}H and ^{2}H NMR spectroscopy. A nearly equal-volume blend of hFPI and dFPI was obtained by mixing 0.189 g of hFPI and 0.201 g of dFPI in THF, filtering through a 0.2 μm PTFE filter, precipitating the polymer in methanol, and drying the polymer under vacuum at room temperature for 12 h. Three SANS cells were made from the nearly equal-volume FPI blend ($\phi_{hFPI} = 0.493$) and two pure homopolymers using the following procedure: the polymers were annealed under 10 mTorr at 90 °C for 7 h and then pressed into an aluminum ring with a thickness of 1.0 mm under 10 mTorr at 90 °C. The polymer disk was sandwiched by two quartz disks and sealed using a high-temperature silicone adhesive (General Electric). Three PI cells were also made from the hPI, dPI, and PI blend (0.355 g of hPI and 0.382 g of dPI; $\phi_{hPI} = 0.496$) using similar procedures.

Small-Angle Neutron Scattering (SANS). SANS measurements of the FPI samples were performed at the National Institute of Standards and Technology Cold Neutron Research Facility on the NIST/Exxon/University of Minnesota 30 m instrument (NG-7). The incident neutrons had a wavelength of $\lambda = 6.0$ Å and a resolution of $\Delta\lambda/\lambda = 0.10$. The detector was placed 7 m from the sample, which was maintained at 100 °C. Scattering data were corrected for detector sensitivity, background, empty cell scattering, and transmission factors, azimuthally averaged, and then converted to an absolute scale using the direct beam method. The two-dimensional data were reduced to the one-dimensional form of scattered intensity versus scattering wavevector $|\vec{\mathbf{q}}| = q = 4\pi\lambda^{-1}\sin(\theta/2)$, where θ is the scattering angle. SANS measurements on the PI cells were performed at the Risø National Laboratory in Denmark. Neutrons with $\lambda = 5.6$ Å and $\Delta\lambda/\lambda = 0.09$ were incident on the samples at room temperature. The sample-to-detector distance was 6 m. The samples produced azimuthally isotropic two-dimensional scattering patterns that were averaged to the one-dimensional form of intensity versus scattering wavevector. The scattering data were corrected for background and cell scattering, detector sensitivity, sample thickness, and transmission.

Small-Angle X-ray Scattering (SAXS). Before the SAXS and rheological measurements, the samples were pressed in a 1 mm thick stainless steel mold, sandwiched by two Teflon sheets under vacuum (<100 mTorr) at 120 °C for 5 h. SAXS measurements were performed at the University of Minnesota on a home-built beamline. Cu Kα X-rays ($\lambda = 1.542$ Å) were generated by a Rigaku RU-200BVH rotating anode fitted with an 0.2 × 2 mm^2 microfocus cathode and Franks mirror optics. Sample temperature was controlled using a water-cooled, electrically heated brass block inside an evacuated sample chamber. Two-dimensional diffraction images were recorded using a Siemens area detector located at the end of a 2 m 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 versus *q*.

Rheology. All of 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. A strain sweep was first performed to establish the linear viscoelastic regime. Strain amplitudes of 2% were found to be sufficiently small to ensure linear response. Temperature ramps were performed at a frequency of 1 rad/s and a heating rate of 0.5 or 2 °C/min. The dynamic storage (G') and loss (G'')

Table 2. Molecular and Morphological Characteristics of CF_2-Modified PSPI(10, 8) Diblock Copolymers

entry	10^3 M_n[a]	PDI[a]	F (mol %)[26]	sample code	D (Å)[b]	a (Å)[c]	N[d]	T_{ODT} (°C)[e]	T_{ODT} (°C)[f]
1	20	1.04	0	PSPI(10, 8)F00	165	7.1	187	130 ± 1	131 ± 1
2	20	1.04	3.3	PSPI(10, 8)F03		7.1	187		126 ± 1
3	21	1.04	5.4	PSPI(10, 8)F05	164	7.1	188	124 ± 0.5	124 ± 1
4	21	1.04	7.7	PSPI(10, 8)F08		7.1	188	124 ± 0.5	123 ± 1
5	21	1.04	12.6	PSPI(10, 8)F13	165	7.1	190	125 ± 0.5	125 ± 1
6	23	1.04	15.7	PSPI(10, 8)F16		7.1	190	128 ± 0.5	128 ± 1
7	23	1.04	17.1	PSPI(10, 8)F17	167	7.1	191	132 ± 0.5	
8	23	1.05	29.2	PSPI(10, 8)F29	174	7.1	193	167 ± 0.5	167 ± 1
9	23	1.04	36.9	PSPI(10, 8)F37	179	7.1	195	196 ± 1	194 ± 1
10	23	1.04	41.5	PSPI(10, 8)F42	182	7.1	196	217 ± 1	>215
11	24	1.04	43.6	PSPI(10, 8)F44	186	7.0	197	234 ± 2	
12	23	1.05	55.2	PSPI(10, 8)F55	195	7.0	200	>240	>215
13	23	1.05	63.4	PSPI(10, 8)F63	204	7.0	201		
14	25	1.05	87.9	PSPI(10, 8)F88	225	7.0	207		>215
15	26	1.06	>99	PSPI(10, 8)F100	234	7.0	210		

[a] Measured by HP SEC system calibrated by PS standards. [b] Measured by SAXS at 110 °C. [c] Average statistical segment length of the copolymer calculated using eq 11. [d] The degree of polymerization (using the PS repeat unit as the reference volume) calculated from the M_n of the precursor and F. [e] Measured by rheology. [f] Measured by static birefringence.

moduli were recorded as a function of temperature. Frequency sweeps were also conducted at various temperatures to investigate the state of the sample based on the characteristic rheological responses of various ordered microstructures and disordered melts.[2] We were concerned about thermal degradation of the CF_2-modified samples at elevated temperatures. The decomposition temperature (defined as the temperature at 5% weight loss) was found by thermal gravimetric analysis to be 309 °C for fully CF_2-modified polyisoprene (FPI).[12] A PS−FPI polymer sample that was held in the rheometer above 175 °C for 25 min (ramp from 175 to 225 °C at 2 °C/min) and above 210 °C for 22 min (210−221 °C at 0.5 °C/min) was checked for degradation by SEC and NMR. The ^{1}H NMR spectra and SEC chromatographs before and after the measurement were virtually identical, and we concluded that no significant thermal degradation occurred during these experiments.

Static Birefringence. The sample cells used in static birefringence measurements were prepared in a manner similar to the SANS cells. The polymers were pressed in a 1 mm thick aluminum ring, sandwiched by two Teflon sheets under vacuum (<0.1 Torr) at 120 °C for 5 h. The annealed sample was then sandwiched between two polished glass disks and sealed with a high-temperature silicone sealant (General Electric). The home-built apparatus and the protocol for the static birefringence measurements were described previously.[21] The sealed sample cell was placed into a sample holder and heated to a temperature above the T_g of both blocks by use of an electrically heated copper block. A vertically polarized laser beam from a 5 mW He Ne 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. The temperature ramp rate was approximately 1 °C/min.

Results

Synthesis and Molecular Characterization of PS-*b*-(FPI-*s*-PI). We previously reported the synthesis and characterization of fluorinated polydienes using CF_2 generated from the thermolysis of hexafluoropropylene oxide (HFPO).[12] In this section, we describe the molecular characterization of a series of PS-*b*-(FPI-*s*-PI) materials prepared using the same technique. The PSPI starting materials we used in this study are described in Table 1. All of the PSPI copolymers exhibited narrow molecular weight distributions. Good agreement was observed between the molecular weights calculated by the reaction stoichiometry, SEC/LS, and end group analysis by ^{1}H NMR spectroscopy (the CH_3 resonances from the *s*-butyl initiating group were used assuming one initiator per chain). The molecular weights we use for subsequent calculations are based on the average of the SEC/LS and ^{1}H NMR results for entries 3−7 and on the SEC/LS results for entries 1 and 2.

Earlier, we reported the preparation of a completely CF_2-modified PSPI diblock copolymer,[12] and we observed selective incorporation of difluorocarbene into the polyisoprene block (i.e, no reaction was observed with the PS block). Although CF_2 is a strongly stabilized ground-state singlet,[22] it has been reported that dihalocarbenes in the singlet state can insert into very strained carbon−carbon single bonds[23] and some tertiary carbon−hydrogen bonds.[24] To further confirm the inert nature of PS, we investigated the reactivity of a PS homopolymer (M_n = 47.1 kg/mol, PDI = 1.04) under the fluorination protocol described in the Experimental Section. After the fluorination conditions, the polymer was examined by ^{1}H and ^{19}F NMR spectroscopy and SEC. No resonances were observed in the ^{19}F NMR spectrum, the SEC chromatographs before and after fluorination were virtually identical, and the ^{1}H spectrum after fluorination was essentially unchanged. Polystyrene is therefore inert under the fluorination reaction conditions reported here.

In this study, we used this fluorination reaction to modify the polyisoprene block in a variety of PSPI block copolymers. The extent of CF_2 modification was adjusted by controlling the stoichiometric ratio of HFPO to olefinic sites in the PI block. Random incorporation of CF_2 into the PI block is important to our analysis of the corresponding PS-*b*-(FPI-*s*-PI) block copolymer thermodynamics. Because neighboring double bonds in PI are separated by two methylene groups, we anticipate that CF_2 should react randomly with the double bonds in the backbone (i.e., no neighboring group effect).[25] In a partially CF_2-modified PSPI (entry 9 in Table 2), the ^{1}H NMR spectrum showed no significant change in the ratio of 4,3 to 4,1 regiochemistry for the unreacted PI repeat units, indicating that the tri- and disubstituted double bonds have similar reactivities under these conditions. Additionally, analysis of a partially (5%) CF_2-modified PSPI diblock copolymer (entry 3 in Table 2) by ^{19}F NMR spectroscopy revealed that the ratio of cis to trans difluorocyclopropane repeat units was approximately the same as that observed in the completely modified sample (entry 15 in Table 2). This indicates that cis and trans double bonds have similar reactivities under these conditions. Although more detailed experiments are needed to conclusively demonstrate random

Table 3. Molecular and Morphological Characteristics of CF_2-Modified PSPI(34, 27) Diblock Copolymers

entry	10^3 M_n[a]	PDI[a]	F (mol %)[26]	sample code	f_{PS}[b]	D (Å)[c]
1	61	1.05	0	PSPI(34, 27)F00	0.519	378
2	65	1.03	22.1	PSPI(34, 27)F22	0.505	389
3	68	1.03	56.7	PSPI(34, 27)F57	0.485	440
4	68	1.05	66.8	PSPI(34, 27)F67	0.479	455
5	69	1.07	>99	PSPI(34, 27)F100	0.462	528

[a] Measured by the SEC system with Wyatt MALS detector. The inconsistency between the calculated and measured values presumably arises from uncertainty in the calculated refractive index increment. See Experimental Section. [b] Volume fractions of PS calculated from F using $\rho(PS) = 1.04$ g/cm^3, $\rho(PI) = 0.913$ g/cm^3, and $\rho(FPI) = 1.26$ g/cm^3. [c] Measured by SAXS at 30 °C.

incorporation of difluorocarbene, these experiments are consistent with the formation of a statistical co-block (FPI-*s*-PI) upon CF_2 modification.

Two series of PS-*b*-(FPI-*s*-PI) copolymers with different extents of CF_2 modification were synthesized from a high-molecular-weight (61 kg/mol) PSPI (Table 1 entry 1) and a low-molecular-weight (18 kg/mol) PSPI (Table 1 entry 2). In a third series, a variety of PSPI materials (Table 1 entries 3−7) with molecular weights ranging from 6.2 to 10 kg/mol were fully CF_2-modified. These three series of materials were characterized by NMR spectroscopy and SEC and are described in Tables 2−4.

The level of CF_2 modification was calculated from the ^{1}H NMR spectra of the modified block copolymers (Figure 2).[26] We denote the PS-*b*-(FPI-*s*-PI) copolymers as PSPI(*x*, *y*)Fz, where *x* and *y* represent the molecular weights of the PS block and PI block (in units of kilogram/mole) of the precursor, respectively, and *z* represents the molar percentage of polyisoprene repeat units modified by difluorocarbene. SEC was used to determine the molecular weights and polydispersity indices (PDIs) of the PS-*b*-(FPI-*s*-PI) materials. Figure 3 shows representative SEC traces of the PSPI(10, 8)-Fz series with different extents of CF_2 modification (Table 3). The shape of the precursor peak was preserved with increasing CF_2 modification, which confirms no significant chain coupling or scission during the fluorination. With the increasing extent of CF_2 modification, the peak shifts toward a lower elution volume, suggesting a larger hydrodynamic volume in THF. The PDIs of all the block copolymers used in this study were less than 1.1.

Morphological Characterization. Figure 4 shows the SAXS scattering profiles obtained at 30 °C for a series of PS-*b*-(FPI-*s*-PI) copolymers, synthesized from the same precursor, PSPI(34, 27). In all cases, several high-order reflections are clearly observed. The ratios of the peak positions to the primary peak are consistent with a lamellar morphology. The volume fraction of the PS block (f_{PS}) decreases only slightly (from 0.519 in PSPI(34, 27)F00 to 0.462 in PSPI(34, 27)F100), and therefore, the preservation of the lamellar morphology was expected. The principal peak shifts markedly toward lower q with increasing extent of CF_2 modification. From the relationship

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

where q^* is the peak position of the principal peak, we calculated the domain spacing (D) of these block copolymers (Table 3). With increasing levels of CF_2 modification, D increases smoothly.[27]

The SAXS profiles of the PSPI(10, 8)Fz series also indicated the morphologies to be lamellar at 20 °C, based on reflections at $2q^*$ or $3q^*$. This morphological assignment was also supported by rheology. In frequency sweeps at 100 °C, the dynamic moduli (G' and G'') each scale with approximately the $^1/_2$ power with frequency ω as $\omega \rightarrow 0$, characteristic of a lamellar microstructure.[2] From SAXS measurements at 110 °C, we determined D of the modified PSPI(10, 8) series by use of eq 1 (Table 2). These values along with the D values from the modified PSPI(34, 27) series, normalized by that of the corresponding precursor PSPI (D_o), are plotted versus the molar percentage of modification in Figure 5. The domain spacings remain approximately unchanged up to 15% modification and then increase significantly (D for both polymers increased by approximately 40% upon complete CF_2 modification).

Order−Disorder Transitions of the PSPI(10, 8)-Fz Series. We examined the order−disorder transition (ODT) of the PSPI(10,8)Fz as a function of CF_2 modification by 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.[3] Figure 6 shows $G'(T)$ for representative PSPI(10, 8)Fz materials. As the temperature was increased, G' dropped sharply at the ODT. In this manner, we located T_{ODT} for several of the CF_2-modified PSPI(10, 8) block copolymers (Table 2). During the measurement of PSPI(10,8)F55, G' started to increase sharply above 240 °C, and the polymer was subsequently insoluble in organic solvents, consistent with covalent cross-linking of the sample.

Another established method to locate T_{ODT} of block copolymers is static birefringence. Because of the anisotropic nature of the microstructure, a polarized laser beam will be depolarized to some extent upon passing through a lamellar block copolymer. In contrast, the polarized laser beam will retain its state of polarization when going through block copolymer melts in the isotropic disordered state. Therefore, a sharp drop in the transmitted depolarized light intensity can be observed when a lamellar block copolymer undergoes the ODT.[21,28] Figure 7 shows the transmitted depolarized intensity for some of the PSPI(10, 8)Fz series as a function of temperature. Using this method, we determined T_{ODT} for several CF_2-modified PSPI(10, 8) materials (Table 2).[29] The results agreed very well with those from rheology and are plotted as a function of degree of CF_2 modification in Figure 8.

Order−Disorder Transitions of PS-*b*-FPI. We also located T_{ODT} for a series of PS-*b*-FPI copolymers with different molecular weights using static birefringence and rheology (Table 4). In the case of PSPI(3.2, 3.0)-F100, no abrupt decrease in G' was observed with increasing temperature. Static birefringence confirmed that the material was disordered above 75 °C (no birefringence was observed when we slowly cooled the sample cell from 100 to 75 °C and kept it at 75 °C for 16 h). As the molecular weight was increased, ODTs were observed for PSPI(3.8, 2.8)F100, PSPI(4.1, 3.1)-F100, and PSPI(4.2, 3.6)F100. No ODT for PSPI(5.5, 4.5)F100 was observed, and the sample remained ordered over the entire experimental temperature window.

Discussion

The main focus of this section is to extract a semiquantitative measure of the interaction strengths in this

Table 4. Molecular and Morphological Characteristics of PS-*b*-FPI with Different Molecular Weights

entry	10^3M_n[a]	PDI[a]	10^3M_n[b]	F (mol %)	sample code	f_{PS}[c]	N[d]	T_{ODT}[e] (°C)	T_{ODT}[f] (°C)
1	13	1.03	13	>99	PSPI(5.5, 4.5)F100	0.459	114	>240	
2	11	1.03	10	>99	PSPI(4.2, 3.6)F100	0.444	90	178 ± 0.5	178 ± 1
3	10	1.03	9.5	>99	PSPI(4.1, 3.1)F100	0.474	82		159 ± 1
4	9.4	1.04	8.6	>99	PSPI(3.8, 2.8)F100	0.482	75	130 ± 0.5	130 ± 1
5	9.1	1.04	8.5	>99	PSPI(3.2, 3.0)F100	0.420	73	<80	<75

[a] Measured by HP SEC system calibrated by PS standards. [b] Calculated from precursor molecular weights based on reaction stoichiometry. [c] Calculated based on precursor volume fractions and stoichiometry. [d] The degree of polymerization obtained from the calculated M_n using the PS repeat unit as the reference volume. [e] Measured by rheology. [f] Measured by static birefringence.

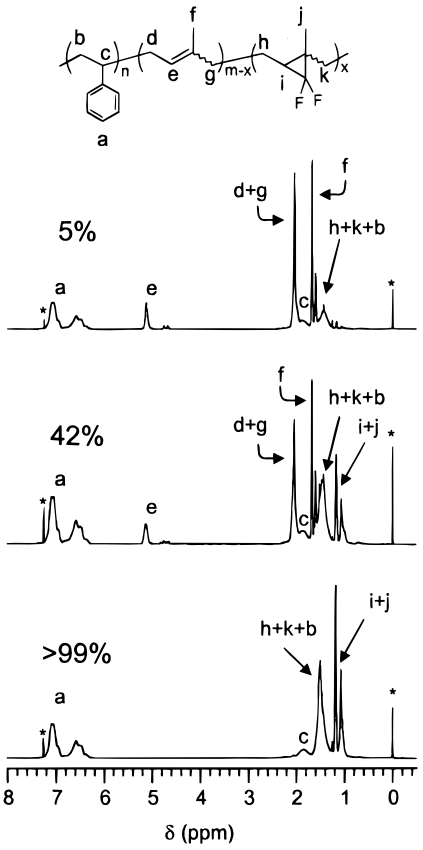


Figure 2. Representative ^{1}H NMR spectra for CF_2-modified PSPI(10, 8). The * denotes resonances associated with the solvent.

system and in so doing to understand the interesting dependence of T_{ODT} on fluorination extent shown in Figure 8. The degree of segregation in a block copolymer system is controlled by χN, where χ is the familiar Flory−Huggins interaction parameter between blocks. From the classic work of Leibler,[30] the mean-field order−disorder transition for a symmetric diblock copolymer occurs when

$$(\chi N)_{ODT} \approx 10.5 \tag{2}$$

In the previous section, we reported T_{ODT} of a series of PS-*b*-FPI with different molecular weights. Using eq 2 and a reference volume (v_o) of 166.3 Å^3 for the calculation of N, we can calculate a mean-field χ_{SFI} between styrene (S) and fully CF_2-modified isoprene (FI). The results are plotted against inverse temperature in Figure 9 and are given by

$$\chi_{SFI} = \frac{86}{T} - 0.074 \tag{3}$$

Leibler noted, and Fredrickson and Helfand[31] later

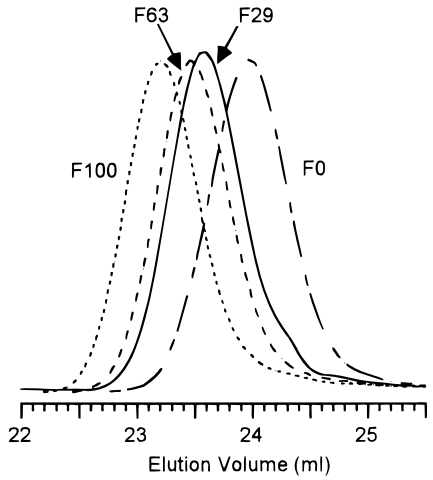


Figure 3. Representative SEC chromatograms of four PSPI-(10, 8)Fz with different levels of CF_2 modification.

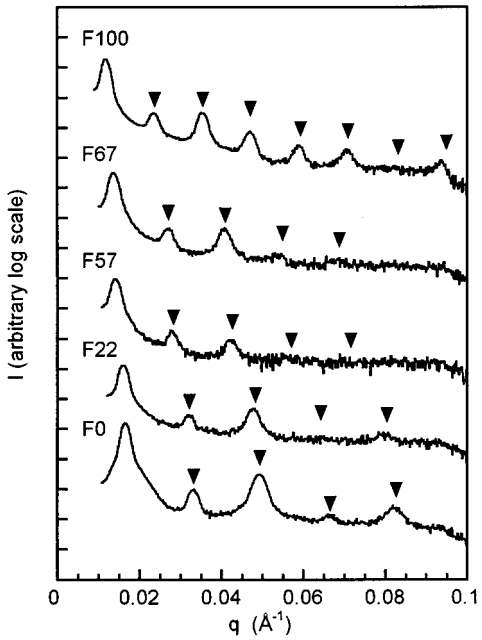


Figure 4. One-dimensional SAXS profiles at 30 °C of a series of PSPI(34, 27)Fz with different degrees of CF_2 modification. The triangles correspond to the positions with integer multiples of q^*. The data were shifted vertically.

showed, that the ODT for a symmetric block copolymer would be shifted to a higher χN due to fluctuations. The resulting prediction (which is still only approximate for low molecular weights) is

$$(\chi N)_{ODT} \approx 10.5 + 41.0\bar{N}^{-1/3} \tag{4}$$

where $\bar{N} = Na^6v_o^{-2}$ and a is the statistical segment length of the block copolymer. Using the values of the

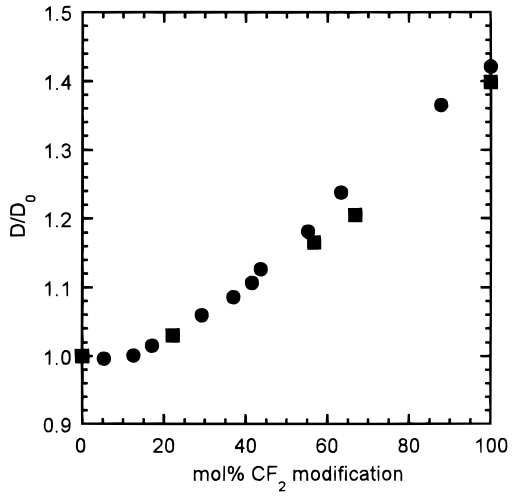


Figure 5. Dependence of the domain spacing, normalized by the domain spacing of the precursor on the molar percentage of CF_2 modification. The filled circles represent the fluorinated PSPI(10, 8)Fz series at 110 °C, and the filled squares represent the CF_2-modified PSPI(34, 27)Fz series at 30 °C.

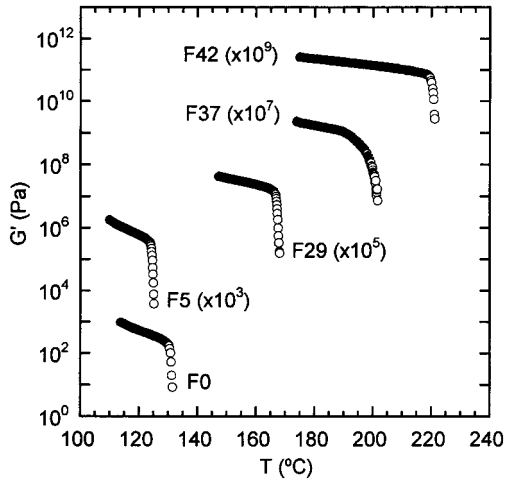


Figure 6. Isochronal temperature dependence of the dynamic storage moduli for representative CF_2-modified PSPI(10, 8)-Fz diblock copolymers with various degrees of CF_2 modification. All of the data were taken at a frequency of 1 rad/s, a strain of 2%, and a heating rate of 0.5 or 2 °C/min. The data were shifted vertically.

average statistical segment length and v_o, we calculated the $\chi_{SFI,fluc}$ at various ODT temperatures using eq 4 and again plotted the $\chi_{SFI,fluc}$ versus $1/T$ in Figure 9. The temperature dependence of $\chi_{SFI,fluc}$ was found to be

$$\chi_{SFI,fluc} = \frac{153}{T} - 0.156 \qquad (5)$$

As expected, the fluctuation theory and mean-field χ_{SFI} values differ, but they have similar temperature dependences. These results may be compared with the mean-field expression for styrene−isoprene (obtained from ODTs of several lamellar melts and solutions):[21a]

$$\chi_{SI} = \frac{33}{T} - 0.0228 \qquad (6)$$

which is also plotted in Figure 9. Clearly, the styrene−CF_2-modified isoprene interaction parameter is greater than that for styrene and isoprene, which is already implied by the overall increase in both T_{ODT} and domain

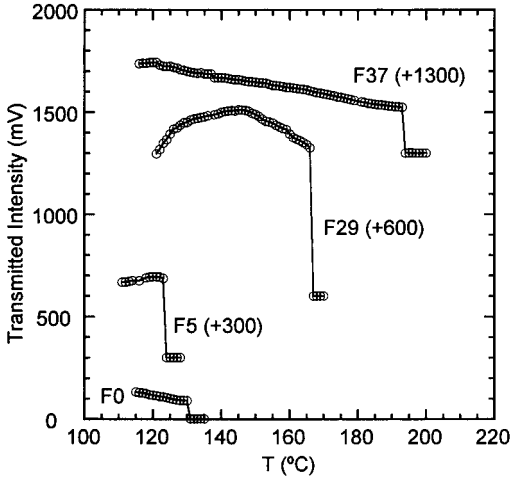


Figure 7. Temperature dependence of the transmitted depolarized light intensity for representative CF_2-modified PSPI-(10, 8)Fz diblock copolymers. The data were shifted vertically.

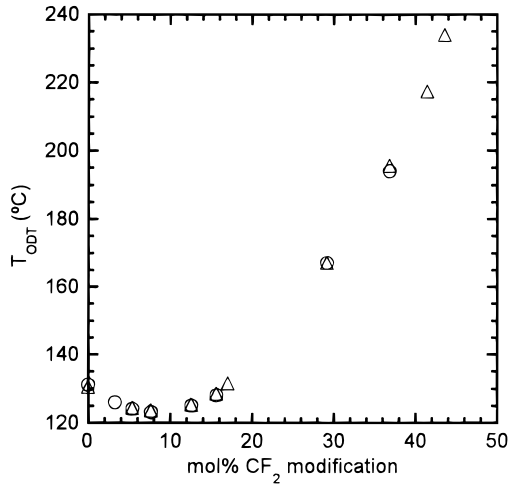


Figure 8. Dependence of the T_{ODT} on the molar percentage of CF_2 modification for the fluorinated PSPI(10, 8)Fz series determined by static birefringence (○) and rheology (△).

spacing (D) with extent of CF_2 modification. In fact, the dependence of D on the extent of CF_2 modification offers a direct route to extracting all three pairwise interaction parameters, χ_{SI}, χ_{SFI}, and χ_{IFI}, as we will now discuss.

The domain spacing is determined by the balance between the unfavorable interfacial energy and the entropic penalty due to the deformation of the polymer coils.[3] Mean-field theory provides an explicit prediction for D in lamellar samples:[32]

$$D = 1.10aN^{2/3}\chi^{1/6} \qquad (7)$$

Equation 7 is strictly applicable only in the strong-segregation regime ($\chi N \geq 100$), whereas the PSPI(10, 8) series at 110 °C falls in the intermediate segregation regime. Nevertheless, eq 8 should provide a reasonable and internally consistent estimate of χ for the following reasons. Matsen and Bates calculated D using self-consistent mean field theory without the traditional approximations and compared the results with eq 7.[4] The results differ by only about 20% when $\chi N = 10$ and by 5% when χN increases to 40. Experimentally, Hadziioannou and Skoulios reported that D for a series of PS-*b*-PI copolymers with molecular weights ranging from 18.7 to 450 kg/mol agreed with-

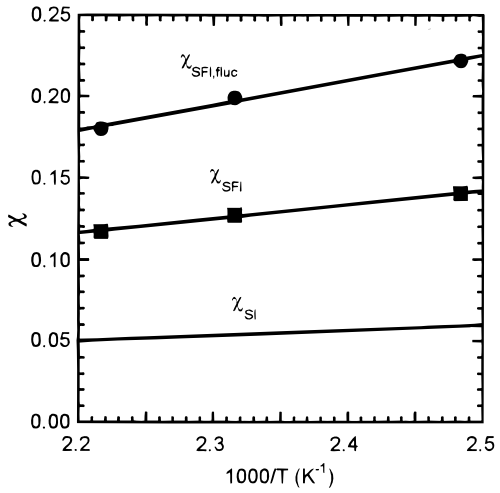


Figure 9. Temperature dependence of the Flory−Huggins interaction parameter between the PS and FPI (χ_{SFI}). The solid squares and circles represent the values calculated from eqs 2 (mean field theory) and 4 (fluctuation theory), respectively. The solid lines are least-squares linear fits to the data points. The temperature dependence of the Flory−Huggins interaction parameter between the PS and PI (χ_{SI}) given by eq 6 is shown for comparison.

in 10% with the calculated value using Helfand's theory with narrow interface approximation (essentially eq 7).[33]

The increase in the domain spacing can be influenced by three different parameters: a, N, and χ. Therefore, we need to examine the effect of fluorination on the first two parameters in order to extract the dependence of χ upon fluorination. The statistical segment lengths of PI and FPI were obtained from SANS measurements on binary hPI/dPI and hFPI/dFPI blends. The experimental intensities were fit to the RPA structure factor $S(q)$ based on the assumption of no interaction between hydrogeneous and partially deuterated polymers (i.e., $\chi_{HD} = 0$):

$$\frac{1}{S(q)} = \frac{1}{\phi_H N_H P_H} + \frac{1}{\phi_D N_D P_D} \tag{8}$$

where ϕ_H and ϕ_D are the respective volume fractions, N_H and N_D are the actual degrees of polymerization, and P_H and P_D are the form factors (Debye functions). The coherent scattering intensities from the blends were fit to eq 8 with the statistical segment length (a) as the only adjustable parameter. As shown in Figure 10, the resulting fits agree well with the scattering data. The statistical segment length for FPI at 100 °C was determined to be 7.0 Å. (Because we chose the PS repeat unit as the reference volume, a_{FI} was adjusted to 7.3 Å using the room temperature densities of FPI (1.26 g/cm^3)[34] and PS (1.04 g/cm^3) for subsequent calculations.) We also calculated the statistical segment length for PI at room temperature to be 6.2 Å, which agrees well with the value of 6.4 Å reported by Krishnamoorti et al.[35]

The average statistical segment length for a PSPI diblock copolymer (a_{SI}) in eq 7 can be written as[36]

$$a_{SI} = \left(\frac{f_{PS}}{a_s^2} + \frac{1 - f_{PS}}{a_I^2}\right)^{-1/2} \tag{9}$$

where f_{PS} is the volume fraction of the PS block.

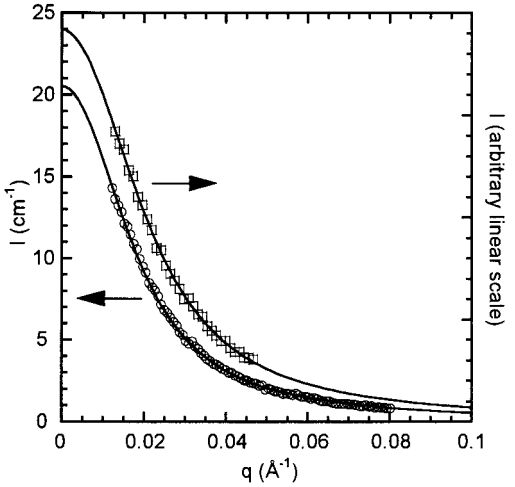


Figure 10. Dependence of coherent SANS intensities from the FPI blend at 100 °C (○) and PI blend at room temperature (□) on the wavevector (q). The smooth curves represent the least-squares fits using the structure factor defined in eq 8.

CF_2 modification should affect the statistical segment length of the PI block as

$$a_{IFI}^2 = (1 - x)a_I^2 + xa_{FI}^2 \tag{10}$$

where x is the extent of CF_2 modification of the PI block (on a volume basis). Thus, the average statistical segment length of the block copolymer can be expressed as

$$a_{SFI} = \left(\frac{f_{PS}}{a_S^2} + \frac{1 - f_{PS}}{(1 - x)a_I^2 + xa_{FI}^2}\right)^{-1/2} \tag{11}$$

Given $a_{FI} = 7.3$ Å at 100 °C from SANS, we then were able to calculate a_{SFI} for a PS-*b*-(FPI-*s*-PI) using eq 11 with the literature values of $a_{PS} = 6.7$ Å and $a_{PI} = 7.6$ Å (at 140 °C, using the PS repeat unit as the reference volume and $\rho_{PI} = 0.913$ g/cm^3 and $\rho_{PS} = 1.04$ g/cm^3 to adjust a_{PI}).[35] The temperature dependence of the statistical segment length is usually weak,[37] and thus, we neglect it. As seen in Table 2 for the PSPI(10, 8)Fz series, the average statistical segment length was found to be nearly constant upon CF_2 modification. The appropriate degree of polymerization, N, is slightly different from the chemical degree of polymerization because the PS repeat unit is chosen as the reference segment. Thus, N increases as the extent of fluorination increases, by 12.5% upon complete CF_2 modification. Experimentally, the domain spacing was observed to increase by approximately 40% upon complete modification by difluorocarbene, whereas the changes in a and N account for only 7% of this based on eq 7; therefore the changing interaction parameter, χ_{eff}, was the major cause of the observed changes in D. By use of the calculated N and a values (Table 2), eq 7 was inverted to generate χ_{eff} as a function of the level of CF_2 modification (Figure 11).

Figure 11 demonstrates an interesting change in χ_{eff} as a function of CF_2 modification. Below 10% CF_2 modification, χ_{eff} decreases, whereas at higher levels of modification, χ_{eff} increases. Initially, CF_2 modification of PI renders the FPI-*s*-PI more miscible with PS. In an effort to understand this interesting behavior, we will utilize a binary interaction model introduced to explain phase behavior for polymer blends composed of a

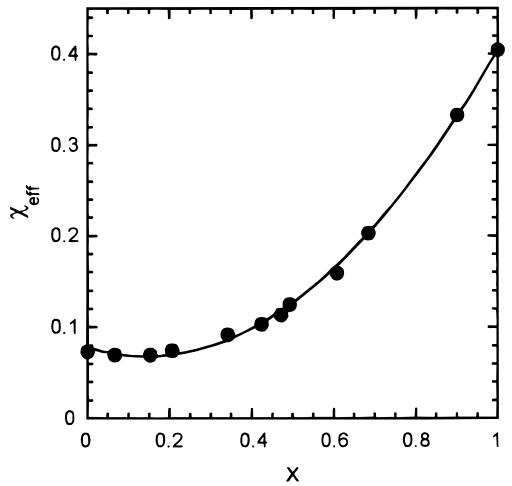


Figure 11. Dependence of the calculated χ_{eff} from eq 7 on the CF_2 modification extent (x). The solid curve is the best-fit quadratic curve ($y = ax^2 + bx + c$). The fitting coefficients are $a = 0.46$, $b = -0.13$, and $c = 0.077$.

homopolymer (A) and a statistical copolymer (B-*s*-C).[38] Because the insertion of difluorocarbene into a PI block is assumed to be random, we applied this binary interaction model to our block copolymer system. The effective interaction parameter (χ_{eff}) in such a three-component system can be expressed in terms of the pairwise interaction parameters and the composition of the statistical co-block as follows:

$$\chi_{eff} = \chi_{SFI}x + \chi_{SI}(1 - x) - \chi_{IFI}x(1 - x) \qquad (12)$$

where χ_{SFI}, χ_{SI}, and χ_{IFI} are the pairwise interaction parameters among the styrene (S), fluorinated isoprene (FI), and isoprene (I) segments, respectively, and x is the extent of CF_2 modification of the PI block (on a volume basis). Equation 12 is thus quadratic in x and fits the experimental χ_{eff} very well, as shown in Figure 11. The resulting values of the pairwise interaction parameters at 110 °C are 0.46, 0.40, and 0.077 for χ_{IFI}, χ_{SFI}, and χ_{SI}, respectively.[39] This result for χ_{SI} is 21% larger than that calculated from eq 6, which is well within the combined uncertainties. Similarly, the value for χ_{SFI} is somewhat larger than that calculated from the T_{ODT} measurements on PS-*b*-FPI copolymers using fluctuation theory ($\chi_{SFI,fluc}$).

As reported in the previous section, T_{ODT} for PSPI-(10, 8)Fz passes through a minimum before increasing sharply with increasing extent of CF_2 modification (Figure 8). This is consistent with the changes in the calculated χ_{eff} with CF_2 modification (Figure 11). The main result from application of the binary interaction model to the χ_{eff} and the T_{ODT} data is the relative magnitude of the pairwise interaction parameters: $\chi_{IFI} \approx \chi_{SFI} > \chi_{SI}$. From eq 12, one concludes that if $\chi_{SI} + \chi_{IFI} > \chi_{SFI}$, there will be a minimum in χ_{eff} at some finite extent of CF_2 modification, x. This accounts for a miscibility directly analogous to that in blends such as PMMA/PSAN[40] and PVC/P(E-s-VAc);[41] although none of the components are pairwise miscible, partial screening of B−C contacts by the interposition of A segments is energetically favorable.[42] These results can also be contrasted with those recently reported by Hashimoto and co-workers[9b] for a PS-*b*-(PEP-*s*-PI) system. They observed a monotonic increase in the domain spacing as they selectively hydrogenated the PI block in a PSPI block copolymer, due to the fact that χ_{SEP} is greater than the sum of χ_{SI} and χ_{IEP}.

Table 5. Solubility Data for PI, PS, and FPI[a]

solvent	δ (MPa)$^{1/2}$	PI	PS	FPI
hexane	14.9	■	□	□
cyclohexane	16.8	■	●	●
dimethoxyethane	17.6	■	■	■
toluene	18.8	■	■	■
chloroform	19.0	■	■	■
tetrahydrofuran	19.4	■	■	■
methylene chloride	20.3	■	■	■
acetonitrile	24.3	□	□	●
dimethyl sulfoxide	24.6	□	□	■

[a] ■ = soluble at room temperature, ● = soluble when heated, and □ = insoluble.

These results imply that the cohesive energy density or the solubility parameter of FPI exceeds that of PS. This is plausible, given the polar nature of the CF_2 moiety in the FPI repeat unit. Indeed, polyvinylidene fluoride is quite polar (δ = 24.5−25.2 MPa$^{1/2}$)[43] and is soluble in polar solvents such as dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), and hexamethylphosphoramide (HMPA).[44] As a simple check of this conclusion, we compared the solubilities of an FPI homopolymer with those of PS and PI in a range of common solvents, spanning solubility parameters from hexane (δ = 14.9 MPa$^{1/2}$) to acetonitrile (24.3 MPa$^{1/2}$) and DMSO (24.6 MPa$^{1/2}$). The results are shown in Table 5. Only PI is soluble in hexane, whereas FPI is the only one soluble in DMSO. Although qualitative, this analysis is fully consistent with the conclusion that insertion of difluorocarbene into polyisoprene increases the cohesive energy density and does so to the extent that the fully CF_2-modified product is more polar than polystyrene.

Summary

We have characterized a set of PS-*b*-FPI and PS-*b*-(FPI-*s*-PI) block copolymers prepared by the reaction of model PSPI block copolymers with difluorocarbene. We determined the T_{ODT} for a set of PS-*b*-FPI with different molecular weights by rheology and static birefringence. Using the mean-field and fluctuation theories, we were able to extract the temperature dependence of χ_{SFI} (Figure 9). For partially CF_2-modified PSPI block copolymers, we determined the morphologies and domain spacings at different levels of CF_2 modification by SAXS. With the a_{FI} measured by SANS from a binary hFPI/dFPI blend, we determined χ_{eff} between PS and FPI-*s*-PI at different levels of CF_2 modification using eq 7. At low levels of CF_2 modification, PS and FPI-*s*-PI become more miscible. At moderate to high levels of CF_2 modification, PS and FPI-*s*-PI become more immiscible. Upon complete CF_2 modification of a PSPI block copolymer, we found the S/FI interaction parameter to be approximately four times larger than that of the S/I interaction. We have rationalized this behavior quantitatively using a binary interaction model introduced to explain the phase behavior of homopolymer/statistical copolymer blends (Figure 11). From this analysis, we were able to uncover the three pairwise interaction parameters. We found the following relationship: $\chi_{IFI} \approx 1.2\chi_{SFI} \approx 6.0\chi_{SI}$. Because of the strong unfavorable I/FI interaction, dilution of the I/FI contacts by the interposition of S segments is energetically favorable. Thus, the χ_{eff} passes through a minimum at some finite extent of CF_2 modification. T_{ODT} for the PSPI(10, 8)Fz

series, measured by rheology and static birefringence, also passes through a minimum before increasing sharply (Figure 8), which is consistent with the behavior of the calculated changes in χ_{eff}.

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$$\frac{F_{total}}{kT} = \frac{F_{int}}{kT} + \frac{F_{el}}{kT} = \gamma\left(\frac{(N_S + N_I)}{(D_S + D_I)\rho}\right) + \frac{3}{2}\left(\frac{{D_S}^2}{N_S {a_S}^2} + \frac{{D_I}^2}{N_I {a_I}^2}\right)$$

where γ is the interfacial energy between the styrene-rich and isoprene-rich domains, ρ is the block copolymer density, and N_I and N_S, D_I and D_S and a_I and a_S are the degrees of polymerization, domain spacings and statistical segment lengths for the PI and PS blocks, respectively. Because $N_I/N_S = D_I/D_S = (1 - f_{PS})/f_{PS}$, we can simplify the equation above to

$$\frac{F_{total}}{kT} = \gamma\left(\frac{N}{D\rho}\right) + \frac{3}{2}\left(\frac{D^2}{N {a_{SI}}^2}\right)$$

where N and D are the total degree of polymerization and domain spacing for the SI diblock copolymer and a_{SI} is the average statistical segment length defined as

$$\frac{1}{{a_{SI}}^2} = \frac{f_{PS}}{{a_S}^2} + \frac{1 - f_{PS}}{{a_I}^2}$$

Therefore, we use eq 9 to calculate the a_{SI}.

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