A Simple and Mild Route to Highly Fluorinated Model Polymers

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ABSTRACT: We have developed a simple and mild method for the fluorination of polybutadiene based on the addition of perfluoroalkyl iodides (R_fI) to carbon−carbon double bonds. Triethylborane (Et_3B) was utilized to initiate this free radical addition to model polybutadiene (PBD) homopolymers and a polystyrene−polybutadiene block copolymer at room temperature. Optimized reaction conditions led to consumption of more than 95% of the double bonds and preservation of narrow molecular weight distribution after the modification. We propose that the reaction undergoes a cyclization pathway rather than open-chain addition and that five-member ring structures are formed during the addition of R_fI to 1,2-PBD. From ^{1}H NMR spectroscopy, we estimate that 83% of the double bonds in the 1,2-PBD cyclized with their neighbors. This agrees well with a theoretical prediction by Flory for random irreversible cyclization between neighboring polymer repeat units. We also demonstrate the selective fluorination of the 1,2-PBD block in a polystyrene-*block*-1,2-polybutadiene (PS-*b*-1,2-PBD) copolymer. In contrast to the fluorinated homopolymers, subsequent hydrogenolysis of this fluorinated PS-*b*-1,2-PBD copolymer gave a soluble material. The ^{1}H NMR spectrum and elemental analysis confirmed the complete hydrogenolysis. Preliminary physical characterization was performed by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), contact angle measurements, and small-angle X-ray scattering (SAXS). The glass transition temperature (T_g) of the fluorinated 1,2-PBD increases by 75 °C, removal of the iodine in the fluorinated PS-*b*-1,2-PBD copolymer increases the thermal stability by ca. 100 °C, and all fluorinated polymers exhibit very low critical surface tensions (14−16 mN/m).

Introduction

The chemical modification of polymers can expand the scope of materials synthesized from the commercially available monomer/polymer base. Ideally, the molecular parameters (i.e., architecture, degree of polymerization, and molecular weight distribution) designed into macromolecular precursors will be preserved after modification, so the resultant polymers can be used in applications and fundamental investigations requiring well-defined materials. In general, two challenges need to be overcome for the preparation of model polymers through post-polymerization modification. First, polymer chain scission and/or coupling during the modification should be avoided. Second, since the polymer solubility usually changes during the modification, an appropriate solvent or solvent mixture is necessary for the homogeneity of the reaction mixture throughout the modification to enable complete conversion. Polydienes and polydiene-containing block copolymers have received much attention as substrates for post-polymerization modification, due to the available unsaturation sites and the facile controlled preparation by anionic polymerization.[1] Hydrogenation of polydienes has been extensively studied[2] and is a useful tool for both fundamental studies[3] and practical applications.[4] Other chemistries, such as hydrosilylation,[4] hydroboration−oxidation,[5] epoxidation,[6] and addition of CCl_4[7] and thiols,[8] have been applied to polydienes to convert the unsaturation sites to desired functionalities.

We are interested in the fluorination of model polydienes because fluorinated polymers are useful materials with remarkable properties,[9] including low surface energies, low dielectric constants and refractive indices,[10] high chemical and thermal stabilities, and solubility in supercritical CO_2.[11] A variety of strategies have been reported for the fluorination of polydienes. Hydroboration−oxidation and subsequent esterification using fluorinated acid chlorides have been utilized to incorporate fluorinated groups into the polydiene block of model polystyrene (PS)-*block*-polydiene copolymers.[12,13] Dhamodharan and co-workers demonstrated the incorporation of fluorosilanes into the 1,2-polybutadiene (1,2-PBD) block of a model PS-*block*-1,2-PBD copolymer by hydrosilylation.[14] Boutevin and co-workers reported the incorporation of fluorinated thiols into hydroxy-terminated polybutadienes by free radical grafting with photochemical[15] and radical initiation.[16] Fluorination has also been carried out on other polymeric substrates. Direct post-polymerization fluorination methods, involving xenon difluoride,[17] F_2,[18] and CF_4 plasma,[19] have been utilized to fluorinate various polymeric substrates. However, these methodologies employ chemically aggressive reagents and usually cause undesired side reactions. Several fluorination methods utilizing fluorinated intermediates, such as fluoroolefins,[10] fluorinated alcohols,[20] and fluorinated acrylates,[21] have been employed to modify various polymers for different end applications.

We previously reported a mild, one-step reaction to insert difluorocarbene (CF_2) into model polydienes.[22] The narrow molecular weight distribution of the macromolecular precursors was preserved through the modification. We applied this fluorination to polystyrene-*block*-polyisoprene (PS-*b*-PI) copolymers to selectively fluorinate the PI block. We were able to control the extent of CF_2 modification and systematically studied the effect of the CF_2 modification on the block copolymer self-assembly. The effective interaction parameter (χ_{eff}) between the PS and partially CF_2-modified PI blocks passes through a minimum before increasing smoothly by a factor of 4 upon complete CF_2 modification and can be understood in a quantitative manner using a binary

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interaction model.[23] We also found that the cohesive energy density or the solubility parameter of the PI block increases after the CF_2 modification due to the polar nature of the CF_2 moiety in the fluorinated PI repeat unit. To achieve the desired properties of fluoropolymers, such as low cohesive energy density and low surface energy, it is necessary to incorporate more fluorine atoms per repeat unit. Incorporation of more fluorine atoms will also mitigate the polarity of the isolated CF_2 group.

The addition of perfluoroalkyl iodides (R_fI) is an efficient, selective, and versatile reaction to incorporate perfluoroalkyl groups into unsaturated organic compounds[24] and has been extensively studied over the past half century.[25] Many initiation methods have been documented for this free radical chain process. The free radical addition can be initiated by the thermal or photochemical homolysis of carbon−iodine (C−I) bonds in R_fI, as Haszeldine reported in his early work.[26] With initiators such as peroxides and azo compounds this free radical addition can be conducted at lower temperatures.[24] Recently, various single-electron reductants[27] and organoboranes[28,29] were used to initiate this free radical addition under milder conditions. This chemistry has been utilized to prepare perfluoroalkyl-substituted monomers, such as perfluoroalkyl-substituted acrylates,[30] allyl ethers,[31] α-olefins,[32] and thiophenes,[33] which can be polymerized subsequently to yield fluorinated polymers. R_fI have also been used as transfer agents in the controlled telomerization of fluoroolefins[34] and 1,3-butadienes[35] and controlled free radical polymerization of styrene and acrylates.[36] We now report the mild synthesis and characterization of highly fluorinated model polymers by the addition of R_fI into model polydienes.[37]

Experimental Section

Materials. All chemicals were purchased from Aldrich and used without further purification except as noted. Styrene was stirred over CaH_2 at room temperature for about 12 h and distilled into a flask containing dibutylmagnesium. The styrene was stirred over dibutylmagnesium for 5 h at room temperature and then distilled into a flame-dried buret. Butadiene was purified by two successive distillations from *n*-butyllithium after stirring at 0 °C for 1 h and then distilled into a flame-dried buret. Dipiperidinoethane (Sigma) was stirred over CaH_2 at room temperature for about 12 h and then distilled into a flame-dried buret. The concentration of *sec*-butyllithium was determined by the Gillman double-titration method prior to use.[38] Cyclohexane was purified using a home-built solvent purification system described previously.[23]

Synthesis of Model Polymer Precursors. In this study, 1,2-polybutadiene (1,2-PBD), 1,4-polybutadiene (1,4-PBD), and polystyrene-*block*-1,2-polybutadiene (PS-*b*-1,2-PBD) were synthesized by living anionic polymerization. The polymerizations were performed in cyclohexane using *sec*-butyllithium as the initiator. The preparation of PS-*b*-1,2-PBD is described below. A 2 L round-bottom flask equipped with five internal ACETHREDS ports was heated to 250 °C under 5 mTorr for 12 h to remove any adsorbed H_2O. After cooling, cyclohexane (ca.1 L) and *sec*-butyllithium solution (1.2 M in cyclohexane, 5.8 mL, 7.0 mmol) were added to the flask. Purified styrene (55.8 g, 0.536 mol) was then added to the flask and stirred at 45 °C for 4 h to achieve complete polymerization. The reaction mixture was cooled to 10 °C. Five equivalents relative to the initiator of purified dipiperidinoethane (7.5 mL, 35 mmol) was injected as the polar modifier to control the microstructure of the second block.[39] The purified butadiene (17.0 g, 0.315 mol) was slowly added. The reaction mixture was warmed to 18 °C and stirred for 3 h. The living chains were terminated by injection of excess degassed methanol. The polymer was precipitated by pouring the solution slowly into a 1:1 mixture of 2-propanol and methanol and subsequently dried at room temperature under vacuum (<100 mTorr) for 72 h. Size exclusion chromatography (SEC) analysis yielded a polydispersity index (PDI) of 1.04 and a number-average molecular weight (M_n) of 9.7 kg/mol, which agreed with the target molecular weight (M_{PS} = 8.0 kg/mol, $M_{1,2-PBD}$ = 2.4 kg/mol, and M_n = 10.4 kg/mol) calculated from the reaction stoichiometry. From the ^{1}H NMR spectrum, the 1,2-content of the PBD block was calculated to be higher than 99%. The isolated yield was 71.2 g (98%). The 1,2-PBD was synthesized using similar procedures except one equivalent relative to the initiator of dipiperidinoethane was added as the polar modifier. The 1,2-content was calculated to be 95% from the ^{1}H NMR spectrum. The M_n was 8.4 kg/mol, and the PDI was 1.03 as determined by SEC. The 1,4-PBD was also synthesized using similar procedures without any polar modifier. SEC analysis gave M_n = 11.4 kg/mol and PDI = 1.03, and the ^{1}H NMR spectrum indicated the 1,4-content to be 94%.

Reaction with Perfluoroalkyl Iodides. Three polybutadienes with different microstructures were used as polymeric substrates for the addition of perfluoroalkyl iodides. A specific example (entry 7 in Table 1) of the general method is reported here. The 1,2-PBD (0.280 g, 5.18 mmol of olefinic sites) was dissolved in 30 mL of a 1:1 mixture of hexanes and 1,1,2-trichlorotrifluoroethane (CFC-113). Then *n*-perfluorohexyl iodide ($C_6F_{13}I$, 2.24 mL, 10.4 mmol) and triethylborane solution (1.0 M in hexanes, 5.2 mL, 5.2 mmol) were injected into the reaction flask under nitrogen flow. The reaction mixture was stirred at room temperature for 24 h under a slow air flow (30 cm^3/min) through a three-way adapter which connects to the reaction flask and a bubbler. The solution was concentrated on a rotary evaporator and precipitated in 0.2 L of methanol. The precipitated polymer was purified by dissolving in CFC-113 and reprecipitating in methanol twice. The polymer was collected and dried at room temperature under vacuum (<100 mTorr) for 12 h. The isolated yield was 1.172 g.

Hydrogenolysis. The fluorinated polymers were subjected to hydrogenolysis to remove the thermally labile iodine. One representative example is described below. 2.24 g of 5 wt % palladium on calcium carbonate ($Pd/CaCO_3$, 1.05 mmol, Strem) was added into a high-pressure reactor, dried at 120 °C for 1 h under vacuum, and then reduced under 160 psi of H_2 at 120 °C for 1 h. 1.46 g of fluorinated PS-*b*-1,2-PBD (ca. 1.63 mmol of iodine) and 0.436 g of 85% potassium hydroxide (6.60 mmol) were dissolved in a solution of 60 mL of α,α,α-trifluorotoluene ($C_6H_5CF_3$, BTF)[40] and 12 mL of methanol. The polymer solution was degassed and added into the high-pressure reactor. The reactor was pressurized with 500 psi of H_2, and the reaction proceeded at 70 °C for 109 h. The catalyst was removed by vacuum filtration, and the polymer solution was concentrated on a rotary evaporator and subsequently precipitated in 0.2 L of methanol. The polymer was purified by dissolving in BTF and precipitating in methanol, collected, and dried at 110 °C under 10 mTorr for 10 h. The isolated yield was 0.917 g (73%).

Characterization. All the polymers were characterized by 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 Varian 500 VI spectrometer. The NMR samples were prepared by dissolving approximately 30 mg of polymer in 750 μL of deuterated chloroform (Cambridge Isotope Laboratories) or deuterated chloroform/CFC-113 mixtures for the polymers insoluble in deuterated chloroform. Hexafluorobenzene was added to the solutions as the internal standard (δ = −162.9 ppm) for the ^{19}F NMR spectra.[41] 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 SEC measurements were performed at a flow rate of 1.00 mL/min, and tetrahydrofuran (THF) was used as the mobile phase.

Table 1. Reactions of $C_6F_{13}I$ with Model Polybutadienes[a]

entry	precursor polymer	R_fI/[C=C]	Et_3B/[C=C]	time (h)	solvent[b]	C=C conv (%)	isolation yield (%)[c]	recalcd yield (%)[d]	product M_n (kg/mol)[e]	product PDI[e]
1	PBD[f]	4	1	5	H	94			17.0	1.09
2	PBD	4	1	5	BTF	92	43	77	13.3	1.59
3	PBD	4	1	4	THF	53	53	89	14.8	1.08
4	PBD	4	1	19	H/113	86	55	98	16.8	1.03
5	PBD	4	0.1	23	H/113	78	53	94	19.3	1.34
6	PBD[g]	4	1	8	H	72	48	82	17.8	1.18
7	1,2-PBD[h]	2	1	24	H/113	96	47	84	13.5	1.04
8	1,2-PBD	1	0.5	23	H/113	94	42	75	13.5	1.02
9	1,2-PBD	1	0.5	0.5	H/113	95	49	88	13.5	1.03
10	1,2-PBD	0.5	0.25	0.25	H/113	74			13.2	1.09
11	1,2-PBD	0.25	0.125	0.25	H/113	37			12.5	1.05
12	1,2-PBD	0.25	0.125	0.5	H/113	53			12.3	1.04
13	PS-*b*-1,2-PBD[i]	1	0.5	20	H/BTF	93			12.2	1.06
14	PS[j]	1	0.5	20	H/BTF				21.5	1.04
15	1,4-PBD[k]	2	1	24	H/113	88	55	98	17.8	1.18

[a] The reactions were run under an air flow of 30 cm^3/min except entries 11 and 12, which were run under an air flow of 3 cm^3/min. [b] H = hexanes, BTF = α,α,α-trifluorotoluene ($C_6H_5CF_3$), 113 = 1,1,2-trichlorotrifluoroethane. [c] We calculated the isolation yields assuming that one double bond was reacted with one perfluoroalkyl iodide. [d] We recalculated the isolation yields based on the proposed cyclization mechanism; i.e., two double bonds react with one perfluoroalkyl iodide. [e] Measured by SEC system with PS calibration. [f] The polybutadiene precursor used in entries 1−6 was characterized by both NMR and SEC (M_n = 11.5 kg/mol, PDI = 1.03, 1,2-content = 68%, and 1,4-content = 32%). [g] C_4F_9I was used for entry 6. [h] The molecular parameters of the 1,2-PBD precursor used in entries 7−12 are M_n = 8.4 kg/mol, PDI = 1.03, and 1,2-content = 95%. [i] The molecular parameters of the PS-*b*-1,2-PBD copolymer precursor are M_n = 10.4 kg/mol, PDI = 1.04, M_{PS} = 8.0 kg/mol, $M_{1,2-PBD}$ = 2.4 kg/mol, and the 1,2-content of the PBD block >99%. [j] The molecular parameters for the PS homopolymer precursor are M_n = 19.9 kg/mol and PDI = 1.04. 1 equiv of $C_6F_{13}I$ and $^1/_2$ equiv of Et_3B relative to the PS repeat units were employed. [k] The molecular parameters of the 1,4-PBD precursor are M_n = 11.4 kg/mol, PDI = 1.03, and 1,4-content = 94%.

Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC-7 or Perkin-Elmer Pyris 1 instrument. Samples of 5−15 mg were annealed at 150 °C for 10 min, quenched to 0 or −50 °C, and heated at a rate of 10 °C/min. Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 instrument. Samples of 5−15 mg were heated at a rate of 10 °C/min, and nitrogen was used as purge gas. A manual contact angle goniometer (model 100-00, Ramé-hart) was used for the contact angle measurements. The polymer thin films were prepared by spin-casting a 5 wt % polymer solution onto fresh mica surfaces and annealing at 120 °C under vacuum prior to the measurements. The static contact angles were measured using a free drop of liquid (ca. 4 μL), and the contact angles were averaged over five measurements. Linear alkanes (C_nH_{2n+1}, n = 7, 8, 10, 12, 14, 16) were used as the testing liquids to determine the critical surface tensions of the fluorinated polymers.

Small-Angle X-ray Scattering (SAXS). Before the small-angle X-ray scattering (SAXS) measurements, the samples were sandwiched by two Teflon sheets and pressed in a 1 mm thick stainless steel mold under vacuum (<100 mTorr) at 120 °C for ca. 8 h. SAXS measurements were performed at the University of Minnesota on a home-built beamline. Cu K_α X-rays (λ = 1.542 Å) were generated by a Rigaku RU-200BVH rotating anode fitted with a 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 vs scattering wavevector $|\vec{q}| = q = 4\pi\lambda^{-1}\sin(\theta/2)$, where θ is the scattering angle.

Results and Discussion

In an effort to uncover a straightforward method for the preparation of highly fluorinated model polymers, we investigated the addition of perfluoroalkyl iodides (R_fI) to model polydienes under various initiation conditions. As shown in Figure 1, the addition is initiated as the iodine of R_fI is abstracted by a free radical. The perfluoroalkyl radical adds to a double bond, which is followed by transfer to another R_fI to complete the addition cycle.[24] We examined the addition of R_fI to model polydienes initiated by $Pd(PPh_3)_4$, 2,2′-azobis(isobutyronitrile) (AIBN), and Et_3B and found that Et_3B was the most effective initiator of the three. In this section, we report our detailed studies on the addition of R_fI to polybutadienes initiated by Et_3B.

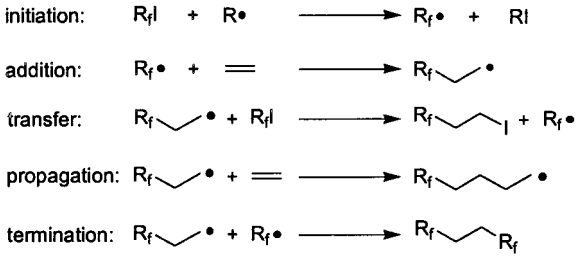

Figure 1. General mechanism of the free radical addition of perfluoroalkyl iodides to double bonds.

Addition of $C_6F_{13}I$ to PBD. When activated by oxygen, organoboranes can initiate free radical processes. As proposed by Brown and co-workers, the displacement of an alkyl radical from the organoborane by oxygen proceeds rapidly due to the strong boron−oxygen bond.[42] A model polybutadiene (M_n = 11.5 kg/mol, PDI = 1.03, 1,2-content = 68%, and 1,4-content = 32%) was used as the test substrate for this addition, and selected experimental results are listed in Table 1. We carried out the reaction at room temperature in hexanes under a slow air flow for 5 h (entry 1 in Table 1), and the polymer precipitated during the modification. A 4-fold excess of $C_6F_{13}I$ was employed to promote the transfer reaction over the propagation and to achieve complete conversion of the double bonds (Figure 1). The ^{1}H NMR spectrum of the product (entry 1 in Table 1) revealed that 94% of the double bonds were consumed.[43] We also tested the reaction in α,α,α-trifluorotoluene ($C_6H_5CF_3$, BTF)[40] and THF which can dissolve both the precursor and product (entries 2 and 3 in Table 1). The molecular weight distribution broadened after the modification in BTF, and the double-bond conversion was only 53% in THF. The reason for the broadening of the molecular weight distribution after the modification in BTF is not immediately apparent,

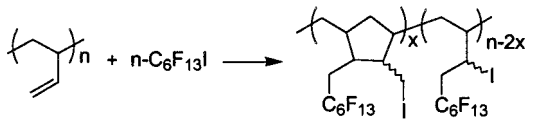

Figure 2. Proposed reaction scheme for the addition of $C_6F_{13}I$ to 1,2-PBD.

and we attribute the low double-bond consumption in THF to possible side reactions between the perfluoroalkyl radical and solvent since ethers are reactive in free radical processes.[44] To avoid the side reaction and ensure the homogeneity of the reaction mixture through the modification, we used a mixture of hexanes and CFC-113 as the solvent. The reaction proceeded in the mixed solvent (entry 4 in Table 1), and the polymer remained in solution after modification. Since Et_3B was used as the initiator, only a catalytic amount of Et_3B should be necessary for the reaction. In entry 5 of Table 1, 0.1 equiv of Et_3B was employed and 78% of the double bonds were consumed after 23 h, but the PDI of the product increased to 1.34.[45] As expected, we also successfully employed *n*-perfluorobutyl iodide (C_4F_9I) instead of $C_6F_{13}I$ in entry 6 of Table 1. Assuming that one R_fI reacted with one double bond, as illustrated in Figure 1, the calculated mass isolation yields were always around 50% (Table 1). This implies that a different reaction mechanism might be operating during the modification. Since 1,2- and 1,4-PBD repeat units might react differently with R_fI under the same conditions, the problem might be complicated by using the polybutadiene precursor with significant 1,2- and 1,4-contents. Therefore, we synthesized both 1,2- and 1,4-PBD and studied their reactions with R_fI separately.

Selected reactions of 1,2-PBD with $C_6F_{13}I$ are listed in Table 1 (entries 7−12). Two equivalents of $C_6F_{13}I$ and 1 equiv of Et_3B were employed (entry 7 in Table 1), and 96% of the olefinic sites in the 1,2-PBD were consumed after 24 h. When we decreased the amounts of $C_6F_{13}I$ and Et_3B, the reaction proceeded as well (entry 8 in Table 1). We conducted preliminary studies on the reaction kinetics. The double-bond conversion was already 95% in approximately 0.5 h when 1 equiv of $C_6F_{13}I$ and $^1/_2$ equiv of Et_3B were used (entry 9 in Table 1). When $^1/_2$ equiv of $C_6F_{13}I$ and $^1/_4$ equiv of Et_3B were used, the double-bond conversion reached a plateau after approximately 15 min (entry 10 in Table 1). When $^1/_4$ equiv of $C_6F_{13}I$ and $^1/_8$ equiv of Et_3B were employed, the reaction reached final conversion in approximately 0.5 h (entries 11 and 12 in Table 1). This preliminary kinetics study shows that this chemistry is expeditious.

When using only $^1/_2$ equiv of $C_6F_{13}I$ and $^1/_4$ equiv of Et_3B, approximately 74% of the double bonds were consumed after 15 min (entry 10 in Table 1). Assuming the simple open-chain addition mechanism shown in Figure 1, only 50% of the double bonds can be consumed using $^1/_2$ equiv of $C_6F_{13}I$. The anomalously high levels of double-bond consumption, low mass isolation yields, and related small molecule studies in the literature[46] lead us to propose that the reaction actually undergoes a cyclization pathway, and five-member ring structures are formed during the addition, as illustrated in Figure 2. Assuming the cyclization mechanism shown in Figure 2, we recalculated the mass isolation yields (Table 1), which range between 75% and 98%.

Distortionless enhancement by polarization transfer (DEPT) ^{13}C NMR spectroscopy was utilized to elucidate the molecular structure of the fluorinated 1,2-PBD (1,2-PBD:$C_6F_{13}I$), and representative spectra are shown in Figure 3. The observation of methylene (CH_2) peaks between 4 and 12 ppm, which correspond to an iodomethyl group, was consistent with the formation of five-member ring structures during the addition. We attributed the two peaks at 4−10 and 10−12 ppm to the cis- and trans-cyclized adducts, respectively, as suggested in related small molecule studies.[47] We also observed a broad methine (CH) peak at 36−46 ppm. Since both the iodomethylene carbon in the open-chain adduct and the methine carbons in the cyclized product appear at 40 ppm, we cannot quantify the extent of open-chain addition from the DEPT ^{13}C NMR spectra.

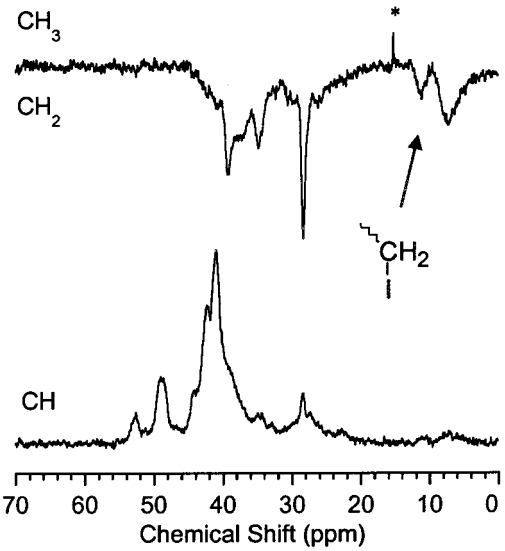

Figure 3. DEPT ^{13}C NMR spectra of 1,2-PBD:$C_6F_{13}I$. The lower spectrum contains only CH carbons, and the upper spectrum contains CH_3 carbons pointing up and CH_2 carbons pointing down. The peak labeled with an asterisk is from residual solvent.

The ^{19}F and ^1H NMR spectra of the 1,2-PBD:$C_6F_{13}I$ provide further information on this cyclization and are shown in Figure 4. In the ^{19}F NMR spectrum, we assigned the peak at −82 ppm to the trifluoromethyl group, the peak between −111 and −117 ppm to the difluoromethylene group connecting to the polymer backbone, and the peaks between −122 and −128 ppm to the remaining difluoromethylene groups in the perfluorohexyl group.[48] The ^{19}F NMR spectrum is consistent with the incorporation of perfluorohexyl groups into the 1,2-PBD. In the ^1H NMR spectrum we observed two small peaks between 4.8 and 5.8 ppm corresponding to the remaining unsaturation, a broad peak between 4.0 and 4.8 ppm corresponding to the iodomethylene protons in the open-chain adducts, a broad peak between 2.8 and 3.6 ppm corresponding to the iodomethyl protons in the cyclized adducts, and a very broad peak from 0.6 to 2.8 ppm corresponding to the remaining aliphatic protons. Since the iodomethyl peak overlaps with the broad aliphatic peak in the ^1H NMR spectrum of the 1,2-PBD:$C_6F_{13}I$, we can only estimate that 83% of the double bonds in the 1,2-PBD cyclized with their neighbors and 13% underwent open-chain addition. The proposed structure was also consistent with elemental analysis.[49] In irreversible random cyclizations between adjacent repeat units, Flory calculated that the maximum possible conversion is 86.5% because some unreacted repeat units become trapped after both of their neighbors have reacted.[50] Our estimated cyclization percentage agrees well with this prediction.

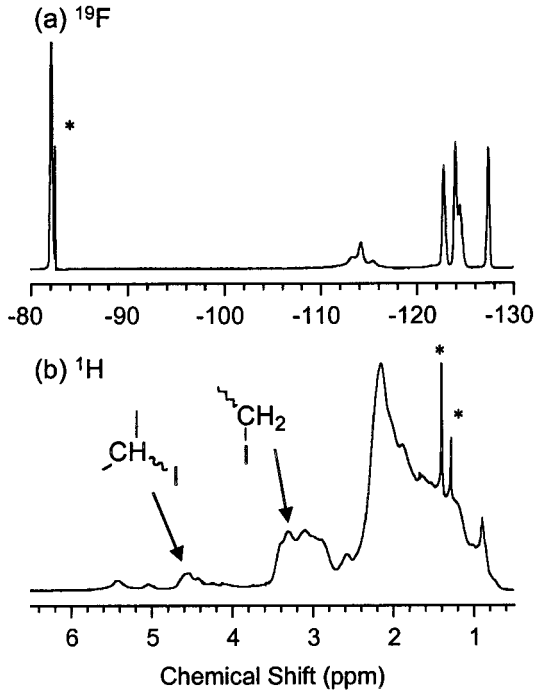

Figure 4. (a) ^{19}F and (b) ^{1}H NMR spectra of 1,2-PBD:$C_6F_{13}I$ (entry 7 in Table 1). The peaks labeled with asterisks are from solvent and impurities.

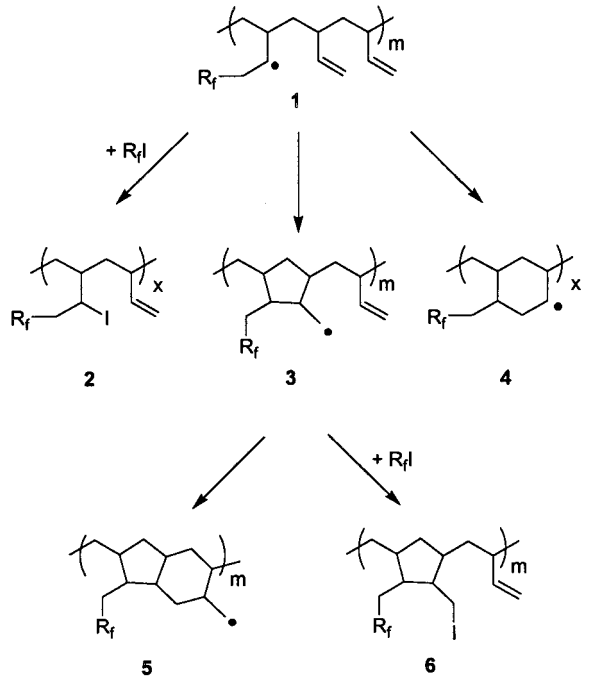

Figure 5. Possible reaction pathways for the addition of R_fI to 1,2-PBD.

As shown in Figure 5, the free radical (structure **1**) is formed by the addition of a perfluoroalkyl radical to the pendant double bond in a 1,2-PBD repeat unit from the terminal end or the abstraction of the iodine from an open-chain adduct. Instead of capturing the iodine from another R_fI to form structure **2**, the free radical (structure **1**) reacts more rapidly with its neighboring double bond three carbons away at the concentrations of R_fI employed. From the DEPT ^{13}C NMR spectra, we observed the iodomethyl peaks between 4 and 12 ppm, which implies that the five-member ring (structure **3**) is preferred over the six-member ring (structure **4**). Our proposed mechanism is consistent with the empirical rules summarized by Baldwin.[51] During free radical processes, the formation of the five-member ring structure is kinetically favored over the six-member ring formation even though the six-member ring structure is thermodynamically more stable.[52] After the cyclization, the free radical (structure **3**) is four carbons away from the neighboring double bond and therefore able to cyclize further to structure **5** according to the Baldwin rules. However, we suspect that the free radical (structure **3**) reacts more rapidly with R_fI to form structure **6** than its neighboring double bond four carbons away at the concentrations of R_fI employed. The conclusion of no significant cyclization to structure **5** is supported by the elemental analysis results of the 1,2-PBD:$C_6F_{13}I$, which agree with the proposed five-member ring structure.[49]

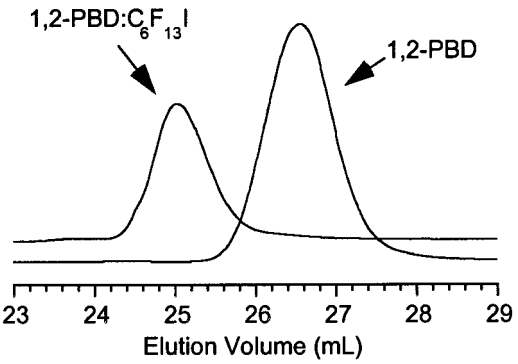

Figure 6. Representative SEC chromatograms of 1,2-PBD:$C_6F_{13}I$ (entry 7 in Table 1) and its precursor. The SEC trace of 1,2-PBD:$C_6F_{13}I$ was shifted vertically.

The five-member ring formation has also been documented in the addition of R_fI to small molecules, and our results are consistent with the studies by Brace and co-workers.[53] In a recent review, Brace summarized his work on the addition of R_fI to different α,ω-alkadienes.[46] Cyclization is the major reaction pathway for the addition of R_fI to 1,6-heptadiene, and a five-member ring structure was preferred over a six-member ring.[53] However, he only observed open-chain adducts for the addition of R_fI to 1,5-hexadiene and 1,7-octadiene. This implies that the free radicals attack R_fI more rapidly than the double bonds two or four carbons away at the experimental R_fI concentrations. This again supports the proposed mechanism of no significant further cyclization to structure **5** after the formation of the five-member ring.

Representative SEC traces of the polymers before and after the modification (entry 7 in Table 1) are shown in Figure 6. The narrow molecular weight distribution was preserved through the modification, which suggests that the chains were modified without significant coupling or scission. The apparent molecular weight of the 1,2-PBD:$C_6F_{13}I$ was determined to be 13.5 kg/mol, which was much smaller than the calculated M_n (45.8 kg/mol) based on the apparent molecular weight of the polymer precursor measured by SEC with PS calibration and reaction stoichiometry. With the incorporation of perfluoroalkyl groups, the solvent quality of THF for the modified polymer deteriorates, which results in an apparent molecular weight smaller than the actual molecular weight. This hypothesis is consistent with the observed solubilities of the polymers in THF before and after the modification. The 1,2-PBD is readily soluble in THF whereas the 1,2-PBD:$C_6F_{13}I$ is only soluble in

Table 2. Properties of Fluorinated Polymers and Their Precursors

sample	T_g (°C)	T_d (°C)[a]	θ (H_2O)[b]	γ_c (mN/m)
1,2-PBD	−20	451	70 ± 2	25[c]
1,2-PBD:$C_6F_{13}I$	55	271	116 ± 2	14.2 ± 1.2
PS-*b*−1,2-PBD	66	488	66 ± 2	32[c]
PS-*b*−1,2-PBD:$C_6F_{13}I$	58, 91	344	109 ± 1	14.7 ± 0.8
PS-*b*−1,2-PBD:$C_6F_{13}H$	55, 89	447	105 ± 1	15.4 ± 0.6

[a] Temperature at 5% weight loss. [b] Static water contact angles in degrees. [c] Literature values from: Lee, L. *J. Polym. Sci., Part A-2* **1967**, *5*, 1103.

THF at low concentrations (≤10 mg/mL). At higher concentrations (150 mg/mL), the THF/polymer mixture phase-separated. We also tested the solubilities of the 1,2-PBD:$C_6F_{13}I$ in a set of common solvents whose solubility parameters (δ) range from 14.9 $MPa^{1/2}$ (hexane and CFC-113) to 24.6 $MPa^{1/2}$ (dimethyl sulfoxide). At room temperature, the 1,2-PBD:$C_6F_{13}I$ is only soluble in fluorinated solvents, CFC-113 (δ = 14.9 $MPa^{1/2}$) BTF (δ = 17.0 $MPa^{1/2}$), and THF (δ = 19.4 $MPa^{1/2}$), at low concentrations.

We also demonstrated the selective fluorination of a PS-*b*-1,2-PBD copolymer under similar conditions (entry 13 in Table 1). 93% of the double bonds in the 1,2-PBD block were consumed, while little reaction with the PS block was observed. The narrow molecular weight distribution of the macromolecular precursor was preserved through the modification. The fluorinated PS-*b*-1,2-PBD (PS-*b*-1,2-PBD:$C_6F_{13}I$) copolymer is readily soluble in common organic solvents, including THF and chloroform. A PS homopolymer was used as the reaction substrate under the same reaction conditions (entry 14 in Table 1). The elemental analysis of the product yielded a fluorine composition of 4.95%. This corresponds to approximately 2 mol % of the PS repeat units substituted by perfluorohexyl groups, which agrees well with the estimate from the ^{19}F NMR spectrum. We suspect that perfluoroalkyl radicals attack the aromatic rings and undergo substitution reactions since similar reactions on small aromatic molecules, PS homopolymers, and copolymers have been reported in the literature.[54,55]

We conducted preliminary studies on the addition of $C_6F_{13}I$ to 1,4-PBD under similar conditions (entry 15 in Table 1). In contrast to 1,2-PBD, there are two carbons between adjacent double bonds in 1,4-PBD. Thus, it is possible that cyclization might not occur. Interestingly, the cyclization appears to be the major reaction pathway (Figure S1, Supporting Information), but this work is still in progress.

Removal of Iodine by Hydrogenolysis. The removal of the iodine is desirable to improve the thermal stability of these fluorinated materials (Table 2). We have focused on catalytic hydrogenation because the replacement of the iodine by hydrogen and saturation of the remaining double bonds can occur simultaneously. Palladium on calcium carbonate ($Pd/CaCO_3$) was employed, and potassium hydroxide (KOH) was added to neutralize the hydrogen iodide generated from the hydrogenolysis.[56] After the hydrogenolysis of the 1,2-PBD:$C_6F_{13}I$, the polymer became insoluble in all the solvents we tested at room and elevated temperatures. Thus, we were unable to isolate the material or characterize its properties. To ensure polymer solubility throughout the modification, we hydrogenated the PS-*b*-1,2-PBD:$C_6F_{13}I$ copolymer under similar conditions as the 1,2-PBD:$C_6F_{13}I$. After hydrogenation the block

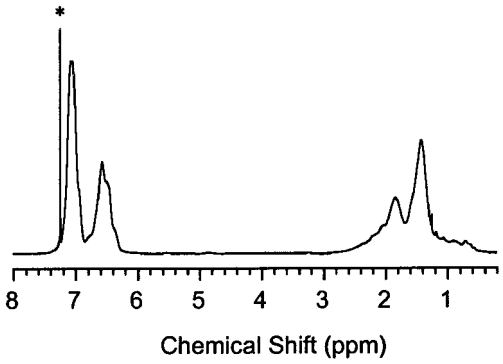

Figure 7. ^1H NMR spectrum of the PS-*b*-1,2-PBD:$C_6F_{13}H$ copolymer. The peak labeled with an asterisk is from solvent.

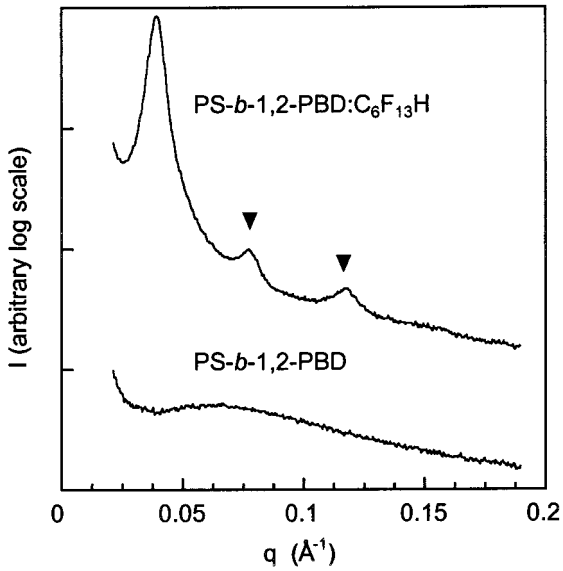

Figure 8. One-dimensional SAXS profiles at 120 °C of the PS-*b*-1,2-PBD copolymer precursor and PS-*b*-1,2-PBD:$C_6F_{13}H$ copolymer. The triangles correspond to the positions of integer multiples of q^*. The data for the PS-*b*-1,2-PBD:$C_6F_{13}H$ copolymer were shifted vertically.

polymer (PS-*b*-1,2-PBD:$C_6F_{13}H$) was still soluble in common organic solvents, including THF and chloroform. The C−I bonds and remaining unsaturation were completely removed as evidenced by the absence of resonances between 2.6 and 5.6 ppm in the ^1H NMR spectrum (Figure 7). Elemental analysis further confirmed the essentially complete replacement of the iodine by hydrogen. The iodine mass composition was 569 ppm after the reaction, which corresponds to an extent of hydrogenolysis of 99.7%.[57]

We did preliminary characterization on the block copolymer morphology. Figure 8 shows the SAXS scattering profiles obtained at 120 °C for the PS-*b*-1,2-PBD copolymer precursor and the PS-*b*-1,2-PBD:$C_6F_{13}H$ copolymer. Prior to fluorination, the PS-*b*-1,2-PBD copolymer precursor is in the disordered, liquid state. After fluorination and hydrogenolysis, several high-order reflections are clearly observed. The ratio of the peak positions to the principal peak is consistent with a lamellar morphology. This indicates a substantial increase in segregation strength upon fluorination, as expected.

Physical Characterization. We measured the glass transition temperatures (T_g) of the 1,2-PBD before and after the fluorination using DSC (Table 2). After the addition of $C_6F_{13}I$, the T_g increases from −20 to 55 °C

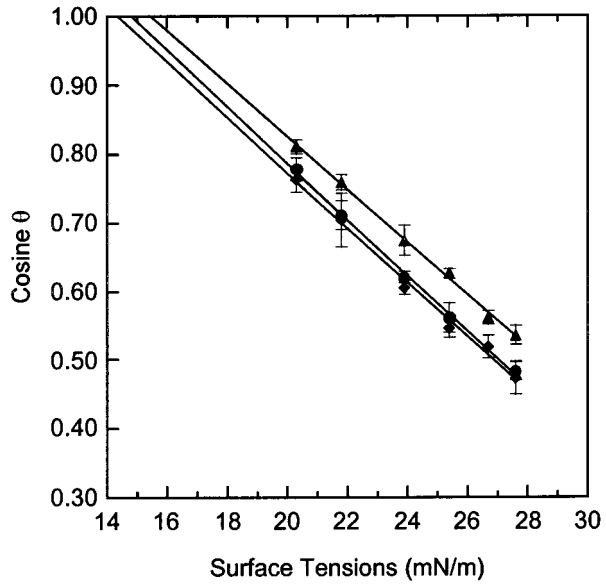

Figure 9. Zisman plots for the fluorinated polymers. The cosines of the average contact angles with various testing liquids on 1,2-PBD:$C_6F_{13}I$ (filled diamonds), PS-*b*-1,2-PBD:$C_6F_{13}I$ copolymer (filled circles), and PS-*b*-1,2-PBD:$C_6F_{13}H$ copolymer (filled triangles) are plotted against the surface tensions of the testing liquids. Linear alkanes (C_nH_{2n+1}, n = 7, 8, 10, 12, 14, 16) were used as the testing liquids.

for the 1,2-PBD:$C_6F_{13}I$. We also determined the T_g of the PS-*b*-1,2-PBD copolymer before the fluorination, after the fluorination, and after the hydrogenolysis. Before the fluorination, the PS-*b*-1,2-PBD copolymer only exhibits one glass transition at 66 °C in the DSC trace. This observation implies that the PS-*b*-1,2-PBD copolymer is disordered, which is consistent with the result from the SAXS experiment. After the fluorination, the PS-*b*-1,2-PBD:$C_6F_{13}I$ copolymer exhibits two glass transitions at 58 and 91 °C, which are assigned to the 1,2-PBD:$C_6F_{13}I$ and PS blocks, respectively. The observation of two glass transitions suggests that the PS-*b*-1,2-PBD:$C_6F_{13}I$ copolymer is phase-separated. After the hydrogenolysis, we again observed two glass transitions at 55 and 89 °C, which are attributed to the 1,2-PBD:$C_6F_{13}H$ and PS blocks, respectively. The observation of two glass transitions for the PS-*b*-1,2-PBD:$C_6F_{13}H$ copolymer is expected since the PS-*b*-1,2-PBD:$C_6F_{13}H$ copolymer exhibits a lamellar morphology, as revealed by the SAXS experiment.

We studied the thermal stabilities of the fluorinated PBD homopolymers and block copolymers using TGA (Table 2). Because of the weak C−I bonds, these adducts exhibit poor thermal stability. The polymer retained 95% of its original weight up to 271 °C for the 1,2-PBD:$C_6F_{13}I$ and 344 °C for the PS-*b*-1,2-PBD:$C_6F_{13}I$ copolymer. After the removal of iodine the thermal stability of the block polymer was significantly improved, and the decomposition temperature (T_d) of the block copolymer increased to 447 °C.

Thin films of these fluorinated materials prepared by spin-casting were annealed (120 °C, vacuum, overnight) for contact angle measurements. As an important measure of the surface properties, the static contact angles of deionized water on these polymer thin films are listed in Table 2. The critical surface tensions extrapolated from Zisman plots (Figure 9) are also included in Table 2.[58] Incorporation of $C_6F_{13}I$ into polybutadienes significantly increases the water contact angles and decreases the critical surface tensions for both the homopolymer and block copolymer. The critical surface tensions of these fluorinated materials are consistent with the results from the semifluorinated block copolymers studied by Ober and co-workers.[59] The PS-*b*-1,2-PBD:$C_6F_{13}I$ copolymer exhibits similar critical surface tension and water contact angle as the 1,2-PBD:$C_6F_{13}I$ since the fluorinated segments in the PS-*b*-1,2-PBD:$C_6F_{13}I$ copolymer are presumably enriched at the surface, as studied in detail by Ober and co-workers.[60] The critical surface tensions and water contact angles are similar for the fluorinated block copolymers before and after hydrogenolysis. All these fluorinated polymers exhibit critical surface tensions which are significantly lower than that of PTFE (19 mN/m), indicating that such polymers could be utilized in low surface energy applications.

Summary

We have developed a mild and convenient method to prepare highly fluorinated homopolymers and block copolymers utilizing the addition of R_fI to double bonds. We propose that cyclization is the major reaction pathway for the addition of R_fI to 1,2-PBD. The observation of iodomethyl groups in the DEPT ^{13}C NMR spectra of the 1,2-PBD:$C_6F_{13}I$ was consistent with the proposed mechanism. The free radical (structure **1** in Figure 5) reacts more rapidly with the neighboring double bond three carbons away, rather than abstracting the iodine from another R_fI at the experimental R_fI concentrations. Five-member rings (structure **3** in Figure 5) are kinetically favored over six-member rings (structure **4** in Figure 5). From the ^1H NMR spectrum we estimate that roughly 83% of the double bonds in the 1,2-PBD cyclize with their neighbors, which agrees well with the theoretical limit predicted by Flory for random irreversible cyclization between adjacent repeat units. The narrow molecular weight distribution of the macromolecular precursors was preserved through the modification. We also demonstrated the selective fluorination of the 1,2-PBD block in a PS-*b*-1,2-PBD copolymer. The C−I bonds in the PS-*b*-1,2-PBD:$C_6F_{13}I$ copolymer were completely transformed to C−H bonds by catalytic hydrogenation. The decomposition temperature (T_d) increases by about 100 °C after the hydrogenolysis. We determined water contact angles and critical surface tensions of the fluorinated materials. Incorporation of $C_6F_{13}I$ into polybutadienes significantly increases the static water contact angles and decreases the critical surface tensions for both the homopolymer and the block copolymer. All these fluorinated polymers exhibit very low critical surface tensions (14−16 mN/m) and could be of utility in low surface energy applications.

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Supporting Information Available: Experimental results and discussion on the addition of $C_6F_{13}I$ to 1,4-PBD. This

information is available free of charge via the Internet at http://pubs.acs.org.

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