Macromolecules **2004,** *37,* 6355−6361

Star Polymer Synthesis Using Hexafluoropropylene Oxide as an Efficient Multifunctional Coupling Agent

Karen A. Switek,[†] **Frank S. Bates,**[‡] **and Marc A. Hillmyer***[,†]

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455-0431, and Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455-0132

Received December 17, 2003; Revised Manuscript Received June 5, 2004

ABSTRACT: Well-defined polyisoprene three-armed star polymers (PI_3) were synthesized through a combination of living anionic polymerization and an efficient coupling process using hexafluoropropylene oxide (HFPO). Anionic polymerization of isoprene followed by termination with HFPO yielded three-armed stars with narrow molecular weight distributions. Under optimized conditions, at least 97% of the chains can be coupled. Molecular characterization of the star polymers (SEC, NMR and IR spectroscopy, and MALDI-TOF mass spectrometry) gave data consistent with the star structure and proposed mechanism of formation. The effects of HFPO concentration and the molecular weight of the arm precursors on the extent of star polymer formation were investigated. End-functionalized polyisoprene stars were also prepared and have potential application as trifunctional precursors to branched block copolymers.

Introduction

The incorporation of long-chain branches in polymers is a useful methodology for modifying physical properties and processing characteristics of these ubiquitous commodity materials.[1,2] Crystallinity, melting point, solution and melt viscosities, and mechanical and viscoelastic properties are all affected, and the structure−property relationships in branched polymers is a subject of continuing research. Because many types of branched polymers do not have well-defined, uniform branch patterns, fundamental correlation of property changes with specific branching architectures can be challenging.[1]

Star polymers have long captured the attention of polymer scientists since, with only one branch point, they constitute the simplest branched materials, and therefore are of the utmost importance for fundamental structure/property relationship studies.[3] However, the synthesis of well-defined star polymers of narrow molecular weight distribution and consistent architecture has not been straightforward. While Schaefgen and Flory[4] were the first to successfully synthesize star polymers in 1948, their use of condensation polymerization and problems with termination reactions led to broad molecular weight distributions and heterogeneous star structures. An important advance was made in 1962 when, taking advantage of living anionic polymerization, Morton et al.[5] were able to synthesize homogeneous model four-arm polystyrenes with polydispersities less than 1.1 using tetrachlorosilane as a linking agent. Since then, several other molecules have been used as linking agents for living polymer anions, including divinyl compounds, chloromethylbenzene derivatives, triazine compounds, and tin and phosphorus chlorides.[3]

While chlorosilane chemistry can be used to prepare very regular and monodisperse star polymers, an excess of the living polymer chains must be added to the chlorosilane compound in order to drive the reaction to completion since the reactivity of the chlorosilane moieties at the juncture decreases as each polymer chain is added.[3] Therefore, after the reaction, the products must be painstakingly separated to remove undesired products, including excess homopolymer and partially formed stars.[6] To combat this problem, divinyl coupling agents, such as divinyl benzene, are often employed. Unfortunately, it is difficult to control the amount of branching and the stars are inherently heterogeneous due to the statistical nature of the reaction.[3] Therefore, despite its limitations, the chlorosilane approach has remained the method of choice for producing well-defined star polymers.[6]

In this study, a simple, unique method for star polymer synthesis was investigated. Living anionic polyisoprene (PI^-) chains were terminated by addition of hexafluoropropylene oxide (HFPO). Through a series of fluoride ion (F^-) eliminations (creating carbonyl groups) and nucleophilic attacks by additional PI^- chains,[7] each molecule of HFPO coupled three chains, forming regular three-armed stars (PI_3). In contrast to chlorosilane systems, we propose that each polymer chain adds to the HFPO-functionalized juncture more readily than the previous chain. This eliminates the need for fractionation of the resultant polymer since unreacted homopolymer and two-chain coupling products are negligible under appropriate reaction conditions. We studied the effect of HFPO concentration on the extent of star polymer formation, as well as the molecular characteristics of the resultant stars. We also efficiently prepared end-functionalized star polymers that have potential utility in the synthesis of branched block copolymers.

Experimental Section

Materials. Isoprene (Aldrich) was twice distilled from *n*-butyllithium (Aldrich) under reduced pressure. Hexafluoro-

---

* To whom correspondence should be addressed (e-mail: hillmyer@chem.umn.edu).

[†] Department of Chemistry.

[‡] Department of Chemical Engineering and Materials Science.

10.1021/ma035936h CCC: $27.50

propylene oxide (HFPO) (Aldrich) was purified by passage through a column of KOH, followed by a column packed with CaH_2.[8] Cyclohexane and tetrahydrofuran (THF) were rigorously purified using a home-built column system, connected to a Schlenk manifold for anhydrous and anaerobic collection.[9,10] Tetrabutylammonium fluoride (TBAF) (Aldrich, 1.0 M in tetrahydrofuran), *sec*-butyllithium (Aldrich, 1.3 M in cyclohexane), and 1-*tert*-butyldimethylsiloxypropyllithium (FMC Lithium Corporation, 11 wt. % in cyclohexane) were used as received. The Gilman double-titration method was used to determine the concentration of *sec*-butyllithium and 1-*tert*-butyldimethylsiloxypropyllithium prior to use.[11]

Methods. Two different size exclusion chromatography (SEC) systems were used in this study. The molecular characteristics (M_n, M_w, and PDI) of the polymers were determined on a Hewlett-Packard series 1100 liquid chromatography system equipped with a Hewlett-Packard 1047A refractive index (RI) detector. The system was fitted with three Jordi polydivinylbenzene columns of 10^4, 10^3, and 500-Å pore sizes, calibrated with polystyrene standards (Polymer Laboratories). In addition, a second system, consisting of a Wyatt Optilab RI detector, a Wyatt Dawn multiangle light scattering detector, and three Phenogel (Phenomenex) columns of 10^5, 10^4, and 10^3-Å pore sizes, was used to determine the absolute molecular weight of the polymers in conjunction with a d*n*/d*c* value for PI in THF of 0.124 mL/g.[12] Tetrahydrofuran was used as the mobile phase (40 °C and 1 mL/min) for both instruments.

^1H NMR spectra of all samples were acquired on a Varian Inova 500 spectrometer at room temperature. ^{13}C and ^{19}F NMR spectral data were acquired on a Varian Inova 300 spectrometer at room temperature. Polymer samples were dissolved in $CDCl_3$ (~40 mg/mL) with hexafluorobenzene as an internal reference for ^{19}F NMR spectra.

Infrared (IR) spectra were obtained using a Nicolet Magna-IR 550 spectrophotometer equipped with Omnic 5.1 software. Polymer samples were pressed between two NaCl salt plates.

Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry data were acquired using a time-of-flight (TOF) detector on an Applied Biosystems QSTAR XL instrument equipped with a pulsed nitrogen laser MALDI source and an orthogonal acceleration reflectron-TOF mass analyzer. A dithranol matrix (20 mg/mL) and cationizing agent of silver trifluoroacetate (2 mg/mL) were used for polymer solutions in THF (10 mg/mL).

Star Polymer Synthesis. The procedure for the anionic polymerization of a typical hexafluoropropylene oxide-terminated polyisoprene (PI_3) sample is described. A 1-L, 5-necked reaction flask equipped with a magnetic stir bar, 4 Teflon bushings fitted with Viton O-rings, and a Y-connector with three ports (Ar/vacuum manifold, manometer, and septum) was evacuated (~10^{-3} mbar) and heated overnight (260 °C). Meanwhile, a solution of HFPO was prepared by passing the gas (4.7 g, 0.028 mol) through columns of KOH and CaH_2[8] and bubbling directly into cyclohexane (300 mL) in a two-necked flask equipped with a magnetic stir bar and attached to a manometer. This dilute HFPO solution was estimated to be ~0.1 M, based on the amount of HFPO collected; however, it was not determined how much of the gas was actually dissolved and how much resided in the headspace of the flask. After cooling the reaction flask to room temperature, a solvent flask containing cyclohexane (250 mL), a flask containing the HFPO solution, and a buret containing isoprene (10.6 g, 0.156 mol), were connected under positive Ar pressure. The apparatus was evacuated and backfilled with Ar (6x), setting the pressure to 2−3 psig. The cyclohexane was added to the flask, followed by *sec*-butyllithium (5.4 mL, 7.5×10^{-3} mol) through the septum. The isoprene was added, and the solution was stirred and heated slowly to 40 °C using a water bath. After 4 h, the reaction was cooled to room temperature, and the HFPO solution was added. The reaction was allowed to stir overnight, then was quenched by 20 mL of methanol. The product was precipitated into 2.5 L of a 1:1 mixture of methanol and 2-propanol. The colorless, viscous polymer was collected and dried under vacuum at room temperature for 24 h and 40 °C for 24 h. Yield = 8.5 g, 80%; SEC (THF, relative to PS standards): $M_n = 5.2$ kg/mol, PDI = 1.09; ^1H NMR ($CDCl_3$, 500 MHz): *resonances from PI repeat unit:* 5.1 (b, $-CH_2-C\mathbf{H}=C(CH_3)-CH_2-$), 4.7 (m, $-CH_2-C(H)-C(CH_3)=C\mathbf{H}_2$), 2.1 (b, $-C\mathbf{H}_2-CH=C(CH_3)-C\mathbf{H}_2-$ and $-CH_2-C(\mathbf{H})-C(CH_3)=CH_2$), 1.7 (m, $-CH_2-CH=C(C\mathbf{H}_3)-CH_2-$ and $-CH_2-C(H)-C(C\mathbf{H}_3)=CH_2$), and 1.4 ppm (m, $-C\mathbf{H}_2-C(H)-C(CH_3)=CH_2$), *resonances from initiator:* 1.2 (m, $-C\mathbf{H}_2-$) and 0.9 ppm (m, $-C\mathbf{H}_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): *resonances from PI repeat unit:* 148 ($-CH_2-C(H)-\mathbf{C}(CH_3)=CH_2$), 135 ($-CH_2-CH=\mathbf{C}(CH_3)-CH_2-$), 125 (cis $-CH_2-\mathbf{C}H=C(CH_3)-CH_2-$), 124 (trans $-CH_2-\mathbf{C}H=C(CH_3)-CH_2-$), 112 ($-CH_2-C(H)-C(CH_3)=\mathbf{C}H_2$), 48 ($-CH_2-\mathbf{C}(H)-C(CH_3)=CH_2$), 40 (trans $-CH_2-CH=C(CH_3)-\mathbf{C}H_2-$), 32 (cis $-CH_2-CH=C(CH_3)-\mathbf{C}H_2-$), 31 ($-\mathbf{C}H_2-C(H)-C(CH_3)=CH_2$), 27 ($-\mathbf{C}H_2-CH=C(CH_3)-CH_2-$), 23 (cis $-CH_2-CH=C(\mathbf{C}H_3)-CH_2-$), 19 ($-CH_2-C(H)-C(\mathbf{C}H_3)=CH_2$), and 16 ppm (trans $-CH_2-CH=C(\mathbf{C}H_3)-CH_2-$); ^{19}F NMR ($CDCl_3$, 282 MHz): −70 to −80 (m, $-C\mathbf{F}_3$) and −175 ppm (b, $-C\mathbf{F}(CF_3)-$); IR: *resonances from PI repeat unit:* 2961 (s), 2925 (s), 2854 (s), 2726 (m), 1664 (m), 1449 (s), 1376 (s), 1311 (b), 1187 (b), 1130 (b), 1092 (b), 1038 (b), 889 (m), 837 (m), and 742 cm^{-1} (b).

The functionalized polyisoprene $(TBDMSO-PI)_3$ star polymer was synthesized according to the method above with the exception of 1-*tert*-butyldimethylsiloxypropyllithium used as the initiator in place of *sec*-butyllithium. SEC (THF, relative to PS standards): $M_n = 7.6$ kg/mol, PDI = 1.21; ^1H NMR ($CDCl_3$, 500 MHz): *resonances from initiator:* 3.6 (t, $-Si(CH_3)_2-O-C\mathbf{H}_2-CH_2-$), 0.9 (s, $(C\mathbf{H}_3)_3C-$), and 0.1 ppm (s, $-Si(C\mathbf{H}_3)_2-$);^{13}C NMR ($CDCl_3$, 75 MHz): *resonances from initiator:* 63 ($-Si(CH_3)_2-O-\mathbf{C}H_2-CH_2-$), 26 ($(\mathbf{C}H_3)_3C-$), 18 ($(CH_3)_3\mathbf{C}-$), and −5 ppm ($-Si(\mathbf{C}H_3)_2-O-$); ^{19}F NMR ($CDCl_3$, 282 MHz): −71 (m, $-C\mathbf{F}_3$) and −175 ppm (b, $-C\mathbf{F}(CF_3)-$); IR: *resonances from initiator:* 1101 (m) and 775 cm^{-1} (b).

The $(TBDMSO-PI)_3$ star polymer (0.50 g, 2.9×10^{-4} mol end groups) was dissolved in THF (5 mL) and stirred vigorously with concentrated acetic acid (0.06 mL, 1.0×10^{-3} mol) and TBAF (1.0 mL, 1.0×10^{-3} mol) for 48 h to remove the TBDMS protecting group. After concentrating the solution by evaporation, the polymer was washed with H_2O (3x) to neutral pH, then dissolved in cyclohexane and again washed with H_2O (3x). After removal of most of the solvent by evaporation, the colorless, viscous polymer was collected and dried under vacuum at room temperature for 24 h and 40 °C for 24 h. Yield = 0.39 g, 80%; SEC (THF, relative to PS standards): $M_n =$ 7.0 kg/mol, PDI = 1.22; ^1H NMR ($CDCl_3$, 500 MHz): *resonances from initiator:* 3.6 ppm (t, $HO-C\mathbf{H}_2-CH_2-$);^{13}C NMR ($CDCl_3$, 75 MHz): *resonances from initiator:* 63 ppm ($HO-\mathbf{C}H_2-CH_2-$); ^{19}F NMR ($CDCl_3$, 282 MHz): −71 (m, $-C\mathbf{F}_3$) and −175 ppm (b, $-C\mathbf{F}(CF_3)-$).

Results and Discussion

Three-armed star polymers were synthesized using living anionic polymerization techniques. As shown in Scheme 1, isoprene was polymerized in cyclohexane at 40 °C using *sec*-butyllithium as the initiator. The coupling of living polyisoprene (PI^-) chains was accomplished by adding an excess of hexafluoropropylene oxide. The reaction was quenched with methanol, and the resultant polymer was isolated through precipitation in methanol/2-propanol followed by removal of the solvent. The resultant star polymers exhibited a peak in the size exclusion chromatograph (SEC) at a molecular weight, determined using a light scattering detector, of approximately three times that of their PI^- chain precursors (Table 1, Figure 1).[13] By adjusting the addition method and amount of HFPO added relative to the concentration of living polyisoprenyl anions (PI^-) in solution, relatively low molecular weight PI^- could be coupled very efficiently. We found that the most effective method for adding HFPO was to add a dilute cyclohexane solution of HFPO to the reaction. Using this technique, we were able to reduce the experimental

Scheme 1. Synthesis of Polyisoprene Star Polymer Using HFPO as a Multifunctional Coupling Agent

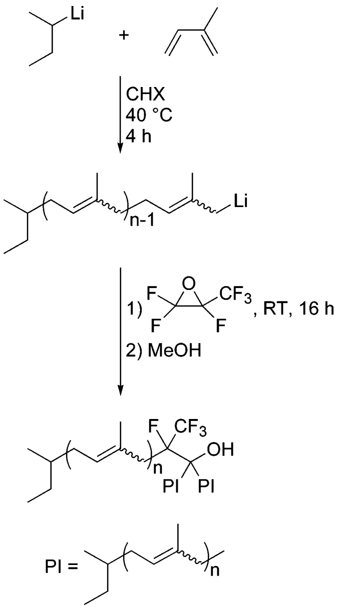


Table 1. Characterization of Polyisoprene Star Polymer Samples

entry	$[HFPO]_0/[PI^-]_0$	M_n (arm) (kg/mol)[a]	M_n (arm) (kg/mol)[b]	M_n (star) (kg/mol)[b]	*PDI*[b] arm/star	coupling efficiency (%)[c]
1	0.3	2.2	2.2	5.5	1.10/1.16	86
2	2	1.8	2.0	5.0	1.10/1.08	96
3	4	1.4	1.6	4.5	1.11/1.07	>97[d]
4	6	2.3	2.4	5.7	1.06/1.09	93
5	8	1.7	1.9	4.5	1.08/1.09	94
6	17	2.4	2.6	5.8	1.08/1.16	84

[a] Calculated from integrations of the appropriate ^{1}H NMR resonances. [b] Calculated using a d*n*/d*c* for PI in THF of 0.124 mL/g[12] from SEC light scattering data. [c] Percent of PI^- chains coupled, estimated from the relative intensities of the appropriate regions of the SEC trace.[14] [d] No low-molecular-weight shoulder was observed for Entry 3; however, because the two distributions overlap slightly (see Figure 1), the coupling efficiency is underestimated[14] and cannot be definitively quantified. We estimate that, at minimum, 97% of the chains coupled.

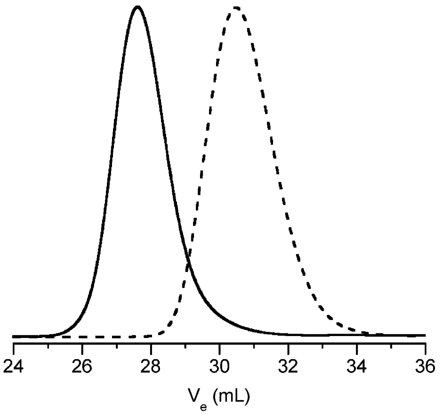
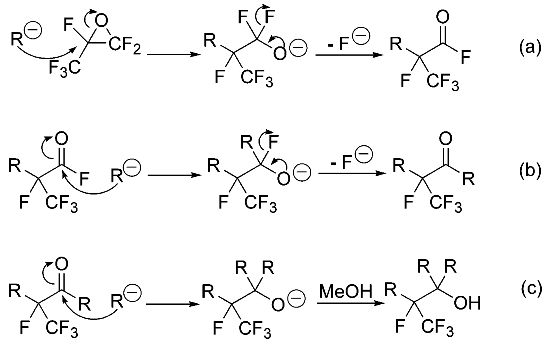


Figure 1. SEC traces of polyisoprene star polymer (solid line) and the respective uncoupled PI^- precursor (dashed line) (Table 1, Entry 3).

difficulties associated with handling the gas and more accurately measure the amount of HFPO added to the reaction. The ratio of initial HFPO concentration to initial PI^- concentration ($[HFPO]_0/[PI^-]_0$) was varied from 0.3 to 17 for low molecular weight polyisoprenes (Table 1). Based on the polydispersities of the resultant SEC peaks and estimation of the fraction of PI chains coupled to form the three-armed star polymer, we found the optimal $[HFPO]_0/[PI^-]_0$ ratio was between 2 and 4. Under these optimal reaction conditions, essentially all of the PI^- chains coupled into star polymers (PI_3), as evidenced by the lack of a peak or shoulder at higher elution volumes in the SEC trace of the final product (Figure 1).

Scheme 2. Proposed Mechanism



We propose the mechanism shown in Scheme 2 to explain the three-chain coupling observed. The first PI^- chain (R^-) attacks the substituted carbon of HFPO, opening the ring. Once the ring is opened, LiF is quickly eliminated, leaving the acid fluoride open for attack of a second PI^- chain. Again, a fluoride ion is eliminated, leaving a ketone, which can then be attacked by a third PI^- chain. After three chains have been added, there is no longer a fluorine atom available for elimination; the carbon adjacent to the oxygen is fully substituted. Therefore, only three PI^- chains will add to one HFPO molecule, and the final oxygen anion is protonated upon addition of methanol to form a hydroxyl group at the center of the star. This mechanism is supported by Watts' and Tarrant's observation of the same type of reaction with a series of low molecular weight alkyllithium reagents; they proposed the same mechanism, where R = Me, Et, *n*-Pr, *n*-Bu, and *n*-pentyl.[7] The reaction is also reminiscent of the carbonation work by Quirk and co-workers,[15,16] where two or three polymer chains were coupled by CO_2.

The essentially complete shift in molecular weight seen in the SEC traces (Figure 1) after addition of an excess of HFPO suggests that the rate-determining step in the coupling reaction is the initial ring-opening of the HFPO molecule, the first step (a) shown in Scheme 2. Once the first PI^- chain (R^-) attacks the HFPO molecule, rapid elimination of LiF ensues, and attack of the (b) second and (c) third PI^- chains follow. This mechanism can be simplified to three basic steps of adding the (a) first, (b) second, and (c) third PI^- chains, with rate constants k_1, k_2, and k_3, respectively. Consider two limiting cases: if k_1 is much less than k_2 and k_3, the great majority of the product would be three-armed PI stars as described above. Conversely, if the ring-opening of the HFPO molecule were fast relative to the subsequent coupling steps (i.e., $k_1 > k_2 > k_3$), an excess of HFPO could not couple three chains. Each PI^- chain would add an HFPO molecule in step (a), and become incapable of coupling. There would not be any free PI^- chains left available to couple with the PI^- chains that had added HFPO in steps (b) and (c). Similar to the chlorosilane coupling agents, to achieve star polymer formation, an excess of polymer would be required to drive the coupling reaction to completion. However, in

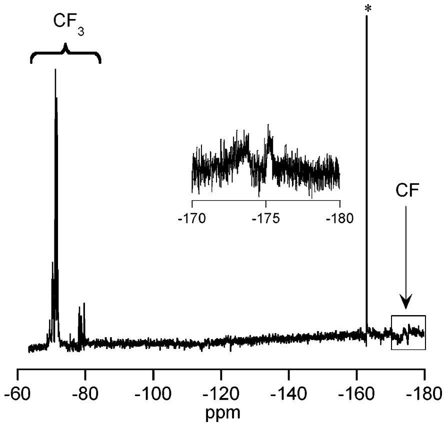


Figure 2. ^{19}F NMR spectrum of polyisoprene star polymer (Table 1, Entry 3) in $CDCl_3$ with standard C_6F_6 (marked *).

the case of excess HFPO, a fast ring-opening step would result in a product simply end-capped with HFPO and the significant shift of molecular weight in the SEC trace would not be seen.

To complement our SEC data, a basic kinetic modeling study was performed. Starting with our initial experimental conditions (reactant concentrations and reaction time), we were able to estimate the rate constants for the experiment by matching the final theoretical product distribution to that obtained from SEC traces. As proposed, we found k_1 much less than k_2 and k_3. The relative values of the three rate constants were particularly sensitive to the difference between k_1 and k_2, but generally $k_1 \ll k_2 \leq k_3$ with typical relative values on the order of approximately 1, 10^2-10^3, and 10^3-10^4, respectively. When these rate constants were applied to optimize experimental conditions, we found that for the best star polymer formation, the ideal ratio of HFPO to PI^- chains ($[HFPO]_0/[PI^-]_0$) was approximately equal to 2. This finding corresponded well with our experimental results of maximum coupling occurring in the range of $[HFPO]_0/[PI^-]_0 \approx 2-4$.

In addition to SEC, the polyisoprene star polymers were characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, IR spectroscopy, and MALDI-TOF mass spectrometry. The ^{1}H NMR spectra were used to calculate M_n of the star arms by end group analysis (Table 1). The typical ^{19}F NMR spectrum (Figure 2) displays the expected signals for the CF_3 and CF groups in the proposed star structure (Scheme 1) at −70 to −80 ppm and near −175 ppm, respectively. The region from −70 to −80 ppm was much more complex than expected; the extraneous peaks could possibly be attributed to many factors, including a statistical combination of arms with both 4,1- and 4,3-polyisoprene microstructures at the chain ends that might slightly affect the chemical shift of the fluorine atoms at the juncture or contamination by minor amounts of uncoupled or partially formed stars. We hoped to identify the hydroxyl group expected at the junction point of the star by spectroscopy, but no signals beyond those expected for polyisoprene were visible in the ^{13}C NMR and IR spectra; perhaps they were hidden by overlapping peaks or due to the low −OH concentration compared to isoprene repeat units.

However, MALDI analysis of the least-contaminated star polymer (Table 1, Entry 3) supports the proposed star structure and mechanism for formation. The mass spectrum (Figure 3) shows three regions of appreciable intensity, at approximately 1500, 3000, and 4000 *m/z*, corresponding to 1, 2, and 3 PI^- chains coupled. Although the relative intensities of the peaks across this broad molecular weight range are not reliable,[17] the corresponding masses provide valuable information. At the larger molecular weights, the peaks correspond to the molecular formula expected for the PI star polymer (i.e., $3(C_4H_9) + (C_5H_8)_n + C_3F_4OH + Ag$) as evidence of the central hydroxyl group, and match molecular weights calculated from SEC light scattering data (M_n = 4.5 kg/mol) and ^{1}H NMR spectroscopy ($M_n = 3(M_{n\,(arm)}) + M_{HFPO\,(core)}$ = 4.4 kg/mol). In support of the proposed mechanism, the peaks in the middle molecular weight range correspond to the two-chain ketone structure (i.e., $2(C_4H_9) + (C_5H_8)_n + C_3F_4O + Ag$). At the lower molecular weights, the peaks correspond to the molecular formula for single PI^- chains simply terminated by a proton (i.e., $C_4H_9 + (C_5H_8)_n + H + Ag$). The presence of single chains and two-armed coupled products in the mass spectrum, not observed by SEC, is attributed to either amplification of minor amounts of uncoupled or partially formed stars or fragmentation of star polymers to smaller species during the ionization process.[18]

Using the information obtained from the low-molecular-weight polymers, we extended this reaction to higher-molecular-weight polymers. At $[HFPO]_0/[PI^-]_0$ ratios between 2 and 4, the majority of PI^- chains (~90%) coupled into three-armed stars; however, complete coupling was never observed using arm molecular weights of approximately 20 kg/mol. Uncoupled chains were visible in the SEC trace (Figure 4) as a lower-molecular-weight peak or shoulder, and the peak corresponding to the coupled product was often broad, suggesting that a portion of the polymer product had

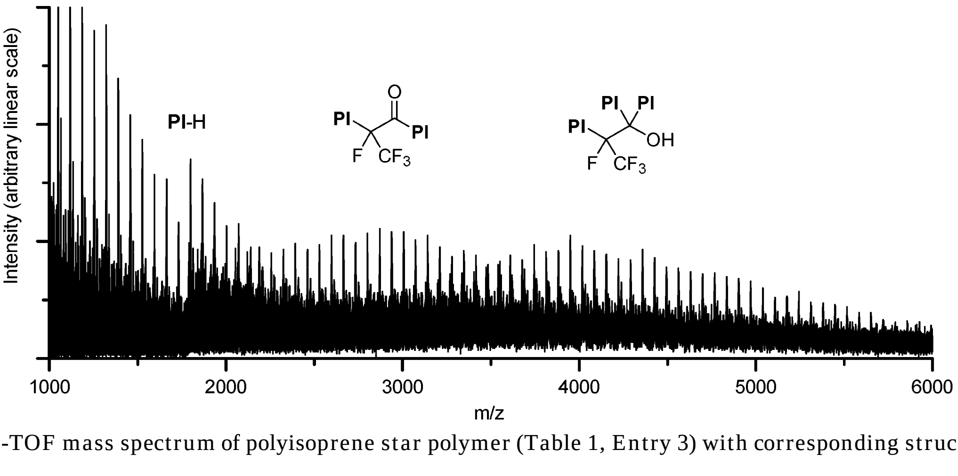


Figure 3. MALDI-TOF mass spectrum of polyisoprene star polymer (Table 1, Entry 3) with corresponding structural assignments.

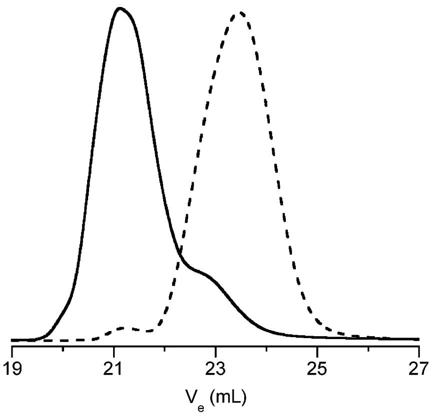
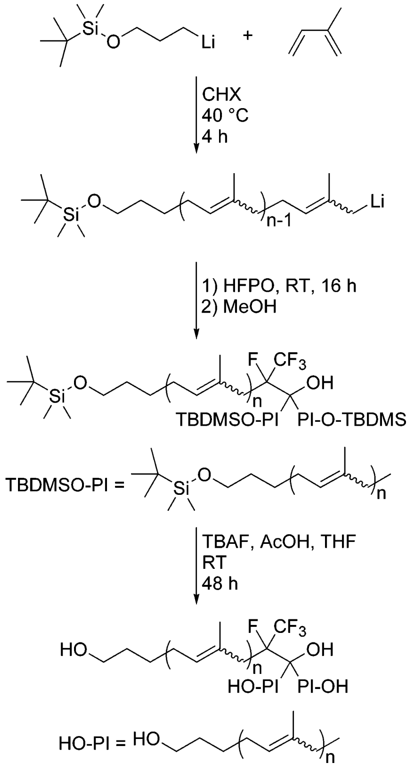


Figure 4. SEC traces of high-molecular-weight polyisoprene star polymer, $M_n = 33.7$ kg/mol, $PDI = 1.13$ (solid line); and the respective uncoupled PI^- precursor, $M_n = 21.6$ kg/mol, $PDI = 1.08$ (dashed line). Molecular weights were determined using light scattering detection.

Scheme 3. Synthesis of Hydroxyl-Functionalized Polyisoprene Star Polymer



only two chains coupled. After many attempts at 20 kg/mol arms, a smaller arm, 10 kg/mol, was tried, with similar results. We found that star polymers could be synthesized with high efficiency using this method up to an arm M_n of approximately 5 kg/mol for a total star molecular weight of 15 kg/mol. For larger molecular weights, we suspect that as the size of the polymer chains increases, steric constraints limit the ability of the third chain to efficiently reach the junction at the center of the molecule, leading to a slightly lower yield of the three-armed star. Therefore, while not quite as effective, this coupling reaction is still valuable for producing star polymers in good yield.

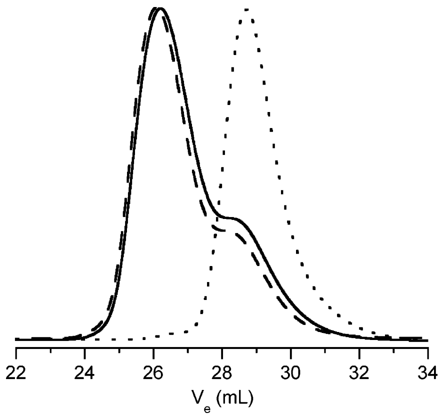


Figure 5. SEC traces of hydroxyl-functionalized polyisoprene star polymer, $M_n = 5.5$ kg/mol, $M_p = 7.1$ kg/mol, $PDI = 1.15$ (solid line); TBDMS-protected end-functionalized PI star polymer, $M_n = 5.2$ kg/mol, $M_p = 6.9$ kg/mol, $PDI = 1.17$ (dashed line); and the respective uncoupled $TBDMSO-PI^-$ precursor, $M_n = 2.5$ kg/mol, PDI = 1.08 (dotted line). Molecular weights were determined using light scattering detection.

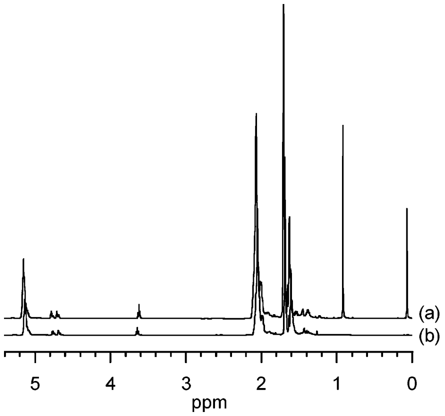


Figure 6. ^1H NMR spectra of (a) TBDMS-protected end-functionalized polyisoprene star polymer and (b) hydroxyl-functionalized PI star polymer in $CDCl_3$.

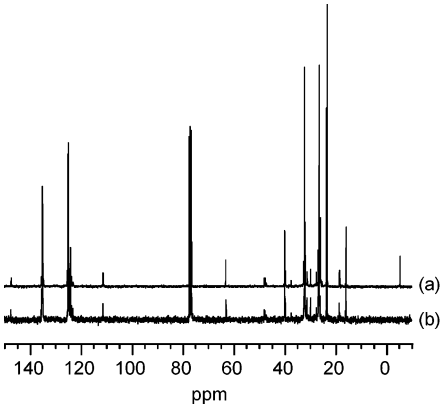


Figure 7. ^{13}C NMR spectra of (a) TBDMS-protected end-functionalized polyisoprene star polymer and (b) hydroxyl-functionalized PI star polymer in $CDCl_3$.

Taking advantage of the excellent efficiency of this reaction at lower molecular weights, we have been able to synthesize a star polymer with arms of 1.7 kg/mol, possessing hydroxyl functionality at the ends of the polymer arms. Using a protected initiator for the polymerization of isoprene and coupling the chains with HFPO, the protecting group was removed to liberate the three arm-end hydroxyl groups (Scheme 3). Polymers of similar triol structure and low molecular weight have been previously synthesized through more complex procedures, and are typically reacted with difunctional small molecules or relatively low-molecular-weight polymers to form higher-molecular-weight polymers.[19−22]

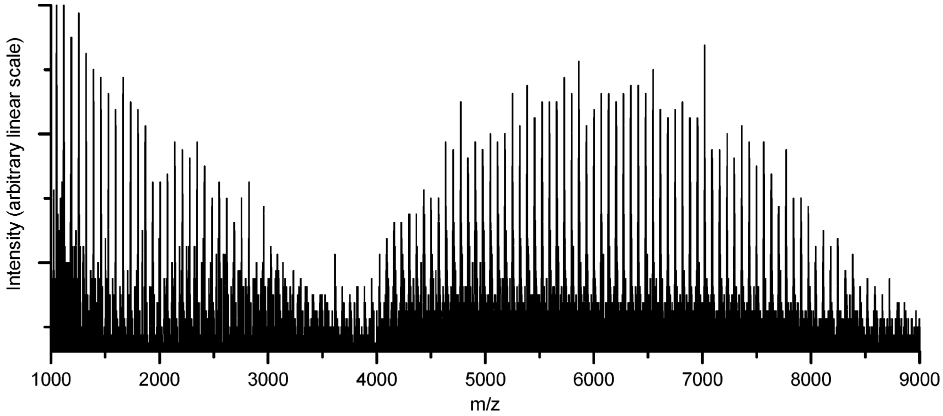


Figure 8. MALDI-TOF mass spectrum of hydroxyl-functionalized polyisoprene star polymer.

For example, diisocyanates have been used in combination with such trifunctional telechelic precursors to produce polyurethanes. In addition, these end-functionalized star polymers could be used as multifunctional macroinitiators for the polymerization of a second block to produce star block copolymers.[23,24] At these low molecular weights, amphiphilic star polymers would have great potential as branched block copolymer surfactants, and because of their unique properties as compared to their linear analogues,[25,26] very useful to study the effects of branching on the formation of vesicles, wormlike micelles, and more complex network morphologies in solution.[27]

The resultant trifunctional polyisoprene star polymer was characterized before and after removal of the *tert*-butyldimethylsilyl (TBDMS) protecting group by SEC, ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, IR spectroscopy, and MALDI mass spectrometry, with results similar to those for the PI_3 star polymer. Although only 80% coupling efficiency was achieved for this example,[28] the star polymer was successfully deprotected without degradation of molecular weight or the star structure (Figure 5).

The ^{19}F NMR spectra for both the TBDMS-protected and deprotected star polymers displayed the expected signals for the CF_3 and CF groups in the proposed star structure at -71 and -175 ppm, respectively, and were not complicated by extraneous peaks in the CF_3 region. The ^{1}H NMR spectra (Figure 6) were used to calculate M_n of the star arms (1.7 kg/mol) by end group analysis. Once the TBDMS groups were removed, the signal corresponding to the methylene protons adjacent to the hydroxyl end groups at 3.6 ppm shifted slightly downfield ($\sim$0.05 ppm), and the resonances corresponding to the TBDMS group at 0.9 and 0.05 ppm were absent. In the ^{13}C NMR spectra (Figure 7), the signal for the methylene carbon adjacent to the hydroxyl end groups was observed at 63 ppm. When deprotected, the signals at 26, 18, and -5 ppm corresponding to the TBDMS group were no longer observed.

While the majority of the IR spectrum resembles that of PI homopolymer, peaks at 1101 and 775 cm^{-1}, in the range expected for Si$-$O$-$C and Si$-$C stretches, respectively, were visible in the $(TBDMSO{-}PI)_3$ star polymer, but absent after deprotection, further supporting the complete removal of TBDMS protecting groups to yield exposed hydroxyl end groups. In addition, MALDI analysis of the hydroxyl-functionalized product supports the proposed star structure. The mass spectrum (Figure 8) shows only two major regions of intensity, at approximately 2000 and 6000 *m*/*z*, corresponding to PI$-$OH homopolymer and the three-armed star. Again, the relative intensities of the peaks across this broad molecular weight range are not reliable,[17] but the corresponding masses do support the molecular formula of the $(HO{-}PI)_3$ star structure (i.e., $3(C_3H_7O) + (C_5H_8)_n + C_3F_4OH + Ag$) at the highest *m*/*z* region. As observed for the PI_3 star polymer, the peaks at low molecular weights correspond to the molecular formula for single HO$-$PI chains simply terminated by a proton (i.e., $C_3H_7O + (C_5H_8)_n + H + Ag$). However, the mass spectrum, like the NMR and IR spectra, still indicates that the polymer was completely deprotected, and in combination with SEC data, provides strong evidence of the three-armed, end-functionalized star structure.

Conclusion

Three-armed star polymers of polyisoprene (PI_3) were efficiently synthesized through a combination of living anionic polymerization and coupling with hexafluoropropylene oxide (HFPO). Under optimal conditions, the polymers possessed narrow molecular weight distributions with little evidence of uncoupled chains by SEC. No fractionation or purification steps were required to achieve this result. Both the star structure and proposed mechanism of formation are supported by SEC, ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, IR spectroscopy, and MALDI-TOF mass spectrometry characterization of the star polymer product. We found that polyisoprene arm precursors of M_n up to 5 kg/mol could be coupled with very high efficiency at $[HFPO]_0/[PI^-]_0$ ratios of 2 to 4. In addition, polyisoprene stars end-functionalized with hydroxyl groups were prepared with arms of 1.7 kg/mol, suitable for potential application as trifunctional precursors to segmented multiblock copolymers and amphiphilic branched block copolymer surfactants.

Acknowledgment. This work was supported primarily by Medtronic, Inc. and in part by the MRSEC Program of the National Science Foundation under Award Number DMR-0212302. The authors thank Dr. Dana Reed for acquiring the MALDI-TOF data and for helpful discussions.

References and Notes

(1) Quirk, R. P.; Lee, Y.; Kim, J. In *Star and Hyperbranched Polymers*; Mishra, M. K.; Kobayashi, S., Eds.; Marcel Dekker: New York, 1999; Vol. 53, pp 1−25.

(2) Roovers, J. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Kroschwitz, J. I., Ed.; Wiley-Interscience: New York, 1985; Vol. 2, pp 478−499.

(3) Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 857−871.
(4) Schaefgen, J. R.; Flory, P. J. *J. Am. Chem. Soc.* **1948**, *70*, 2709−2718.
(5) Morton, M.; Helminiak, T. E.; Gadkary, S. D.; Bueche, F. *J. Polym. Sci.* **1962**, *57*, 471−482.
(6) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747−3792.
(7) Watts, R. O'B.; Tarrant, P. *J. Fluorine Chem.* **1975**, *6*, 481−490.
(8) Darling, T. R. U.S. Patent 4,356,291, 1982.
(9) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.
(10) Schmidt, S. C.; Hillmyer, M. A. *Macromolecules* **1999**, *32*, 4794−4801.
(11) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447−454.
(12) *Polymer Handbook*, 4th ed.; Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; Wiley: New York, 1999.
(13) The ratios of M_n (star) to M_n (arm) based on the data in Table 1 are somewhat less than the expected value of 3. However, for most samples, the coupling is not optimized and the low-molecular-weight shoulder in the SEC analysis contributes to a lower overall M_n (star). Under optimal conditions, the low polydispersity and the absence of a shoulder or asymmetric peak shape indicate that the product is comprised of predominantly one polymer species (e.g., Table 1, Entry 3 with M_n (star)/M_n (arm) = 2.8). Since the ratios are all well above 2 and three-armed star polymers have been observed by MALDI, we are confident in our assignment of the three-armed stars.
(14) The relative intensities of the main peak corresponding to PI_3 and the signal at the position of the PI^- precursor peak were compared to estimate the coupling efficiency.
(15) Quirk, R. P.; Chen, W.-C. *Makromol. Chem.* **1982**, *183*, 2071−2076.
(16) Quirk, R. P.; Yin, J.; Fetters, L. J. *Macromolecules* **1989**, *22*, 85−90.
(17) Nielen, M. W. F. *Mass Spectrom. Rev.* **1999**, *18*, 309−344.
(18) Feast, W. J.; Hamilton, L. M.; Rannard, S. *Polym. Bull.* **1997**, *39*, 347−352.
(19) Handlin, D. L., Jr.; Willis, C. L.; Goodwin, D. E.; St. Clair, D. J. Eur. Patent 0,632,075, 1995.
(20) Letchford, R. J.; Kamienski, C. W.; Schwindeman, J. A. U.S. Patent 5,919,870, 1999.
(21) Cuscurida, M. U.S. Patent 3,331,791, 1967.
(22) Weissmüller, M.; Burchard, W. *Polym. Int.* **1997**, *44*, 380−390.
(23) Pitsikalis, M.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. *Adv. Polym. Sci.* **1998**, *135*, 1−137.
(24) Charleux, B.; Faust, R. *Adv. Polym. Sci.* **1999**, *142*, 1−69.
(25) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31−71.
(26) Fukui, H.; Yoshihashi, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1996**, *29*, 1862−1866.
(27) Jain, S.; Bates, F. S. *Science* **2003**, *300*, 460−464.
(28) Due to experimental difficulties encountered when using the functionalized 1-*tert*-butyldimethylsiloxypropyllithium initiator, unrelated to the HFPO coupling reaction, only 80% coupling efficiency was observed for this sample. However, when using *sec*-butyllithium, our results were very reproducible and we consistently observed the three-armed star polymer in excellent yield under the reported optimal conditions.

MA035936H