Synthesis and Characterization of Triptych μ-ABC Star Triblock Copolymers

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ABSTRACT: We describe a general procedure for the synthesis of miktoarm star triblock copolymers with a hydrocarbon, a fluoropolymer, and a hydrophilic segment. Several μ-(polyethylethylene)(poly(ethylene oxide))(poly(perfluoropropylene oxide)) [μ-(PEE)(PEO)(PFPO)] star triblock copolymers were prepared using two successive anionic polymerization steps and one polymer−polymer coupling reaction. Initially, living polybutadienyllithium chains were end-capped with 2-methoxymethoxymethyloxirane forming a heterobifunctional 1,2-polybutadiene (PBD) precursor, with a hydroxyl group and a protected hydroxyl group at one chain end. Catalytic hydrogenation of this PBD gave the corresponding polyethylethyene (PEE) while preserving the end group structures. Transformation of the terminal hydroxyl group in the PEE precursor to a potassium alkoxide followed by addition of ethylene oxide and subsequent end-capping with ethyl bromide generated polyethylethylene−poly(ethylene oxide) (PEE−PEO) diblock copolymers with a protected hydroxyl group at the junction. Deprotection of the methoxymethyl group followed by coupling with acid chloride end-capped PFPO yielded well-defined μ-(PEE)(PEO)(PFPO) star triblock copolymers. Detailed molecular characterization of these products and their precursors confirmed the composition and architecture of these new star block copolymers. This modular strategy represents a new, straightforward, and versatile methodology for the preparation of mixed arm star block copolymers.

Introduction

Polymeric micelles formed in aqueous solution using amphiphilic block copolymers have been extensively studied for their potential and realized applications,[1,2] and the micellization behavior of two-component AB diblock and ABA triblock copolymers is quite well understood.[2,3] Spherical, cylindrical, vesicular, and more complex structures have been reported for these systems.[4−11] With only two components, control over the self-assembled structure is typically achieved by changing either the molecular weight or the composition of the material. Addition of a third component in ABC triblock copolymers provides another way to tune micelle structure and design even more intricate micelle morphologies (e.g., micelles with structured cores).[12−20]

Understanding the detailed relationship between the micellar and molecular structures (e.g., block components, composition, architecture) is central to the engineering of new micelle structures with potentially enhanced properties and functionality. Some examples of linear ABC triblock copolymer self-assembly in solution have been published. For example, Gohy et al.[13] reported the formation of core−shell−corona micelles with pH-responsive shells from a polystyrene−poly(2-vinylpyridine)−poly(ethylene oxide) (PS−P2VP−PEO) linear triblock copolymer in water.[14] Zhou et al.[16] reported a micellar shape transition and internal segregation induced by chemical modification of a linear ABC triblock copolymer. Core−corona spherical micelles were formed from a 1,2-polybutadiene (PBD)−PS−PEO linear triblock copolymer in dilute aqueous solution. Upon fluorination of the PBD block, the micelles formed were best described as core−shell−corona ellipsoidal disks. The internal segregation of the micelle core was attributed to the large segment−segment interaction parameter (χ) for the fluorinated-PBD/PS pair.[21] ABC linear triblock copolymers can also be manipulated to form micelle-like structures with compartmentalized coronas, as in so-called Janus micelles[18−20] and starlike micelles.[22]

In addition to molecular weight and composition, architectural changes in ABC block copolymers (e.g., ACB and BAC structures) can lead to different micelle morphologies.[23] One such structural variation in ABC block copolymers that has been receiving attention lately is the mixed arm (μ) ABC star architecture. Forcing three relatively incompatible blocks to meet at one junction point can produce interesting morphologies in the bulk state as documented by experiment[24−27] and simulation.[28−31] Fujimoto et al.[32] reported the synthesis of the first well-defined μ-ABC star triblock copolymers wherein a living anionic polymer chain of the first block was coupled with a macromonomer of a second block to generate an active site at the block junction. A third component is then grown from that site. A well-defined μ-(PS)(poly(dimethylsiloxane) [PDMS])(poly(*tert*-butyl methacrylate) [PtBMA]) was prepared using this methodology. Iatrou et al.[33] developed a second strategy consisting of successive coupling reactions between a multifunctional chlorosilane and various living anionic polymer chains. Using this multifunctional chlorosilane technique, μ-(PS)(polyisoprene [PI])(PBD), μ-(PS)(PI)(poly(methyl methacrylate) [PMMA]),[34] and μ-(PS)(PI)(PDMS)[35] star triblock copolymers have been prepared by this group. Other mixed arm ABC star block copolymers have been prepared using related strategies, some by combining more than one polymerization mechanism.[36−40]

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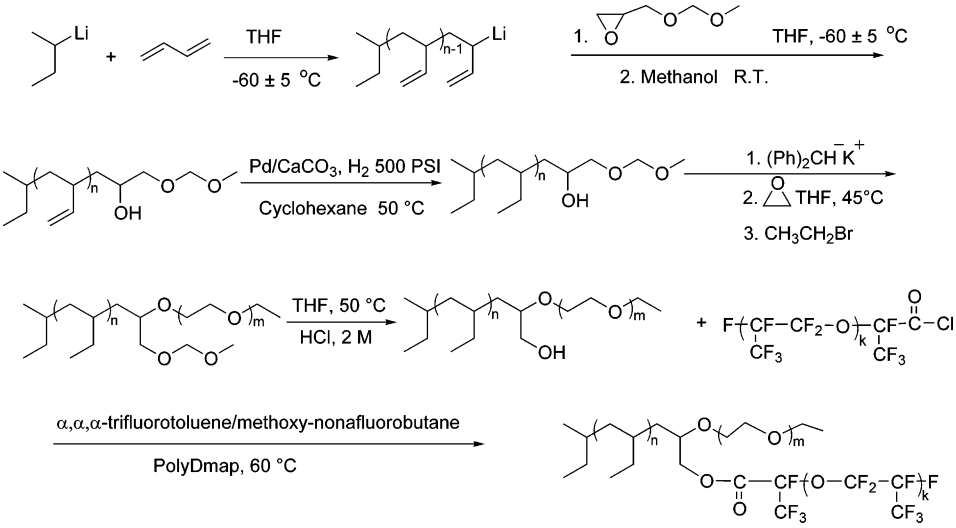
Scheme 1. Synthetic Route to μ-(PEE)(PEO)(PFPO) Star Triblock Copolymers



We have been interested in the synthesis and self-assembly of fluorinated block copolymers over the past several years.[16,21,41−45] In particular, we have shown that fluorinated ABC block copolymers can form interesting micellar structures provided the fluorinated block is incompatible with the nonhydrophilic component.[16] This is typically the case since most fluorinated polymers are immiscible with common hydrophobic polymers such as PS and PBD. Given the interesting bulk morphologies formed in μ-ABC and the high hydrophobicity and lipophobicity of fluorinated polymers, we were motivated to prepare μ-ABC star triblock copolymers in which one of the blocks is water-soluble, one is a hydrocarbon, and one is a fluorinated polymer. These kinds of molecules should exhibit significant "triple philicities". In fact, there have been very few reports on the solution phase behavior of μ-ABC materials,[37,46] and these would certainly be of interest in this regard.

In this paper, we describe the synthesis and molecular characterization of this kind of triptych surfactant,[16] where the fluorinated polymer, polymeric hydrocarbon, and water-soluble component are poly(perfluoropropylene oxide) (PFPO), polyethylethylene (PEE), and poly(ethylene oxide) (PEO), respectively. The general procedure consists of two successive anionic polymerization steps and a polymer−polymer coupling reaction (Scheme 1). Polybutadienyllithium is end-capped by 2-methoxymethoxymethyloxirane, resulting in the formation of a heterobifunctional PBD precursor. The corresponding polyethylethylene (PEE) was obtained by subsequent catalytic hydrogenation. This polymeric hydrocarbon contained one free hydroxyl group and one protected hydroxyl group at the same chain end. A mid-hydroxyl functionalized PEO−PEE diblock copolymer was then prepared by successive polymerization of ethylene oxide from the corresponding alkoxide macroinitiator, end-capping of the PEO chain, and deprotection of the protected alcohol located at the juncture of the PEO and PEE blocks. Mono-end-functionalized PFPO was then used to react with this hydroxyl group to form the well-defined μ-(PEE)(PEO)(PFPO) star triblock copolymers. This synthetic strategy represents a modular approach to μ-(PEE)(PEO)(PFPO) star block copolymers and can be generally applied to a variety of distinct μ-ABC materials.

Results and Discussion

Synthesis of 2-Methoxymethoxymethyloxirane (MMO). The functionalized end-capping molecule MMO was synthesized by reacting chloromethylmethyl ether with an excess of sodium oxiranylmethoxide (prepared by treating oxiranylmethanol with a large excess of NaH) in anhydrous THF.[47] After the reaction, only unreacted NaH, unreacted sodium oxiranylmethoxide, and MMO remained in the THF solution. MMO was concentrated by fractional distillation, and a dry and pure solution of MMO in THF was isolated (as confirmed by ^{1}H NMR spectroscopy). This anhydrous MMO solution was used directly for end-capping polybutadienyllithium.

Synthesis of Heterobifunctional PBD. Anionic polymerization of butadiene was initiated by *sec*-butyllithium in THF at low temperature. After complete consumption of the monomer, the polymerization was terminated using an excess of the MMO solution described above (Scheme 1). This procedure yielded PBD samples with narrow molecular weight distributions as determined by SEC (PDIs < 1.1). The number-average molecular weight, number-average functionality, and repeat unit microstructure were determined by ^{1}H NMR spectroscopy (Figure 1). Integration of the vinyl and vinylidene protons was consistent with approximately 90% 1,2 regiochemistry in the PBD backbone. Assuming exactly one initiator per chain, both the molecular weight and degree of functionalization by MMO were determined. Although an excess of MMO was used to terminate the living polybutadiene chain, only one MMO group was incorporated per chain.[48] For all MMO end-capped PBD samples the number-average functionalities were between 0.95 and 1.00 from ^{1}H NMR spectroscopic analysis. Furthermore, the protected hydroxyl group in MMO was not compromised during the termination reaction. These data are consistent with the well-established efficiency of oxirane and its derivatives as end-capping reagents in anionic polymerizations.[49,50] Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI−TOF MS) confirmed the structure for mono-MMO end-capped PBD as depicted in Scheme 1 (Figure S1). We did observe another set of peaks in the MALDI−TOF MS that were consistent with a low level of termination by chloromethylmethyl ether. This was undetected in the ^{1}H NMR spectrum of

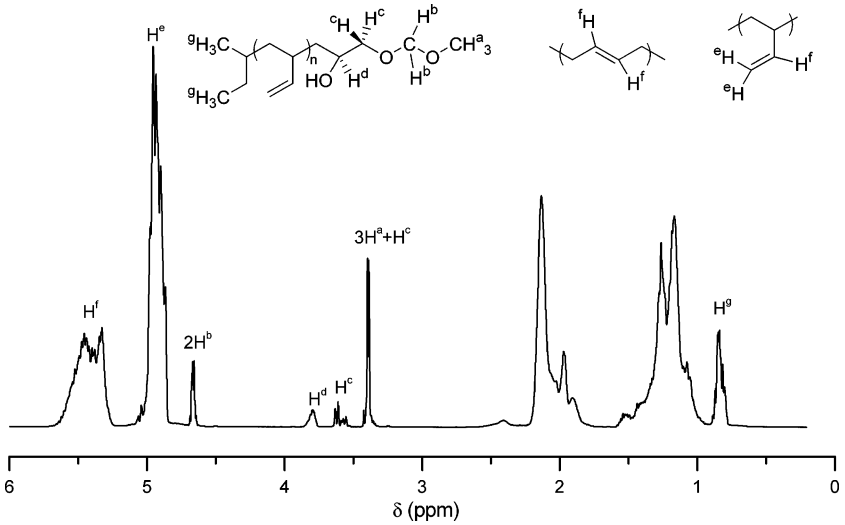


Figure 1. ^{1}H NMR spectrum of (PBD)(OH)($CH_2OCH_2OCH_3$) homopolymer precursor.

either the purified THF solution of MMO or the MMO end-capped PBD. The presence of a small amount of this impurity did not interfere with our synthetic route to the target μ-ABC star block copolymer.

While we determined that mono-MMO terminated PBD was effectively prepared, there are two regioisomeric forms of the MMO moiety that are potentially present. In reactions with substituted oxirane derivatives, the addition of propagating anionic polymer chains exhibits high levels of regioselectivity, e.g., termination of polystyryllithium with propylene oxide resulted in 97% of addition at the least substituted ring carbon.[49] In addition, given the chirality of the ultimate butadiene unit upon 1,2 addition and the chirality of the MMO, various diastereomers can result. Analysis of the ^{1}H NMR spectrum suggests that the predominant structure stems from attack of the PBD anion at the unsubstituted carbon in the ethylene oxide ring of MMO, as supported from ^{1}H NMR structural analysis (Figure 1 and Figure S2). However, we cannot definitively rule out the presence of species resulting from attack at the monosubstituted carbon. The complexity of ^{1}H NMR spectra of the subsequent diblock and μ-ABC triblocks suggests that the regioselectivity of the MMO end-capping is good though not perfect.

Hydrogenation of the MMO End-Capped PBD. Since the pendant double bonds in PBD are susceptible to spurious free radical cross-linking, we explored the hydrogenation of the MMO functionalized PBD. Heterogeneous hydrogenation of the functional PBD gave the corresponding polyethylethylene (PEE), as confirmed by ^{1}H NMR spectroscopy, while retaining a narrow molecular weight distribution (PDIs < 1.1 in all cases by SEC). The retention of the MMO end group on the PEE was confirmed by ^{1}H NMR spectroscopy (Figure S3) and MALDI−TOF MS (Figure 2). The number-average functionality in the MMO end-capped PEE samples was quantitatively consistent with the values found for the MMO end-capped PBD samples.

Synthesis of Mid-Functional PEE−PEO Diblock Copolymers. Transformation of the free hydroxyl group in MMO end functionalized PEE materials to the corresponding potassium alkoxide was accomplished by titration with diphenylmethylpotassium in THF (Scheme 1).[51] In all cases, the calculated number of moles of hydroxyl end group from mass of the sample, degree of functionalization, and molecular weight information

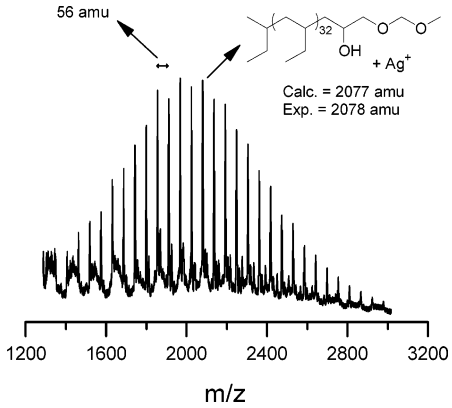


Figure 2. MALDI−TOF spectrum of heterobifunctionalized (PEE)(OH)($CH_2OCH_2OCH_3$) homopolymer precursor (see Experimental Section for details).

from the above analysis were confirmed by the number of moles of diphenylmethylpotassium needed for complete titration. This corroborates both the ^{1}H NMR and MALDI−TOF MS data described above. After titration, ethylene oxide was added as a liquid at room temperature, and the reaction solution was stirred at 45 °C for 24 h to ensure complete conversion.[50] The PEO alkoxide end group was terminated by addition of a 10-fold molar excess of ethyl bromide after additional diphenylmethylpotassium solution was added to convert any possibly dormant hydroxyl groups into the corresponding potassium alkoxides.

In all ^{1}H NMR spectra of the mid-functional PEE−PEO diblock copolymer precursors, two characteristic resonances from the methoxymethyl protecting group were observed. Resonances at $\delta = 4.6$ ppm and $\delta = 3.3$ ppm correspond to the protons of $-O-CH_2-O-$ and $-O-CH_3$ in the protecting group, respectively. Under the conditions of the ethylene oxide polymerization the hydroxyl protecting group appeared to remain intact. The molar ratio of methylene protons ($-O-CH_2-O-$) in the protecting group and all the protons from the PEE blocks was consistent with predicted values to within 10% (based on the known molecular weights of the PEE precursors). These data are consistent with no significant loss of the methylmethoxy protecting group during the polymerization of ethylene oxide and subsequent end-capping. The methoxymethyl protecting group for the mid-hydroxyl group is rather robust to strongly basic

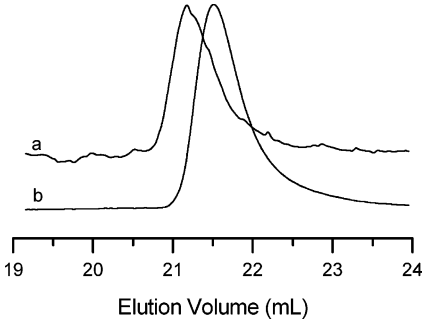


Figure 3. SEC traces of PEE−PEO(2−13) diblock copolymer precursor labeled by 1-naphthnyl isocyanate: (a) fluorescence detection; (b) RI detection. The shift in elution volume is due to the serial connection of the detectors.

conditions. In fact, this protecting group has been shown to be stable in the presence of excess potassium *tert*-butyl oxide at 60 °C for 20 h in a relevant small molecule study.[52] This combination of two successive living anionic polymerizations followed by deprotection of the methoxymethyl protecting group, which was accomplished by a treatment of PEE−PEO precursor with HCl in THF,[53] gave mid-hydroxyl functional diblock copolymers with narrow molecular weight distributions by SEC (PDI < 1.15 in most cases).

To confirm the presence of an active hydroxyl group at the junction of the PEE and PEO blocks, we treated the deprotected diblock with 1-naphthnyl isocyanate, a hydroxyl reactive fluorescent label. SEC analysis of the product using a fluorescence detector showed that the polymeric fraction contained the fluorescent label and gave a peak shape that was nearly identical to the refractive index detector response (Figure 3). These data confirm the presence of a hydroxyl group in the PEE−PEO diblock copolymers.[54] In addition, we treated the deprotected PEE−PEO diblock copolymer with trifluoroacetic anhydride and analyzed the product by ^{1}H NMR spectroscopy. The methylene protons alpha to the hydroxyl group were observed as multiple resonances centered around 4.3 ppm. As mentioned above, the multiplicity associated with these resonances is presumably due to the two-diastereotopic protons alpha to a chiral carbon. Assuming exactly two protons for the envelope of peaks centered around 4.3 ppm (i.e., one −OH group per chain), we calculated molecular weights for the PEE that were consistent with predicted values based on the PBD precursor to within 10%.

Synthesis of μ-(PEE)(PEO)(PFPO). The preparation of μ-(PEE)(PEO)(PFPO) [μ-EOF] star triblock copolymers was accomplished by reacting the mid-hydroxyl functionalized PEE−PEO diblock copolymer precursors with mono acid chloride end-capped poly(perfluoropropylene oxide) (PFPO−COCl) homopolymer (Scheme 1). The PFPO−COCl was prepared by converting the commercially available mono carboxylic acid end-capped PFPO homopolymer (PFPO−COOH) to the corresponding acid chloride using oxalyl chloride following a similar procedure established by Yazdi and Beckman.[55] The ^{19}F NMR spectrum of PFPO prepared in this way was in excellent agreement with the published data of Karis et al.[56] On the basis of ^{19}F NMR spectra, the degree of polymerization of PFPO−COCl was calculated.

Because of the dramatically different solubility characteristics between the mid-hydroxyl functional PEE−PEO precursors and PFPO, identification of an appropriate solvent for the coupling was difficult. In fact, no reaction (as determined by SEC) was observed using conventional solvents wherein the PEE−PEO/PFPO−COCl formed heterogeneous mixtures. After testing of several different solvent pairs, we determined that a mixture of α,α,α-trifluorotoluene, methoxynonafluorobutane, PEE−PEO, and PFPO−COCl formed a homogeneous solution at mild temperature. In this work, the coupling reaction was performed at 60 °C employing a large excess of PFPO−COCl. The products were carefully purified to remove the excess unreacted PFPO−COCl (see Experimental Section).

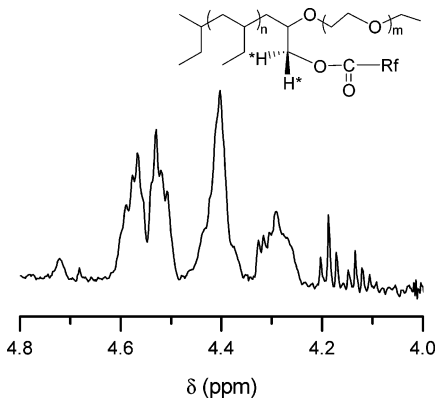


Figure 4. ^{1}H NMR spectra of μ-EOF(2−7−2) (Table 1). The resonances shown are for the protons labeled with an asterisk.

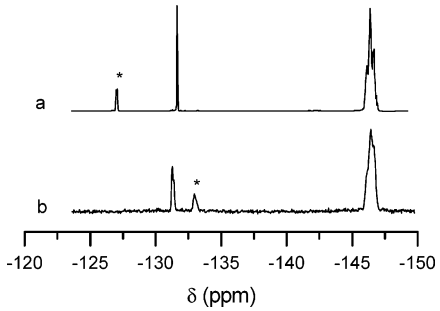


Figure 5. ^{19}F NMR spectra of (a) PFPO−COCl and (b) μ-EOF(2−7−2) star triblock copolymer. The resonance marked with a * denotes the F adjacent to the carbonyl group in the poly(perfluoropropylene oxide) segment.

Analysis of the reaction products by ^{1}H and ^{19}F NMR spectroscopy provided evidence for the suggested coupling reaction. Upon reaction of the acid chloride in PFPO−COCl with the hydroxyl group in PEE−PEO the methylene protons alpha to this hydroxyl group were observed as a multiple set of peaks centered around 4.5 ppm (as in the case for the reaction with trifluoroacetic anhydride). A representative ^{1}H NMR spectrum of μ-EOF product is shown in Figure 4. Although the detailed multiplicity was not fully resolved, the integration of this set of resonances gave a consistent molecular weight for the PEE block using the known PBD homopolymer precursor molecular weight, assuming that the total integration was for two protons. The ^{19}F NMR spectra of the same μ-EOF product and the PFPO−COCl precursor are shown in Figure 5. The resonance associated with the characteristic F adjacent to the carbonyl group of the acid chloride in PFPO−COCl shifted from $\delta = -127$ ppm to $\delta = -133$ ppm upon conversion to the ester, resulting from reaction of the hydroxyl group in PEE−PEO with PFPO−COCl.

The molecular weight distributions of the μ-EOF star triblock copolymers were analyzed by SEC under identi-

Table 1. Molecular Parameters of μ-EOF Star Triblock Copolymers

sample ID[a]	N_{PEE}[b]	N_{PEO}[b]	N_{PFPO}[c]	f_{PEE}[d]	f_{PEO}[d]	f_{PFPO}[d]	M_n[e] (kg/mol)	M_n[f] (kg/mol)	PDI μ-EOF[f]
μ-EOF(2−6−2)	31	128	14	0.26	0.59	0.15	10.1	8.3	1.32
μ-EOF(2−7−2)	31	148	14	0.24	0.62	0.14	10.9	12.0	1.06
μ-EOF(2−9−2)	31	197	14	0.19	0.69	0.12	13.1	11.9	1.10
μ-EOF(2−9−3)	31	197	20	0.19	0.66	0.15	14.0	9.8	1.27
μ-EOF(2−9−5)	31	197	31	0.17	0.61	0.22	15.9	11.4	1.24
μ-EOF(2−13−2)	31	285	14	0.15	0.76	0.09	17.0	14.3	1.11
μ-EOF(2−13−3)	31	285	20	0.14	0.74	0.12	17.9	16.6	1.08

[a] The numbers after the sample name correspond to the molecular weight of PEE, PEO, and PFPO blocks, respectively, in kg/mol. The molecular weights were calculated using NMR spectroscopy. [b] Calculated using ^{1}H NMR spectroscopy. [c] Calculated using ^{19}F NMR spectroscopy. [d] The volume fractions were calculated using the molecular weight and the RT densities of ρ(PEE) = 0.815 g/cm^3,[57] ρ(PEO) = 1.12 g/cm^3 (amorphous),[58] and ρ(PFPO) = 1.9 g/cm^3.[59] [e] The total molecular weight of each triblock copolymer was calculated from the NMR spectra. [f] The PDI was determined by SEC using PS standards and THF as solvent at 40 °C.

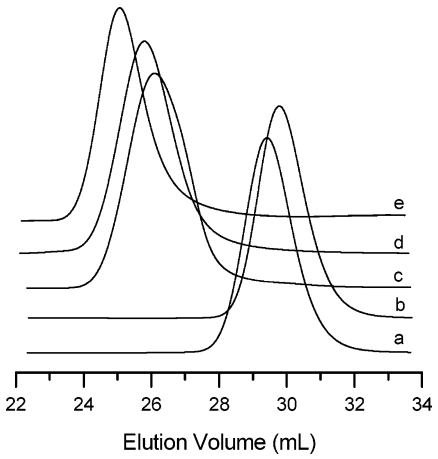


Figure 6. SEC traces of polymer at different synthesis stages: (a) (PBD)(OH)($CH_2OCH_2OCH_3$) precursor; (b) (PEE)(OH)($CH_2OCH_2OCH_3$) precursor; (c) protecting PEE-PEO(2−7) diblock copolymer; (d) deprotected PEE-PEO(2−7) diblock copolymer; (e) μ-EOF(2−7−2) star triblock copolymer.

cal conditions as those for all the PBD, PEE, and PEE−PEO precursors. Representative SEC traces for the MMO terminated PBD, the MMO terminated PEE, the protected and deprotected mid-functional PEE-PEO precursors, and the final μ-EOF star block copolymer are shown in Figure 6. All the μ-EOF star triblock copolymers showed relatively narrow molecular weight distributions (PDIs ≤ 1.3), indicating insignificant chain degradation or cross-linking during the coupling reaction. Characterization data for seven μ-EOF star block copolymers are given in Table 1. The degree of polymerizations for the PEE, PEO, and PFPO were all determined by end group analyses as described above. The volume fractions of the respective blocks were calculated using reported amorphous densities for the three blocks at RT, and the molecular weight distributions were obtained by SEC using THF as the eluent and PS standards (Table 1). To confirm the compositions of these materials, we examined the μ-EOF samples by elemental analysis. The theoretical compositions could be calculated for each product using the molecular weight data from NMR spectroscopy. In general, the calculated values agreed well with the experimentally determined C, H, O, and F compositions (Table S1). Taken together, the characterization data strongly support the formation of a new set of μ-ABC star block copolymers containing three blocks that are both mutually and strongly incompatible.

Summary

We have described the preparation and detailed molecular characterization of a set of well-defined μ-(polyethylethylene)(poly(ethylene oxide))(poly(perfluoropropylene oxide)) (μ-EOF) star triblock copolymers. The synthetic protocol combined two living anionic polymerization steps and one efficient polymer−polymer coupling reaction. This combination gave the obtained miktoarm star triblock copolymers with well-defined structure and composition. Seven μ-EOF star triblock copolymers were prepared with a range of molecular weights and component volume fractions. Preliminary results show that these materials exhibit interesting self-assembly characteristics both in the melt state and in aqueous solutions.[60]

Experimental Section

General Methods. Size exclusion chromatography (SEC) was performed on a Hewlett-Packard series 1100 liquid chromatography system equipped with a Hewlett-Packard 1047A refractive index (RI) detector and three Jordi poly(divinylbenzene) columns of 10^4, 10^3, and 500 Å pore sizes, calibrated with polystyrene standards (Polymer Laboratories). THF was used as the mobile phase (40 °C and 1 mL/min). The SEC analysis with fluorescence detection was performed on a Waters 150C ALC/GPC equipped with three Phenomenex Phenogel columns (5 mm bead size), an internal refractive index detector, and a Hitachi F1050 external fluorescence detector. The fluorescence detector excitation and emission wavelengths were 227 and 348 nm, respectively.[61] THF was used as the mobile phase (ambient temperature and 1 mL/min). ^{1}H NMR spectra were recorded on a Varian Inova 500 MHz spectrometer at room temperature. All samples were dissolved in $CDCl_3$. ^{19}F NMR spectra were recorded on a Varian Inova 300 MHz spectrometer at room temperature. PFPO was dissolved in Freon-113. The μ-EOF star triblock copolymers were dissolved in a mixture of $CDCl_3$ and Freon-113 (ca. 40% v/v). Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI−TOF MS) data were acquired on a Bruker Reflex III instrument equipped with a 337 nm nitrogen laser, a delayed extraction Scout ion source, a high-resolution multichannel plate (MCP) detector in the reflector mode, and a 2 GHz digitizer. Dithranol (20 mg/mL) and silver trifluoroacetate (2 mg/mL) were used as the matrix and cationizing agent for polymer solutions in THF (10 mg/mL). The volume of matrix solution, silver trifluoroacetate solution, and polymer solution are 10, 2, and 10 μL, respectively. Elemental analysis was performed by Atlantic Microlab (Georgia), and the experimental error was within 0.3%. All the analyses were duplicated, and the averaged results were used.

Materials. All commercial solvents and chemicals were used as received with the following exceptions. Tetrahydrofuran (THF) as a reaction solvent was rigorously purified by passing through a supported copper catalyst.[62,63] (±)Oxiranylmethanol (Aldrich, 96%) was distilled under reduced pressure before use. Butadiene (Aldrich, 99.8%) was sequentially vacuum distilled from dibutylmagnesium and *n*-butyllithium after stirring in a sealed flask for 4 h at 0 °C on each. Ethylene oxide (Aldrich, 99.5%) was vacuum-distilled from *n*-butyl-

lithium after stirring in a sealed flask at 0 °C for 1 h. The concentration of *sec*-butyllithium (Aldrich) was determined by the Gilman double titration method.[64] Mono carboxylic acid end-capped poly(perfluoropropylene oxide) (PFPO−COOH) was provided by Dupont. α,α,α-Trifluorotoluene (Aldrich) and methoxynonafluorobutane (HFE-7100, 3M) were stirred on CaH_2 for 2 days before distillation and stored on 3 Å molecular sieves (Fisher).

Synthesis of 2-Methoxymethoxymethyloxirane ($C_5H_{10}O_3$). 12.8 g (0.46 mol) of sodium hydride (NaH) powder (Aldrich, 95%) was added to a 500 mL round-bottom flask equipped with a mechanical stir bar under an argon atmosphere. 300 mL of anhydrous THF was added to the flask under an argon purge. The NaH slurry was stirred in an ice/water bath for 1 h. 16.1 g (0.217 mol) of freshly distilled (±)oxiranylmethanol was dissolved in 80 mL of anhydrous THF and added to the NaH/THF slurry slowly under an argon purge. After the evolution of H_2 ceased, the slurry mixture was stirred at 0 °C for 1 h. 12.0 mL (0.154 mol) of chloromethylmethyl ether (Aldrich) was then added into the flask dropwise via a syringe. After 1 h of stirring at 0 °C, most of the THF and unreacted chloromethylmethyl ether (~300 mL) were condensed into a buret under reduced pressure at liquid nitrogen temperature. All remaining liquid was then condensed into a second buret. The unreacted NaH and sodium oxiranylmethoxide were quenched with 2-propanol followed by water. 9.8 g (0.083 mol) of 2-methoxymethoxymethyloxirane was obtained in 54% yield from ^{1}H NMR spectroscopy.

Synthesis of Heterobifunctional PBD Homopolymer Precursor. A typical polymerization procedure is briefly described below. A more detailed description of the equipment and general procedures can be found elsewhere.[50] The polymerizations were performed in a 2 L round-bottom glass reactor fitted with five ACE-THREADS connectors and containing a glass-coated magnetic stir bar. The reactor was evacuated to 30 mTorr and baked at ca. 270 °C overnight. After cooling to room temperature, the pressure in the system was kept constant and positive under an argon purge (20 Torr) via a mercury bubbler. Purified THF (500 mL) was added, and the reactor was cooled to −60 ± 5 °C with a dry ice/2-propanol bath. *sec*-Butyllithium (0.0426 mol) was injected, causing the reaction mixture to become yellow immediately. After 15 min, purified butadiene (1.5 mol) was added to the reactor and the solution became peach color within a few seconds. The reaction solution was stirred for 5 h at −60 ± 5 °C, after which the 2-methoxymethoxymethyloxirane solution (0.083 mol) was added. The reaction mixture became colorless within 30 s. The reaction solution was stirred for 2 h and slowly warmed to room temperature before adding degassed methanol.

The crude product solution was concentrated on a rotary evaporator and redissolved in 1.5 L of cyclohexane. The solution was washed with DI water eight times to remove salt. The solution was concentrated on a rotary evaporator again, and the resulting viscous product was dissolved into 300 mL of THF and precipitated into methanol to obtain purified PBD. The product was dried under vacuum for 2 days at room temperature and 3 days at 50 °C.

Hydrogenation of PBD Homopolymer Precursor. Hydrogenations were performed in cyclohexane in a 1 L high-pressure stainless steel reactor equipped with a Teflon-coated stir bar and heating band.[65] The PBD homopolymer solution with a concentration of 20 g/L was purged with argon for 1 h before hydrogenation. Pd on calcium carbonate (5% Strem) was used as the catalyst in an amount ~2 mass equivalents of the PBD precursor. The catalyst was first heated to 120 °C under vacuum for 2 h in the reactor and then reduced at 120 °C under 100 psi of H_2 for 2 h. The reactor was evacuated and cooled below 30 °C before the PBD solution was added. The reaction was performed under 500 psi of H_2 at 50 °C for 24 h. Upon completion, the reactor was cooled to room temperature, and the catalyst was removed by filtration. The polymer solution was then concentrated on a rotary evaporator, and the recovered PEE homopolymer precursor was dried in a vacuum to constant weight prior to subsequent polymerization of ethylene oxide.

Synthesis of Mid-Hydroxyl Functional PEE−PEO Diblock Copolymer. The polymerization of ethylene oxide was performed using a similar setup as the polymerization of butadiene. The completely dried PEE homopolymer precursor was dissolved in THF. The initiator, a dark red diphenylmethylpotassium solution, was freshly prepared by the reaction of potassium naphthalenide with diphenylmethane in THF and allowed to stir overnight.[51]

The PEE/THF solution (500 mL) with concentration ranging from 5×10^{-3} to 1×10^{-2} mol/L was added to the reactor and titrated slowly with the diphenylmethylpotassium solution until a light pink color persisted for 20 min at room temperature. The disappearance of the red color immediately upon addition of diphenylmethylpotassium solution indicated a fast initiation. The cold ethylene oxide monomer was added in to the reactor at room temperature, and the solution was then heated to 45 °C and stirred for 24 h. An additional 10 mL of diphenylmethylpotassium solution was injected into the reaction mixture, and a pink color persisted before the termination with ethyl bromide. A white salt (KBr) was observed upon addition of ethyl bromide. The cloudy solution was stirred at 45 °C for 2 h before cooled to room temperature. An aliquot of the solution was taken for characterization by SEC and ^{1}H NMR. The remaining solution was deprotected using a reported method for small molecules.[53] Immediately after termination, the reaction solution was treated with 200 mL of concentrated HCl acid (37%) in the reactor, and the resulting colorless and viscous solution was stirred at 50 °C for 24 h. The mixture was concentrated on a rotary evaporator, and the solution was extracted with 1 L of chloroform. The water layer was washed with 150 mL of chloroform three times. The combined chloroform solution was washed with saturated sodium bicarbonate solution two times and DI water five times. The organic layer was collected and concentrated on a rotary evaporator to attain a slightly yellow solid. The product was first purified by flash column chromatography to remove the initiator and traces of unreacted PEE homopolymer precursor.

Two methods were applied to confirm the presence of the hydroxyl group in the deprotected PEE−PEO diblock copolymer precursors. In the first, 0.10 g (ca. 6.8×10^{-3}−1.3×10^{-2} mmol) of deprotected PEE−PEO diblock copolymer precursors and 0.10 g (5.9×10^{-1} mmol) of 1-naphthyl isocyanate (Aldrich, 98%) were dissolved in 15 mL of anhydrous THF and stirred at room temperature for 12 h. The resultant solution was then diluted to ca. 1 mg/mL for SEC with refractive index (RI) and fluorescence (FL) detections. In the second method, 0.5 mL of trifluoroacetic anhydride was mixed with a solution of 30 mg of deprotected PEE−PEO diblock copolymer precursor in 0.75 mL of $CDCl_3$ 30 min before observation by ^{1}H NMR spectroscopy.

Synthesis of PFPO−COCl. 50.0 g of PFPO−COOH and a glass-coated stir bar were added to a 250 mL round-bottom flask with a Teflon valve inlet and a 24/40 glass outer joint. The flask was then evacuated to 30 mTorr for 4 h at room temperature before the addition of 60 mL of methoxynonafluorobutane and 25.0 g of oxalyl chloride (Aldrich) under an argon purge. The reaction mixture was connected to a reflux condenser capped with a silicon oil bubbler and stirred at 60 °C under a slow argon purge for 12 h. After cooling to room temperature, the solution was concentrated on a rotary evaporator, and the resultant viscous yellow liquid was dried in a vacuum to constant weight and stored in a desiccator.

Synthesis of μ-(PEE)(PEO)(PFPO) Triblock Copolymers. A typical coupling reaction between mid-hydroxyl functionalized PEE−PEO diblock and PFPO−COCl is described briefly as follows. 4.2 g (0.548 mmol) of PEE-PEO(2−7) diblock copolymer precursor, 13.8 g (5.52 mmol) of PFPO−COCl, and 1.2 g of polyDMAP were added to a 250 mL round-bottom flask equipped with a glass-coated stir bar, a 24/40 glass outer joint, and an inlet with a Teflon valve, which was connected to a vacuum/argon manifold. The mixture was evacuated to 30 mTorr for 4 h before adding 100 mL of α,α,α-trifluorotoluene and 60 mL of methoxynonafluorobutane under an argon purge. The reaction mixture was connected to a reflux condenser capped with a silicon oil bubbler and stirred at 60

°C for 24 h under a slow flow of argon. After cooling to room temperature, some product and unreacted PFPO−COCl precipitated. 200 mL of THF was added to the flask to help dissolve the products. The insoluble polyDMAP was removed by filtration. The resulting cloudy solution was concentrated on a rotary evaporator, yielding a mixture of white solid and viscous polymers, which were presumably the desired μ-EOF star triblock copolymer and unreacted PFPO−COCl. The product was dissolved in 500 mL of THF to form a ~1 wt % dilute solution. Most of the unreacted PFPO−COCl was removed by successively centrifuging the cloudy solution, utilizing the insolubility and high density of PFPO in THF, and the remainder was removed by washing the μ-EOF triblock copolymer THF solution with PF-5060 (C_6F_{14}, 3M) five times to result in a clear solution. The product was dried in a vacuum to constant weight after removal of the THF.

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Supporting Information Available: MALDI−TOF spectrum of a PBD homopolymer precursor, 2D ^{1}H NMR spectrum of a PBD homopolymer precursor, ^{1}H NMR spectrum of a PEE homopolymer precursor, and elemental analysis results for the μ-EOF star triblock copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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