Synthesis and Characterization of Model Polyalkane−Poly(ethylene oxide) Block Copolymers

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ABSTRACT: We describe the preparation of a new set of amphiphilic block copolymers with well-defined molecular weights and block volume fractions. The synthesis of a variety of polyalkane−poly(ethylene oxide) block copolymers was accomplished by a new polymerization−hydrogenation sequence. Initially, anionic polymerization of either butadiene or isoprene was performed followed by end capping with ethylene oxide. The resulting hydroxyl-terminated polydienes were catalytically hydrogenated to give the corresponding hydroxyl-terminated polyalkanes. These polymeric alcohols were then titrated with potassium naphthalenide to yield the analogous potassium alkoxides. This type of macroinitiator was employed in the polymerization of ethylene oxide. Seventeen polyalkane−poly(ethylene oxide) block copolymers were prepared in near quantitative yields with molecular weights ranging from (1.4 to 8.7) $\times$ 10^3 and poly(ethylene oxide) volume fractions ranging from 0.29 to 0.73. These polymers are model materials for block copolymer phase behavior studies.

Introduction

Fundamental studies on AB block copolymer thermodynamics rely on the preparation of monodispersed materials with well-defined molecular weights (MWs) and block volume fractions (f_a = volume fraction of A block).[1] This is typically accomplished through a living polymerization technique by sequential monomer addition. Due to the absence of chain transfer and chain termination, living polymerizations allow for precise definition of MW and f_a. The most widely used technique for the preparation of model block copolymers is living anionic polymerization. However, cationic, ring-opening metathesis,[2] group transfer, and radical[3] polymerizations have all been used for the purpose of producing block copolymers with novel pairs of polymeric segments.[4] One limitation of the sequential monomer addition technique is that both of the monomers must be compatible with the chosen polymerization mechanism. Side reactions such as termination and chain transfer must be avoided in the polymerization of both monomers, and the chosen monomers must both be reactive enough to undergo propagation. These requirements limit the number of possible block combinations for a given polymerization mechanism, and the synthesis of new materials that cannot be obtained by a single polymerization mechanism necessitates a different approach.

A two-step process can also be employed for the preparation of block copolymers. In this type of polymerization the first block is polymerized by a living technique, and the propagating center is modified such that the living polymerization of the second monomer can be accomplished without complication. An example of this is the attenuation of the polystryl anion reactivity by the addition of 1,1-diphenylethylene followed by polymerization of methyl methacrylate.[5] Without this modification of the active species, side reactions between the polystyryl anion and the methyl methacrylate will occur. This type of approach can also be extended to the preparation of block copolymers where the reactive end group of the first block is modified such that it can be subsequently transformed into a macroinitiator for the second. Each of the blocks can then be prepared by completely different mechanisms. An example of this was demonstrated by Risse and Grubbs with the ring-opening metathesis polymerization of norbornene and end capping with terephthaldehyde, followed by the aldol group transfer polymerization of a vinyl silyl ether.[6] The resultant polymer was hydrolyzed to give a polynorbornene−poly(vinyl alcohol) block copolymer with a narrow molecular weight distribution. A block copolymer with this particular structure cannot be obtained by a single polymerization mechanism. This type of "change of mechanism" polymerization can be very useful for the preparation of block copolymers that contain highly incompatible blocks such as amphiphilic block copolymers.

Over the past decade we have been studying the thermodynamics and dynamics of a variety of block copolymer systems.[7] All of the materials employed in these studies have been synthesized by anionic polymerization using both sequential monomer addition and active center modification techniques.[8] Of central importance is the determination of block copolymer "phase diagrams." A block copolymer phase diagram establishes the equilibrium morphology as a function of both temperature and block volume fraction. The mapping of a block copolymer phase diagram typically requires the synthesis of a relatively large number (10−20) of discrete block copolymers varying in both molecular weight and block volume fraction, and thus the synthetic techniques must be both precise and easily utilized.[9] In a series of block copolymer systems studied and prepared by Bates and co-workers, it became evident that the complexity of the general block copolymer phase diagram near the order−disorder transition (ODT), the transition at which the system melts into an isotropic state, increased as the overall molecular weight of the block copolymer system decreased.[7] This feature was the driving force for investigating block copolymers with molecular weights that approached the monomeric limit. Low-molecular-weight block copolymers will allow the investigation of self-assembly in the intermediate regime between high-molecular weight

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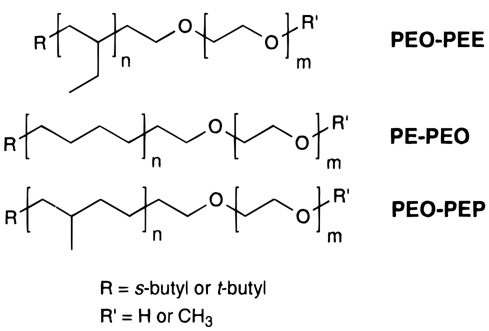

Figure 1. Structure of polyalkane−poly(ethylene oxide) block copolymers.

block copolymers and monomeric thermotropic liquid crystals.[10]

For ordered block copolymers, the combination parameter χN, where χ is the Flory−Huggins segment−segment interaction parameter and N is the overall degree of polymerization, determines the degree of block segregation. Therefore, a small value of N requires a large value of χ to remain in the ordered regime. Studies on the bulk phase behavior of block copolymers have generally dealt with hydrocarbon-based polymer pairs such as polyisoprene-*b*-polystyrene (PI−PS).[11] Although the molecular weights required to exhibit microphase separation in PI−PS block copolymers are relatively low ($\approx 3.0 \times 10^4$), the investigation of block copolymers with even lower molecular weights was desirable.[12] We set out to investigate this low-molecular-weight regime through the synthesis of a new set of amphiphilic block copolymers. Amphiphilic block copolymers have a variety of uses such as polysoaps, polymeric surfactants, solution modifiers, emulsifiers, wetting agents, and foam stabilizers.[13−15] A number of successful synthetic schemes for the preparation of amphiphilic block copolymers have been reported; however, most of the published work focuses on the solution behavior of this class of polymers. Bulk block copolymer phase behavior in the weak-segregation regime has generally been restricted to block copolymers in which neither block is water soluble.[16] In this paper we describe the synthesis and characterization of new amphiphilic block copolymers with well-defined molecular weights and block volume fractions (Figure 1).[17]

Results

Polymerization Scheme. Scheme 1 illustrates our strategy for the preparation of the polyalkane−poly(ethylene oxide) block copolymers using poly(ethylene oxide)-*b*-poly(ethylethylene) (PEO−PEE) as an example.[18] Anionic polymerization of butadiene followed by end capping with ethylene oxide (EO) leads to monohydroxyl-terminated polybutadiene (PBD−OH). This polybutadiene precursor is then catalytically hydrogenated to yield the analogous monohydroxyl-terminated poly(ethylethylene) (PEE−OH). The PEE−OH is converted to the corresponding potassium alkoxide and used as a macroinitiator for the subsequent polymerization of EO. The polymerization of EO can be terminated by acids or other electrophilic reagents such as methyl iodide. The molecular weights of both the PBD−OH and the PEO−PEE are set by the ratio of monomer to initiator, and the volume fraction of PEO is set by the relative amounts of PEE−OH and EO. The following sections describe each of the polymerization steps in detail.

Preparation of Polybutadiene Precursors. The anionic polymerization of butadiene was carried out in THF at −60 to −50 °C using either *tert*-butyl- or *sec*-butyllithium as the initiator. Anion concentrations employed ranged from 11 to 71 mM. The polymerizations were allowed to proceed for 3−6 h depending on anion concentration. End capping was accomplished by adding EO at a low temperature upon complete conversion of the butadiene. A large excess of EO was added although only one $-CH_2CH_2O-$ unit was incorporated as a result of using a lithium counterion.[19,20] Acidic methanol (HCl) was then used to liberate the polybutadiene alcohol which was isolated by evaporation of the solvent (eq 1). The inorganic salts left in the polymer do not affect the subsequent hydrogenation step and are removed by filtration during the purification of the PEE−OH. Alternatively, the salts can be removed by extraction of a cyclohexane solution of the polymer with distilled water.

The yields of polymerization were very high, indicating complete conversion of butadiene and end capping under these reaction conditions. The polymerization results for six hydroxyl end capped polybutadienes are given in Table 1. The first three samples were prepared using C_4H_6, and samples 4−6 were prepared using $C_4D_4H_2$.[21] Deuterium labeling was used to enhance the neutron scattering contrast between the PEO and PEE chains for subsequent phase behavior studies.[17] Labeling with deuterium in the subsequent hydrogenation step is effective; however, low molecular weights and the high 1,2 content (see below) of the polybutadienes generally lead to the incorporation of only two D's per repeat unit.[22] This level of labeling does not signifi-

Scheme 1. Poly(ethylethylene)-*b*-poly(ethylene oxide) Synthetic Route

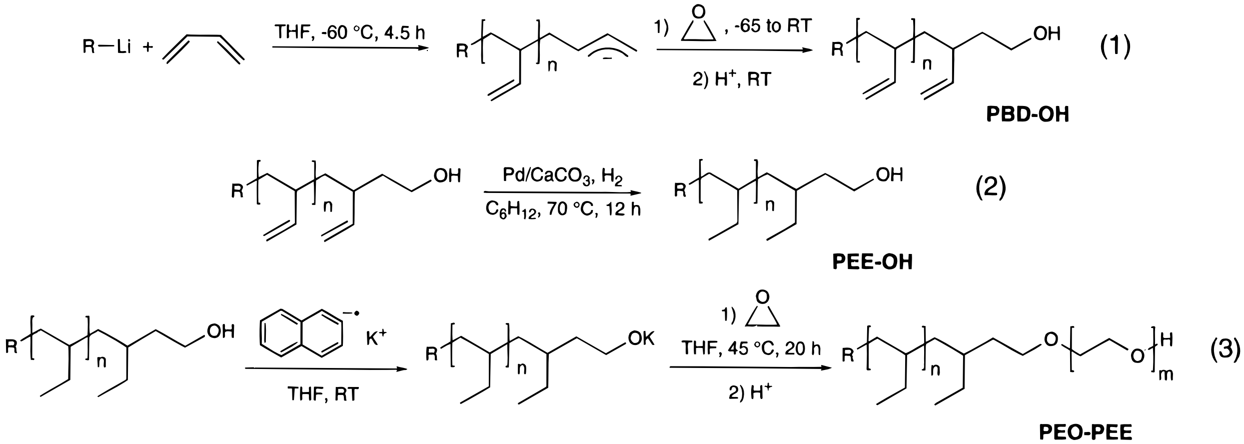

Table 1. Hydroxyl Terminated Polybutadiene (PBD−OH) Data

entry	$\bar{X}_n$(stoich)	$\bar{X}_n$(NMR)	1,2 content (%)[a]	[EG]/[I][a,c]	PDI (GPC)	d content[d]	butyllithium initator structure	yield (%)
PBD-1	37	35	88	1.09	1.05	d_0	tert	99
PBD-2	31	28	90	1.05	1.07	d_0	tert	99
PBD-3	38	36	91	1.01	1.07	d_0	sec	97
PBD-4	31	34	(90)	1.02	1.07	d_4	sec	
PBD-5	10	8.8	(90)	0.98	1.09	d_4	tert	
PBD-6	15	15	89[b]	1.02	1.09	d_4	sec	98

[a] Determined from ^{1}H NMR spectrum. [b] Determined from ^{13}C NMR spectrum. [c] EG: end group, I: initiator. [d] Deuterium content per C_4 repeat unit.

cantly enhance the scattering contrast relative to the natural contrast, and the use of $C_4D_4H_2$ was required.[23]

The relatively low number of repeat units in these polymers (<40) allowed the precise determination of microstructure, molecular weight, and end capping efficiency by ^{1}H and ^{13}C NMR spectroscopy. The polymerization of butadiene at low temperatures in a polar solvent like THF results in a polybutadiene with ≈90% 1,2 repeat units. This was measured by ^{1}H NMR spectroscopy for all of the hydrogenous samples (Table 1, entries PBD-1−PBD-3) and by ^{13}C NMR spectroscopy[24] for a representative d_4 polybutadiene sample (Table 1, entry PBD-6) prepared under similar conditions. The initiator fragment (aliphatic methyl groups), the end group fragment ($-CH_2-OH$), and the repeat unit resonances were well resolved in the ^{1}H NMR spectra. From inspection of the end group fragments in both the ^{1}H and ^{13}C NMR spectra it appears that the ultimate butadiene unit is a mixture of 1,2 and 1,4 regioisomers. Presumably, a larger percentage of the end groups are of the 1,2 type, in analogy to the propagation reaction. A mixture of end groups should not affect the initiation of EO in the final polymerization step. Since the polymerizations were run to high conversions, the number average degree of polymerization determined by ^{1}H NMR spectroscopy ($\bar{X}_n$(NMR)) compares favorably with the value calculated from the reaction stoichiometry ($\bar{X}_n\text{(stoich)} = [M]_o/[I]_o$). The mole ratios of end groups (EG) to initiator (I) fragments for the PBD−OH samples were very close to 1.0 in all cases. This indicates that the end capping efficiency was near quantitative and that there was no unwanted termination during the polymerization. (The end capping efficiency was also verified by titration in the final EO polymerization step and lack of PEE−OH homopolymer in the final PEO−PEE products.) This is in accord with the well-established efficiency of EO as an end capping reagent for anionic polymerizations.[5,25]

The polydispersity indices were determined by GPC using polystyrene standards and a set of columns that gave a linear calibration curve for polystyrenes down to a polystyrene molecular weight of 760. The GPC molecular weights were not used for molecular weight determination; however, the polydispersity indices calculated from the GPC traces were found to be less than 1.1 for all PBD−OH samples.

Polybutadienes with one hydroxyl end group per chain with well-defined molecular weights and low polydispersities were prepared in near quantitative yields. The effectiveness of the second step relies on a highly efficient hydrogenation reaction that results in a complete saturation of the polymer without affecting the hydroxyl end group.

Hydrogenation of the Polybutadiene Precursors. Catalytic hydrogenation of the polybutadiene precursor polymers was carried out in cylohexane at 70 °C using a supported palladium catalyst under ≈500 psi of H_2 or D_2 in a suitable high-pressure reactor. Reactions were typically run overnight. Upon completion, the polymer solution was filtered, and the crude cyclohexane solutions were concentrated and dried to give the corresponding PEE−OH (eq 2). These hydrogenation conditions do not reduce the terminal hydroxyl group.[26] This was confirmed by ^{1}H NMR spectroscopy and subsequently by titration of a known amount of PEE−OH in the following synthetic step. In six of the seven PEE−OH samples no residual olefin resonances were observed in the ^{1}H NMR spectra. One of the samples (PEE-3) contained a small amount of residual double bonds estimated to be less than 1% of the total number of repeat units. The hydrogenation results are shown in Table 2.

Table 2. Hydroxyl-Terminated Poly(ethylethylene) (PEE−OH) Data

entry	PBD precursor	d content[a]	PDI (GPC)	$\bar{M}_n$[b]	mol of K/mol of PEE−OH[c]
PEE-1	PBD-1	d_0	1.06	2100	1.05
PEE-2	PBD-2	d_0	1.07	1700	0.91
PEE-3	PBD-3	d_0	1.06	2200	1.01
PEE-4	PBD-3	d_2	1.07	2200	1.04
PEE-5	PBD-4	d_6	1.06	2000	1.06
PEE-6	PBD-5	d_6	1.08	600	0.97
PEE-7	PBD-6	d_6	1.08	960	0.99

[a] Approximate deuterium content per C_4 repeat unit. [b] Calculated from the $\bar{X}_n$(NMR) of the PBD precursor + 1 for the initiator fragment. The molecular weights of the deuterated polymers are reported as hydrogenous equivalent molecular weights. [c] The ratio of the average number of moles of potassium naphthalenide used in subsequent titrations and the calculated number of moles of PEE−OH used as the macroinitiator.

The molecular weights of the PEE−OH samples were calculated using the number of repeat units measured by ^{1}H NMR spectroscopy for the corresponding PBD−OH precursor ($\bar{X}_n$(NMR)), the molecular weight of the initiator fragment, and the molecular weight of the hydroxyethyl end group. All molecular weights are given as the hydrogenous equivalent molecular weights. This allows for direct comparison of molecular weights between hydrogenous and deuterous samples and avoids confusion associated with deuterium labeling. The deuterium content was based on previous studies in this laboratory that established the incorporation of two deuteriums per repeat unit in the catalytic deuteration of low-molecular-weight 1,2-polybutadiene.[22] In addition, the level of deuterium incorporation was determined by ^{1}H NMR spectroscopy and found to be consistent with the incorporation of approximately two deuteriums per repeat unit.

This catalytic saturation step also led to narrow polydispersity materials, indicating an insignificant amount of chain degradation during the reaction. The next step of the procedure requires the activation of the PEE−OH with a potassium base, followed by the polymerization of EO.

Polymerization of Ethylene Oxide. The preparation of the PEO−PEE block copolymers begins with the

Table 3. PEO−PEE Diblock Copolymer Data

entry	PEE precursor	yield (%)	end group[a]	d content (PEE block)[b]	N_{PEE}[c]	N_{PEO}[d]	N_{TOT}[e]	f_{PEO}	$\bar{M}_n$[f]	PDI (GPC)
OE-1	PEE-1	71[g]	H	d_0	36	32	51	0.34	3400	1.14
OE-2	PEE-2	99	H	d_0	29	44	50	0.48	3600	1.12
OE-3	PEE-2	98	H	d_0	29	20	37	0.29	2500	1.12
OE-4	PEE-3	99	H	d_0	37	49	61	0.44	4300	1.09
OE-5	PEE-3		H	d_0	37	143	113	0.70	8400	1.09
OE-6	PEE-4	100	H	d_2	37	46	59	0.42	4100	1.09
OE-7	PEE-4	100	H	d_2	37	40	56	0.39	3900	1.10
OE-8	PEE-5		H	d_6	35	43	56	0.42	3900	1.09
OE-9	PEE-5	98	H	d_6	35	51	60	0.46	4200	1.10
OE-10	PEE-5	93	H	d_6	35	152	115	0.72	8700	1.07
OE-11	PEE-6		Me	d_6	9.8	19	20	0.55	1400	1.14
OE-12	PEE-7	100	Me	d_6	16	29	31	0.52	2200	1.11
OE-13	PEE-6	94	H	d_6	9.8	45	33	0.73	2500	1.11

[a] R′ from Figure 1. [b] Approximate deuterium content per C_4 repeat unit. [c] Calculated from the $\bar{X}_n$(NMR) of the PBD precursor + 1 for the initiator fragment. [d] Calculated from ([M]/[I]) + 1 from the PEE−OH end group. [e] Based on a common segment volume of 126 Å^3. [f] The molecular weights of the deuterated polymers are reported as hydrogenous equivalent molecular weights. [g] Reaction performed at 21 °C for 23 h, cumyl potassium was used as the base.

transformation of the hydroxyl end group in the PEE−OH polymers to the corresponding potassium alkoxide. This was accomplished by titration with potassium naphthalenide. Potassium naphthalenide acts as a strong base under the conditions employed,[27] and the titration byproducts (naphthalene and dihydronaphthalene) should not affect the subsequent polymerization of EO. In a typical polymerization, a known amount of PEE−OH in anhydrous THF was slowly titrated with a THF/potassium naphthalenide solution of known concentration. At the end point a slight green color was observed and persisted for at least 30 min. The extremely large molar absorptivity of the potassium naphthalenide allows for a precise end point determination such that addition of a very small amount of the solution relative to the total titration volume was necessary to observe the slight green color (<0.5% of the total titration volume).

Using the calculated molecular weight of PEE−OH and the mass of polymer used in a given reaction, the number of mols of PEE−OH was calculated. This was verified by the titration with potassium naphthalenide. If there is one hydroxyl end group per PEE chain, then the number of moles used in the titration should equal the number of moles calculated from the molecular weight. These ratios were always very close to 1.0 and are listed in Table 2. Errors in this ratio arise from inaccuracies in the molecular weight of the PEE−OH, the mass of the polymer added to the reaction flask, the concentration of the potassium naphthalenide solution, and the titration volume. For consistency, the number of moles of initiator for the subsequent EO polymerization was set equal to the number of moles of the PEE−OH used in the polymerization, as calculated from the mass of polymer added to the flask and the calculated molecular weight of the polymer.

After the titration, EO was added to the reaction flask as a liquid, and the reaction mixture was heated to 45 °C. The rate constant for polymerization of EO by a potassium alkoxide propagating species at 45 °C was calculated using published data.[28] A rate constant of approximately 0.035 $\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$ was used as a guideline for the EO polymerizations reported here. The initiator concentrations we employed ranged from 0.005 to 0.02 M. Using a first-order initiator concentration dependence[28] the reaction times for 99.5% conversion were calculated to be 8.5 and 2.1 h for the least and most concentrated initiator solutions, respectively. The polymerizations were typically run for 20 h to ensure complete conversion.

Termination of these polymerizations was accomplished by the addition of slightly acidic (HCl) methanol or by the addition of methyl iodide. The resulting hydroxyl- or methoxyl-terminated block copolymers were isolated by filtration of the polymerization solution (KCl or KI precipitate upon termination), concentrated on a rotary evaporator, and dried at ≈70 °C under dynamic vacuum. This procedure was effective at ridding the polymer samples of inorganics and the titration byproducts (naphthalene and dihydronaphthalene) in most cases. However, elemental analysis showed that there was still 0.3−0.4% potassium remaining in two representative samples (OE-8 and OE-10). Therefore an additional purification procedure was employed. The block copolymers were dissolved in chloroform and washed with distilled water (and sodium bisulfite solution in the case of the KI impurities to rid the sample of I_2). Poly(ethylene oxide) can be quantitatively extracted from water into chloroform,[29] and the poly(ethylethylene) is insoluble in water. A direct comparison of unwashed and washed samples of OE-8 and OE-10 established that this procedure lowers the potassium content to less than 56 and 32 ppm, respectively. The water washes were concentrated and determined to be free of block copolymer.

Table 3 summarizes the data for the PEO−PEE block copolymers. With the exception of OE-1 (polymerization performed at 21 °C for 23 h) conversion of the EO was near quantitative in all cases, as demonstrated by the high yields of recovered polymer. The molecular weights of the PEO blocks were calculated using the PEE−OH initiator concentration and the mass of the EO added to the reaction assuming quantitative conversion (the MW of OE-1 was calculated by multiplying the monomer to catalyst ratio by the measured yield of polymerization). Using the calculated PEE and PEO molecular weights, the volume fraction of the PEO block was calculated using the densities for high-molecular-weight PEE (with 10% linear C_4 units) and PEO reported by Fetters at 140 °C (PEE = 0.806 g/cm^3 and PEO = 1.064 g/cm^3).[30] Although the absolute densities at these molecular weights will be lower than their high-molecular-weight analogs, we estimate that the ratio of the densities will be relatively unaffected. Thus, the absolute differences in density should not significantly affect the calculation of the PEO volume fraction.

The PEO mole fractions were also measured from the ^{1}H NMR spectra of the PEO−PEE block copolymers. A representative ^{1}H NMR spectrum (OE-4) is shown in Figure 2. Calculation of the PEO composition from the

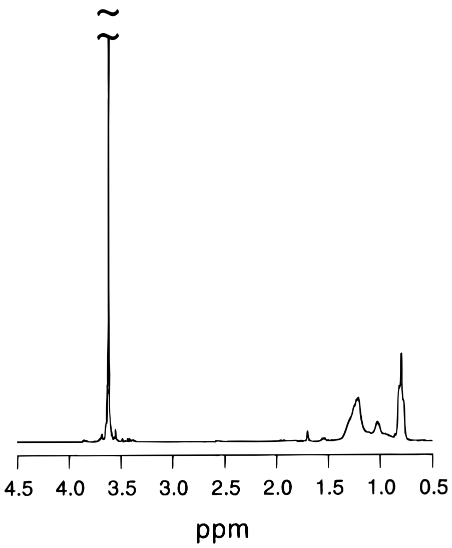

Figure 2. 300 MHz ^1H NMR spectrum of PEO−PEE block copolymer (OE-4 in chloroform-*d*).

Table 4. Elemental Analysis for Representative PEO−PEE Block Copolymers

sample	C_{calc} (%)	C_{meas} (%)	H_{calc} (%)	H_{meas} (%)
OE-2	68.5	68.10	11.6	11.51
OE-4	69.8	69.88	11.8	11.40
OE-8	66.7	66.89	11.9	11.66
OE-10	60.1	60.26	10.4	10.56

^1H NMR spectra followed by the previously stated density correction gives volume fractions within 1% of the volume fractions obtained using the calculation described above.[31] This is in accord with our estimated error of approximately 1% in the calculated PEO volume fractions. As a check of the calculated PEO volume fractions, the elemental analyses of four representative PEO−PEE samples were performed. The results are given in Table 4. All of the calculated percentages agree to within 0.4%, the standard accepted error associated with elemental analysis by thermal conductivity measurements.

The combination of two living polymerizations should lead to block copolymers with relatively narrow molecular weight distributions. In the case of fast initiation relative to propagation, the molecular weight distributions should approach $1 + 1/\bar{X}_n$, where $\bar{X}_n$ is the number average degree of polymerization.[32] Even for the low molecular weights of the polymers described in this paper, the distributions are expected to be less than 1.1. The polydispersity indices ($\bar{M}_w/\bar{M}_n$) for the PEO−PEE block copolymers were measured in THF using polystyrene standards as described above for the PBD−OH and PEE−OH samples. In all cases the PDI was less than 1.15, indicating relatively monodispersed samples.[33] GPC was also useful for the determination of the PEE−OH reinitiation efficiency. The high resolution of the GPC columns used for these studies allowed for the separation of the PEE−OH homopolymer from the PEO−PEE copolymer. Four GPC traces are shown in Figure 3: OE-8, OE-9, OE-10, and the PEE−OH precursor polymer (PEE-5). Clearly, all of the block copolymer curves are devoid of a significant amount of homopolymer. Even if 100% of the PEE−OH was not converted to the corresponding potassium alkoxide, the interconversion of dormant chains and active chains would effectively lead to quantitative initiation.[34] However, in all of the polymerizations a slight excess of potassium naphthalene was added to the reaction mixture. If the differences in acidities between the initiating PEE−OH and the dormant PEE-PEO species were large enough, a broadening of the molecular weight distribution or incomplete initiation may have been detrimental to the precision of the polymerization.[32,35] The narrow polydispersities and the absence of any PEE−OH in the GPC analysis indicates that all of the PEE−OH was activated during the titration step and that there was virtually no unfunctionalized PEE−OH in the final reaction product. In addition, this type of GPC analysis also rules out a significant amount of PEO homopolymer that may result from initiation with the very slight excess of potassium naphthelenide in the reaction mixture.

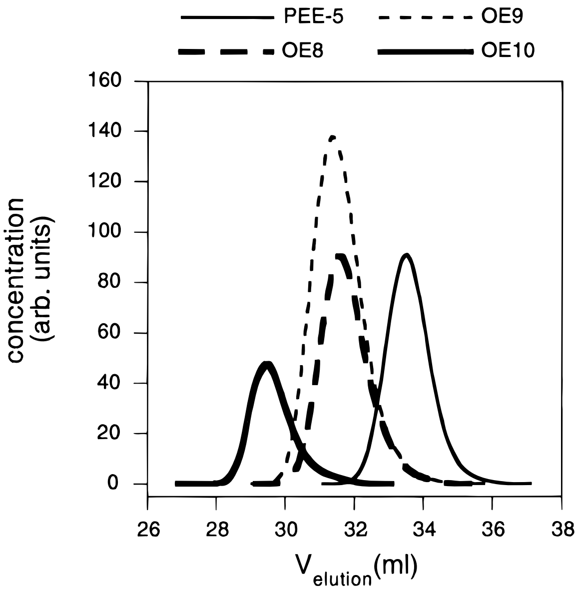

Figure 3. GPC traces for OE-8, OE-9, OE-10, and the PEE−OH precursor polymer (PEE-5) employed in the polymerization.

Other Amphiphilic Block Copolymers. The procedures described above are general and can be applied to the preparation of other polyalkane−poly(ethylene oxide) block copolymers. We have established this by preparing both polyethylene-*b*-poly(ethylene oxide) (PE−PEO)[36,37] and poly(ethylene oxide)-*b*-(polyethylene-*alt*-polypropylene) (PEO−PEP) block copolymers (Figure 1). The alkane precursors for these two types of block copolymers were hydroxyl-terminated 1,4-polybutadiene and hydroxyl-terminated 1,4-polyisoprene, respectively.[38] Both of the polymerizations and the hydrogenation proceeded without complication. However, for the PE−PEO block copolymer it was necessary to modify the general EO polymerization procedure due to the low solubility of the hydroxyl-terminated PE precursor. The titration and EO polymerization were performed at ≈50 and ≈55 °C, respectively. The polydispersity of the PE−PEO and the PEO−PEP block copolymers were determined by GPC vs polystyrene standards to be less than 1.15. The molecular characteristics for these polymers are given in Table 5.

Thermal Analysis. The PEO block in the block copolymers described is semicrystalline. The crystallization behavior of PEO in other block copolymers[39,40] and nonionic surfactants has been extensively studied.[41] For the purpose of this publication we performed limited analysis of five representative polyalkane−poly(ethylene oxide) block copolymers by differential scanning calorimetry (DSC). The results are listed in Table 6. In all cases the PEO block was of sufficient length to

Table 5. Additional Polyalkane−Poly(ethylene oxide) Block Copolymer Data

entry	polyalkane	*d* content[a]	end group	N_{PA}[b]	N_{PEO}[c]	N_{TOT}[d]	f_{PEO}	$\bar{M}_n$[e]	PDI (GPC)
EO-1	PE	d_6	Me	15	28	30	0.52	2100	1.10
EO-2	PE	d_0	Me	20	37	39	0.52	2800	
OP-1	PEP	d_6	Me	13	28	30	0.52	2200	1.11
OP-2	PEP	d_0	Me	20	44	47	0.51	3000	1.08

[a] Approximate deuterium content per C_4 repeat unit. [b] Calculated from the $\bar{X}_n$(NMR) of the polydiene precursor + 1 for the initator fragment. [c] Calculated from ([M]/[I]) + 1 from the polyalkane precursor end group. [d] Based on a common segment volume of 126 Å^3. [e] The molecular weights of the deuterated polymers are reported as hydrogenous equivalent molecular weights.

Table 6. Representative DSC Results

entry	T_m onset PEO (°C)[a]	N_{PEO}	T_m onset polyalkane (°C)[a]	N_{PA}
OE-2	44	44		29
OE-10	57	152		35
OE-12	38	29		16
EO-1	37	28	78	15
OP-1	40	28		13

[a] ±2 °C.

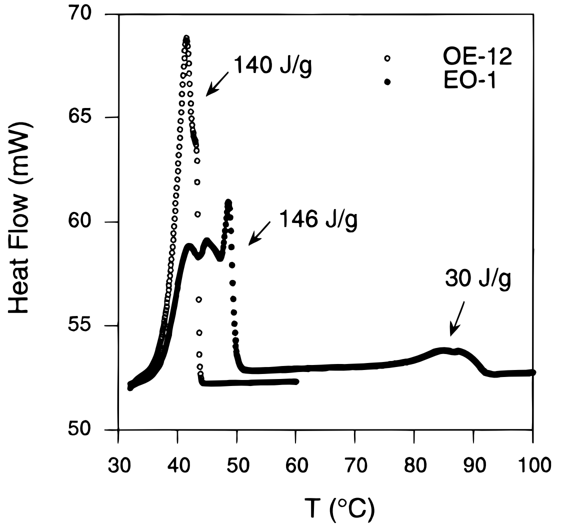

Figure 4. DSC thermogram for OE-12 and EO-1. Samples were held at 120−125 °C for 15 min, quenched to 30 °C, held for 1 h, and then scanned at 5 °C/min. The heats of fusion are based on the weight fraction of the corresponding blocks in the sample.

crystallize at room temperature. The melting temperature (T_m) of the PEO sets the lower limit for amorphous block copolymer thermodynamic studies and was less than 60 °C in all cases. In the PE−PEO block copolymers, the melting temperature of the polyethylene block is the lower limit, and for EO-1 the onset of the most significant melting endotherm was determined to be 78 °C. Depending on annealing conditions and heating rates, the shape and size of the melting endotherms varied. Presumably, these differences are related to the amount of chain folding, overall degree of crystallinity, and constraints imposed by the amorphous block.[40,42]

Figure 4 shows DSC thermograms for OE-12 and EO-1. The PEO blocks in each of these polymers are approximately the same molecular weight and give similar heats of fusion and T_m onset temperatures. The PE block in EO-1 also shows a well-defined melting endotherm. Based on heats of fusion for perfectly crystalline, high-molecular-weight PEO and PE, the calculated degree of crystallinity for the PEO and PE blocks of EO-1 are 71% and 10%, respectively.[43] The PEO block in OE-12 was calculated to be 77% crystalline. In EO-1 the calculated degree of crystallinity of the PE block is probably an underestimate because the melting of this block appears to occur over a much larger temperature range than the most significant melting endotherm used for the heat of fusion calculation. This large range of melting behavior has also been seen in the low-frequency rheological response of EO-1 as a continuous decrease in the dynamic elastic modulus between the PEO melting temperature and the most significant PE melting temperature. We plan to report the crystallization behavior of these new materials in detail in a future publication.[42]

Discussion

There have been a number of synthetic procedures published describing the preparation of amphiphilic block copolymers. Polydiene−poly(ethylene oxide)[44] and polystyrene−poly(ethylene oxide)[14,45] block copolymers have received the most attention. As a model block copolymer system, we chose to investigate polyalkane−poly(ethylene oxide) block copolymers because of their chemical similarity to nonionic surfactants.[46] The lyotropic liquid crystalline phases of nonionic surfactant/water mixtures have been well-documented,[47,48] and it has been noted that these and other lyotropic liquid crystals share a common set of ordered morphologies with high-molecular-weight block copolymers.[7,11,48−50] We feel that the polyalkane−poly(ethylene oxide) block copolymers described above will serve as a bridge between monomeric liquid crystalline systems and high-molecular-weight block copolymer systems.

We have focused on the bulk phase behavior in the weak and intermediate segregation regime,[17,51] and this requires overall molecular weights that are roughly 1 order of magnitude greater than typical nonionic surfactants. We chose the method outlined in Scheme 1 because of a number of advantageous features: (1) The end capping reaction of polydienyl lithium reagents with EO is highly efficient and results in the incorporation of only one EO unit. (2) Catalytic hydrogenation of the polydiene precursor polymer leads to a thermally and oxidatively stable polyalkane and avoids potential complications associated with the hydrogenation of amphiphilic molecules. (3) The exact same PEE block can be used for the preparation of many block copolymers varying in molecular weight and PEO volume fraction. (4) The technique is general to a variety of polyolefins. (5) The end group of the PEO chain can easily be functionalized in a subsequent manipulation for the preparation of ABC triblock copolymers or specifically end capped block copolymers. (6) All of these reactions lead to near quantitative conversions of the starting materials and can be easily carried out on a large scale.

The initial system we chose to investigate was the PEO−PEE block copolymers. The alkane block in the PEO−PEE block copolymers is amorphous ($T_g \approx -30$ °C) unlike typical nonionic surfactants which consist of linear (unbranched) alkane chains. Since the PEO blocks in these block copolymers are all large enough to crystallize, and we are mainly concerned with phase behavior in the amorphous state, the T_m of the crystalline PEO (<60 °C) was the lower bound on the experimental temperature window. Although we have demonstrated that the synthetic scheme allows for the preparation of PE−PEO block copolymers, the T_m of crystalline PE (≈80−110 °C) would have decreased our experimental temperature window for the initial phase behavior studies.

From the low-frequency rheological response of the PEO−PEE block copolymers in addition to small angle scattering studies,[51] it was determined that 15 of the 17 samples formed ordered microstuctures above the T_m of the PEO block. OE-11 and OE-13 were too low in molecular weight and were disordered above the T_m of the PEO. All of the other samples (including the PE−PEO and the PEO−PEP samples) disordered at experimentally tractable temperatures ($T_m < T_{ODT} < 275$ °C). OE-10, with a molecular weight of 8.7×10^3, exhibited the highest ODT temperature of 259 °C. To ensure that degradation of the block copolymer was not problematic at high temperatures, a sample of OE-10 that had been previously heated in the rheometer under a blanket of nitrogen from 30 to 260 °C at 1 °C/min was analyzed by GPC. The GPC curve before and after the rheology were virtually indistinguishable. In addition, samples of OE-10 that had been heated to 260 °C exhibited the same ODT temperature as the initial run. Although a complete stability study on the PEO−PEE block copolymers was not carried out, general precautions should be taken to avoid premature degradation.[52] Generally speaking, these materials appear to be quite robust.

Summary

We have described the preparation of a new set of amphiphilic block copolymers consisting of a polyalkane block and a poly(ethylene oxide) block. The synthetic scheme combines two extremely efficient reactions, anionic polymerization and catalytic hydrogenation, and leads to materials with well-defined molecular weights and block volume fractions. The synthesis is versatile and can be performed on a large scale. Seventeen polyalkane−poly(ethylene oxide) block copolymers have been prepared with a variety of molecular weights and volume fractions. The majority of these block copolymers formed ordered phases above the melting temperature of the highest melting block and disordered at an experimentally tractable temperature. For the range of volume fractions we investigated, this requires the overall molecular weights to be in the range of $(1.4-8.7) \times 10^3$. These polymers represent one of the lowest molecular weight systems employed in the study of block copolymer thermodynamics.

Experimental Section

General Considerations. High-purity argon (>99.5%) was rigorously dried and deoxygenated by passage through a column containing vermiculite and MnO.[53] NMR spectra were recorded on a Varian VXR 500 or a Varian VXR 300. All NMR samples were dissolved in deuterated chloroform (Cambridge) at concentrations of approximately 0.5−1 wt %. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane and referenced to residual protio solvent. For all spectra where quantitative integrations were necessary, a pulse delay time of 30 s was employed to ensure complete relaxation. DSC analysis was performed under nitrogen using a Perkin-Elmer DSC-7. A scan rate of 5 °C/min was used. GPC analyses of the PEO−PEE and the PEO−PEP block copolymers were performed on a homebuilt HPLC system utilizing an Altex dual piston pump, a Rheodyne injector fitted with a 100 μL injection loop, four Phenomex phenogel columns (5×10^5, 5×10^4, 5×10^3, and 500 Å pore sizes), and a Waters R401 differential refractometer. THF was used as the mobile phase, and the columns were calibrated using narrow distribution polystyrene standards (Pressure Chemical Co.). The columns gave a linear calibration curve for polystyrene between MW 760 and 300 000. For the PE−PEO block copolymer a Waters 150C was used with THF as the mobile phase at 55 °C. Three Phenomenex Phenogel columns, 500, 10^3, and 10^4 Å, were employed with a flow rate of 1.0 mL/min. The columns gave a linear calibration curve for polystyrene between 580 and 49 900. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Thermal conductivity measurements were employed for C and H analysis.

Materials. THF for polymerizations was purified by distillation from a purple Na/benzophenone solution under argon. Cyclohexane used for hydrogenations was sparged with argon before use. Methanol, 2-propanol, chloroform, and other common solvents or reagents were used as received. Butadiene-h_6 (Aldrich) was purified by multiple distillations from *n*-butyllithium (Aldrich). Ethylene oxide (EO) (Aldrich) was purified by successive distillations from calcium hydride and dibutyl magnesium (Aldrich). *sec*-Butyllithium and *tert*-butyl lithium were used as received (Aldrich). The concentration of these initiators was determined by the Gilman double titration method.[54] Naphthalene was purified by crystallization from diethyl ether (×3) and stored in a desiccator. Potassium naphthalenide solutions were prepared by adding recrystallized naphthalene to a stirring THF dispersion of freshly cut potassium under a purge of argon. The green color of the potassium naphthalenide appeared immediately, and the solution was allowed to stir at room temperature for at least 12 h before use. The concentrations of the potassium naphthalenide solutions were determined by addition of a 10 mL aliquot of the dark green solution to water and titration with a standardized HCl solution using phenolphthalene as an indicator. The predicted and measured concentration values were typically within 10%. All other chemicals were used as received.

Preparation of Butadiene-*1,1,4,4-d*$_4$. The pyrolysis of butadiene-*2,2,5,5-d*$_4$ sulfone (Aldrich) at ≈150 °C under a slow purge of argon in a round bottom flask was carried out according to established procedures.[21] The outlet of the flask was connected to a glass frit, and the product gases were bubbled through a flask containing a concentrated aqueous solution of sodium hydroxide (≈10 wt %) to remove the SO_2. The outlet of the this flask was connected to a column of $CaCl_2$ containing a small amount of indicating Dririte. The butadiene was collected in a monomer purification flask that was immersed in a dry ice/2-propanol bath (−78 °C). The outlet of this flask was connected to a mineral oil bubbler. The yield of butadiene-*1,1,4,4-d*$_4$ was typically ≈90%. Butadiene-*1,1,4,4-d*$_4$ was purified by repeated distillation from *n*-butyllithium in a manner similar to perprotiobutadiene.

Polymerization and End Capping of Butadiene. A typical polymerization procedure is described below. A more detailed description of the general anionic setup has been previously reported.[55] The polymerization was performed in a 3 L glass reactor fitted with five ACE-THREADS threaded glass connectors and containing a Teflon-coated magnetic stir bar. Using Teflon ferrules and Nylon bushings, a glass thermocouple well, an inlet from the THF still, a Y-adapter (equipped with two Teflon valves (Kontes or Chemglass) and a port capped with a Teflon-coated septum), and two glass plugs were fitted on the secured reaction flask. The two valves on the Y-adapter were connected to a mercury manometer and a vacuum/argon manifold. The entire flask was heated to ≈275 °C with a heating mantle and evacuated to ≈10^{-3} Torr (thermocouple gauge). The connection between the THF still and the reaction flask was also evacuated during this step. The flask was kept under vacuum at 275 °C overnight. After cooling, the two glass plugs were replaced with pretared burets of purified butadiene (57.9 g, 1.07 mol) and EO (28.8 g, 0.654 mol). The burets were connected with flexible glass to metal adapters and Cajon Ultratorr fittings and kept cold by immersion in dry ice/2-propanol cold baths. The reaction flask was evacuated (≈10^{-3} Torr) and back-filled with argon five times. During this procedure the flask was leak tested by filling with $\approx {}^1/_2$ atm positive pressure of argon and monitoring the pressure on the manometer. After the final back-fill, the pressure in the flask was equalized with the pressure in the THF still through the manifold and $\approx$1.5 L of THF was distilled into the flask. The flask was isolated from the still, pressurized with $\approx {}^1/_2$ atm of argon, isolated from the manifold, and cooled to ≈ -65 °C with a dry ice/2-propanol bath. *sec*-Butyllithium (21.0 mL, 1.31 M in cyclohexane, 0.0276 mol) was added via cannula through the Teflon-coated septum. The reaction temperature increased by a few degrees during the addition, and a deep yellow color was observed. After the reaction cooled back to ≈ -65 °C, the butadiene buret was warmed to 0 °C, and all of the butadiene was added to the reaction flask. The reaction temperature warmed to -59 °C and became peach in color. After 2 h the color changed from peach to yellow-orange. The reaction was stirred at ≈ -60 °C for a total of 4.5 h. EO was added in a manner similar to the addition of butadiene. The reaction warmed to -52 °C, and the reaction became colorless in less than 30 s after the addition. The reaction was warmed to room temperature and allowed to stir overnight while still under argon. Acidic methanol (3 mL of concentrated HCl in 50 mL of methanol) was added to the reaction flask by removing one of the burets and pouring in the solution. The slightly cloudy solution became clear and was concentrated on a rotary evaporator to give 59.0 g of a crude product (97%). GPC (THF vs PS): $\bar{M}_w/\bar{M}_n = 1.07$, $\bar{M}_n = 3150$. This product was used without purification for the subsequent hydrogenation.

Hydrogenation of Hydroxyl-Terminated Polybutadiene. Hydrogenations were performed in cyclohexane in a 2 L Parr reactor under $\approx$500 psi of hydrogen (or deuterium) at 70 °C. The concentrations of PBD−OH ranged from 12 to 40 g/L of cyclohexane. A supported Pd catalyst was used (5% on calcium carbonate) in an amount of 1.5−2 times the weight of polymer. The catalyst was typically activated by heating to 100 °C under 100 psi of hydrogen (or deuterium) for a few hours and cooled to room temperature before adding a solution of the polybutadiene. Reactions were typically run overnight ($>$12 h); however, one reaction was run for 4 h and showed no residual unsaturation by ^{1}H NMR spectroscopy. Upon completion the heterogeneous reaction was filtered to remove the catalyst and the cyclohexane solution of polymer was concentrated to yield the PEE−OH. The filtration removes any residual inorganic salts left in the crude hydroxyl-terminated PBD from the anionic polymerization. The isolated yield of polymer was typically greater than 95%. This product can be used without further purification. Most of the hydrogenations were carried out without complication. Reagent grade cyclohexane can be used, and degassing of the cyclohexane solution of polymer can be accomplished by simply sparging with inert gas before adding it to the Parr reactor.

Polymerization of Ethylene Oxide Initiated by a Hydroxyl-Terminated Poly(ethylethylene). These polymerizations were performed using a reaction setup similar to the one described for the polymerization of butadiene in THF. A glass covered stir bar is recommended due to side reactions of the potassium naphthalenide solution with Teflon. A general polymerization procedure is described. After assembly of the reactor and drying at 275 °C, the reactor was cooled to room temperature, one of the glass stoppers was replaced with a pretared buret of purified EO, and the center Y-adapter was removed. A sample of predried PEE−OH was poured into the reactor from a pretared beaker. After the weight of PEE−OH was established, the reactor was resealed, heated to 70 °C, and evacuated. The PEE−OH was stirred and dried by this method overnight. During this period a solution of potassium naphthalenide was prepared in a graduated cylinder fitted with a Teflon valve and a side hose adapter. The deep green potassium naphthalenide solution was stirred under argon overnight while the PEE−OH was being dried. The reactor was cooled to room temperature and 400 mL of fresh tetrahydrofuran was distilled into the flask with continued stirring. The solution of PEE−OH was slowly titrated with the freshly prepared potassium naphthalenide solution (typically 0.1−0.2 M) until a light green solution persisted for at least 30 min at room temperature. The EO was added in one portion to the solution. The reaction mixture became colorless after approximately 1 min. The reaction was heated to 45 °C and stirred for at least 20 h. The reaction was cooled to room temperature, the reactor was vented, and acidic methanol was added directly to the stirring reaction mixture. In cases with a relatively low-molecular-weight PEO block, a white precipitate (LiCl) was observed. The crude reaction mixture was then concentrated on a rotary evaporator and the white, semicrystalline solid was redissolved in chloroform. This chloroform solution was washed at least five times with fresh aliquots of distilled water. The chloroform solution was concentrated on a rotary evaporator, and the white, semicrystalline solid was isolated and spread into Petri dishes or watch glasses as thinly as possible. The Petri dishes were heated to 70 °C in a vacuum oven overnight to remove residual solvents, naphthalene, and dihydronaphthalene. Alternatively, methyl iodide can be used to terminate the polymerization. In that case, the methyl iodide is added via syringe to the reaction mixture at room temperature and then the reaction mixture is reheated to 45 °C for 2−3 h to ensure complete end capping. In the chloroform washing procedure, the first few washes were done with a dilute solution of sodium bisulfite to remove residual I_2 from the decomposition of KI.

NMR Characterization. The following sets of resonances were observed by ^{1}H NMR spectroscopy for the representative polymers described in this work. All resonances are given in ppm (δ) downfield from tetramethylsilane (0.0 ppm). All of the resonances observed were either broad (b) or consisted of multiple overlapping sharp peaks (m). 1,2-PBD−OH: 5.4 (m, $\mathrm{CH_2{-}C}\mathit{H}\mathrm{{=}C}\mathit{H}\mathrm{{-}CH_2{-}}$ and $\mathrm{CH_2{=}C}\mathit{H}\mathrm{{-}CH{-}}$), 4.9 (m, $\mathrm{C}\mathit{H}_2\mathrm{{=}CH{-}CH{-}}$), 3.6 (m, $\mathrm{{-}C}\mathit{H}_2\mathrm{{-}OH}$), 2.0 (b, $\mathrm{C}\mathit{H}_2\mathrm{{-}CH{=}CH{-}C}\mathit{H}_2\mathrm{{-}}$ and $\mathrm{CH_2{=}CH{-}C}\mathit{H}\mathrm{{-}}$), 1.2 (m, $\mathrm{CH_2{=}CH{-}C(R)H{-}C}\mathit{H}_2\mathrm{{-}}$), 0.9 (m, $\mathrm{{-}C}\mathit{H}_3$ resonances from initiator). 1-4-PBD−OH: 5.4 (m, $\mathrm{CH_2{-}C}\mathit{H}\mathrm{{=}C}\mathit{H}\mathrm{{-}CH_2{-}}$ and $\mathrm{CH_2{=}C}\mathit{H}\mathrm{{-}CH{-}}$), 4.9 (m, $\mathrm{C}\mathit{H}_2\mathrm{{=}CH{-}CH{-}}$), 3.6 (m, $\mathrm{{-}C}\mathit{H}_2\mathrm{{-}OH}$), 2.0 (b, $\mathrm{C}\mathit{H}_2\mathrm{{-}CH{=}CH{-}C}\mathit{H}_2\mathrm{{-}}$ and $\mathrm{CH_2{=}CH{-}C}\mathit{H}\mathrm{{-}}$), 1.2 (m, $\mathrm{CH_2{=}CH{-}C(R)H{-}C}\mathit{H}_2\mathrm{{-}}$), 0.9 (m, $\mathrm{{-}C}\mathit{H}_3$ resonances from initiator). PI-OH: 5.1 (m, $\mathrm{{-}CH_2{-}C(CH_3){=}C}\mathit{H}\mathrm{{-}CH_2{-}}$), 4.7 (m, $\mathrm{{-}CH_2{-}C(H)(CH_2){-}C(CH_3){=}C}\mathit{H}_2$), 3.6 (m, $\mathrm{{-}C}\mathit{H}_2\mathrm{{-}OH}$), 2.0 (b, $\mathrm{{-}C}\mathit{H}_2\mathrm{{-}C(CH_3){=}CH{-}C}\mathit{H}_2\mathrm{{-}}$ and $\mathrm{{-}CH_2{-}C(}\mathit{H}\mathrm{)(CH_2{-}){-}C(CH_3){=}C}\mathit{H}_2$), 1.6 (m, $\mathrm{{-}CH_2{-}C(C}\mathit{H}_3\mathrm{){=}CH{-}CH_2{-}}$ and $\mathrm{{-}CH_2{-}C(H)(CH_2{-}){-}C(C}\mathit{H}_3\mathrm{){=}CH_2}$), 1.3 (m, $\mathrm{{-}CH_2{-}C(H)(C}\mathit{H}_2\mathrm{{-}){-}C(CH_3){=}CH_2}$), 0.9 (m, $\mathrm{{-}C}\mathit{H}_3$ resonances from initiator). PEE−OH: 3.6 (m, $\mathrm{-C}\mathit{H}_2\mathrm{-OH}$), 1.2 (m, $\mathrm{CR_3}\mathit{H}$ and $\mathrm{CR_2}\mathit{H}_2$), 0.9 (b, $\mathrm{CR}\mathit{H}_3$). PE-OH: 3.6 (m, $\mathrm{{-}C}\mathit{H}_2\mathrm{{-}OH}$), 1.2 (m, $\mathrm{CR_3}\mathit{H}$ and $\mathrm{CR_2}\mathit{H}_2$), 0.9 (b, $\mathrm{CR}\mathit{H}_3$). PEP-OH: 3.65 (m, $\mathrm{{-}C}\mathit{H}_2\mathrm{{-}OH}$), 1.25 (m, $\mathrm{CR_3}\mathit{H}$, and $\mathrm{CR_2}\mathit{H}_2$), 0.8 (b doublet, $\mathrm{CR}\mathit{H}_3$). PEO−PEE, PE−PEO, and PEP-PEO: All of the polyalkane−PEO block copolymers have a broad $\mathrm{{-}OC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{O{-}}$ resonance centered at $\approx$3.65 ppm, and the alkane region is similar to the corresponding hydroxyl-terminated polyalkane resonances (see Figure 2).

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