Synthesis and Characterization of Poly[1,4-isoprene-*b*-(ethylene oxide)] and Poly[ethylene-*co*-propylene-*b*-(ethylene oxide)] Block Copolymers

Jürgen Allgaier,* Andreas Poppe, Lutz Willner, and Dieter Richter

Institut für Festkörperphysik, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

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ABSTRACT: The synthesis of amphiphilic AB block copolymers, having 1,4-polydiene or corresponding hydrogenated aliphatic polyolefin blocks and poly(ethylene oxide) (PEO) blocks, is described. The materials are obtained in a two-step process. In the first step isoprene is polymerized anionically in a hydrocarbon solvent with *sec*-butyllithium or *tert*-butyllithium as initiator. The end-capping of the living polymer with ethylene oxide (EO) yields polyisoprene, which is functionalized with a hydroxyl end group (PI-OH). This product can be hydrogenated to the aliphatic polyolefin poly(ethylene-*co*-propylene) (PEP-OH). In the second step cumylpotassium is used to deprotonate the OH groups, leading to the macroinitiators PI-OK and PEP-OK. PI−PEO and PEP−PEO block copolymers are obtained by initiating the polymerization of EO with the macroinitiators in THF. The characterization reveals narrow molecular weight distributions, absence of homopolymer in the block copolymers, and complete conversion of monomers in both polymerization steps. The materials form water soluble aggregates even at a PEO content of 41% and a total molecular weight of $M_n = 35\,400$. In *n*-decane all block copolymers synthesized were soluble, the one with the smallest hydrophobic part having a PI content of 24% and a total molecular weight of $M_n = 17\,700$.

Introduction

Block copolymers form micelles in selective solvents for one of the components. Amphiphilic block copolymers, which contain both hydrophilic and hydrophobic segments, can form micelles both in aqueous media and in nonpolar solvents. A well-known example for such polymeric surfactants is the polystyrene−poly(ethylene oxide) (PS−PEO) system. The synthesis[1−3] and colloidal behavior of these polymers have been investigated intensively in water[4−7] and in a few cases in nonpolar solvents.[8] In contrast, little work has been done on the synthesis of polymeric amphiphiles, containing polydiene or aliphatic polyolefin blocks in the hydrophobic part.[9] However, these substances should exhibit interesting properties since most polymers forming the hydrophobic part are low-T_g materials and there are a variety of solvents selectively solubilizing one block. Furthermore, amphiphiles, having aliphatic polyolefin blocks, show almost the same chemical design as the well-known low molecular weight alkane-oxyethylene ($C_n(EO)_m$) surfactants.

The ideal method for the synthesis of block copolymers with a narrow molecular weight distribution and well-defined block structure is the living anionic polymerization. The preparation of polyisoprene (PI), having a high degree of 1,4-microstructure, requires the use of organolithium initiators and hydrocarbon solvents. Initiators with the other alkali metals are only soluble in polar solvents, cause side reactions, and cause an increase of 3,4-microstructure in the polymer. In contrast, the anionic ring-opening polymerization of ethylene oxide (EO) demands sodium organic or, preferably, potassium organic initiators and polar solvents. The reaction of organolithium initiators in nonpolar media with EO exclusively effects hydroxyethylation of the chain end without any propagation taking place.[10,11] However, the polymerization of EO with lithium organic compounds can take place if potassium salts or lithium-complexing agents are added. PS−PEO block copolymers prepared by this technique still contain significant amounts of PEO homopolymer and show incomplete conversion of EO or unsatisfying molecular weight distributions, depending on the synthetic procedure.[12−14] The preparation of PS−PEO block copolymers was also performed by the use of a two-step process.[4] In this case polystyryllithium was hydroxyethylated with EO. The counterion was switched to potassium by protonating the lithium alkoxide with methanol and deprotonating the hydroxyl chain end with potassium methoxide. After the polymerization of the PEO block, the product had a molecular weight distribution of 1.15 and still contained PS and PEO homopolymers.

For the preparation of the 1,4-PI−PEO and PEP−PEO block copolymers, described in this work, we also have chosen a two-step process. Thereby, the conversion of the counterion from lithium to potassium was accomplished by using cumylpotassium. The products obtained showed polydispersities lower than 1.05 and were free of homopolymer.

Experimental Section

Solvents and Monomers. Cyclohexane (Merck) and benzene (Merck) were purified by sequential distillation from CaH_2 and from butyllithium. Tetrahydrofuran (THF) was purified by sequential distillation from sodium−potassium alloy and from the purple benzophenone−potassium adduct. Isoprene (Fluka) was purified by treatment with dibutylmagnesium for 12 h, then distilled onto *n*-butyllithium, and allowed to stand for 30 min at −20 °C immediately before use. EO (Fluka) was distilled onto *n*-butyllithium and allowed to stand for 2 days. Thereafter it was stirred over CaH_2 overnight before being transferred into ampules.

Initiators. *sec*-Butyllithium (Aldrich) and *tert*-butyllithium (Aldrich) were distilled or sublimed under high-vacuum conditions, then diluted with cyclohexane, and subdivided into ampules. Cumylpotassium was synthesized following an established procedure[1] and was stored as a 0.05 M solution in THF at −78 °C. Taking these precautions, the cumylpotassium could be used up to at least 4 months after preparation. The concentrations of the metal organic initiators were determined by hydrolyzing an aliquot with water and titrating the LiOH or KOH formed with standard hydrochloric acid.

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Polymerizations. All manipulations were performed under high vacuum in glass reactors, provided with break seals for the addition of reagents. Living PI was prepared in cyclohexane or benzene with *sec*- or *tert*-butyllithium. PI-OH was formed by reacting the living PI with EO in a 10-fold excess over the initiator concentration. The mixture was stirred for at least 12 h and terminated with acetic acid. The polymer was precipitated in p.a. grade methanol. PEP-OH was obtained by hydrogenation of PI-OH with a $Pd/BaSO_4$ catalyst (Aldrich) according to a known procedure.[15]

The PI-OH and PEP-OH were purified by dissolving the polymers in dry benzene and evaporating the solvent under reduced pressure at room temperature at the vacuum line. The PI-OH was subsequently stirred under high vacuum overnight at room temperature, the PEP-OH at 100 °C. This procedure was repeated twice. Thereafter, the polymer was dissolved in dry THF. These manipulations were done under high-vacuum conditions without allowing the polymer to come in contact with air. The polymer solutions were titrated with the deeply red-colored cumylpotassium solution. The addition of cumylpotassium was stopped after a slight orange color in the polymer solution persisted for 5 min. After the mixture was stirred for 2 h the color disappeared again completely. More THF was added, and the EO was polymerized at 50 °C for 3−4 days. In the case of polymer PI5−PEO15 the polymerization was allowed to proceed for 1 week. The reactions were terminated with acetic acid and the products precipitated twice in acetone at −10 to −20 °C. Polymer PI5−PEO2 could not be precipitated in that way. It was precipitated in water.

Measurements. Size exclusion chromatography (SEC) experiments were carried out at 30 °C, using a Waters 150C instrument. Four μ-Styragel columns with a porosity range from 10^5 to 500 Å and one ultra-Styragel column of continuous porosity were used together with a differential refractometer. For the PI-OH and PEP-OH the eluant was THF, and for the block copolymers a mixture of THF and *N*,*N*-dimethylacetamide (DMA) (90:10 by vol) was used. In all experiments the flow rate was 1 mL/min. PS standards (Tosoh Corp.) were used for the calibration. The molecular weights, calculated with the PS calibration, were transformed into PI and PEP molecular weights considering the different hydrodynamic volumes of the polymers. Based on the Mark−Houwink−Sakurada relationship, the equations $M_{PI} = 0.632M_{PS}$ and $M_{PEP} = 0.446M_{PS}^{1.028}$ were used for the transformation.[16,17]

The number-average molecular weights (M_n) of the PI-OH and PEP-OH were measured with a Knauer vapor pressure osmometer at 45 °C. The solvent was benzene, which was distilled from CaH_2. The M_n values were obtained using a calibration function of the type $(\Delta V/c)_{c=0} = KM_n^{\alpha}$, where ΔV is the change in voltage of the thermistors and c is the concentration.[18] The calibration constants K and α were obtained, using benzil and PS standards of $440 < M_n < 9600$.

The M_n values of some copolymers were determined with a Knauer membrane osmometer at 37 °C. The solvent was toluene, which was distilled from Na. The results were obtained from the square root plot $(\pi/c)^{1/2} = (\pi/c)_{c=0}^{1/2}(1 + 1/2M_nA_2c)$, where π is the osmotic pressure and A_2 is the second virial coefficent.[19]

The copolymer compositions, the microstructures of the PI-OH, and the completeness of the hydrogenation reaction yielding PEP-OH were determined by ^{1}H-NMR spectroscopy in $CDCl_3$, using a 500 MHz Bruker spectrometer.

Solubility Tests. The micellization behavior of the block copolymers was examined in deionized water and in *n*-decane. For these experiments block copolymer samples were used, which were precipitated in acetone. The materials were dried under vacuum conditions until NMR analysis revealed the absence of solvent residues. Polymer solvent mixtures, containing 0.1% polymer, were heated to 60 °C in order to increase the solubilization rate.

Results and Discussion

The preparation of PI−PEO and PEP−PEO block copolymers in the two-step process involves in the first step the synthesis of hydroxyl-end-functionalized PI-OH and PEP-OH (see Scheme 1). To obtain these polymers, isoprene was polymerized with *sec*- or *tert*-butyllithium. The functionalization was achieved by reacting the living PI with an excess of EO. Under these conditions exclusively one unit of EO was added to the PI chain end, leading to PI-OH.[10,11] The microstructure was analyzed by comparing the signal intensities of the olefinic protons associated with the 1,4-structure at 5.1 ppm and the 3,4-structure at 4.7 ppm. It was found that the polymers contain 93−95% 1,4-units and 5−7% 3,4-units. The hydrogenation of PI-OH with a conventional palladium catalyst yielded PEP-OH. The completeness of the reaction was characterized by ^{1}H-NMR. The disappearance of the resonances, associated with the olefinic protons revealed the complete saturation of the double bonds. The molecular weight data of the PI-OH and PEP-OH blocks are collected in Table 1. As expected, the molecular weight distributions, obtained by SEC, are narrow, and the calculated molecular weights are in good agreement with the measured SEC and vapor pressure osmometry (VPO) data.

In the second polymerization step the hydroxyl polymers were deprotonated and transferred into the macroinitiators PI-OK and PEP-OK by the reaction with cumylpotassium. For this purpose protic impurities like methanol, the precipitant for the hydroxyl polymers, had to be removed completely. The impurities would also react with cumylpotassium and initiate the homopolymerization of EO. Therefore, the polymers were dissolved in dry benzene, the solvent was removed

Scheme 1

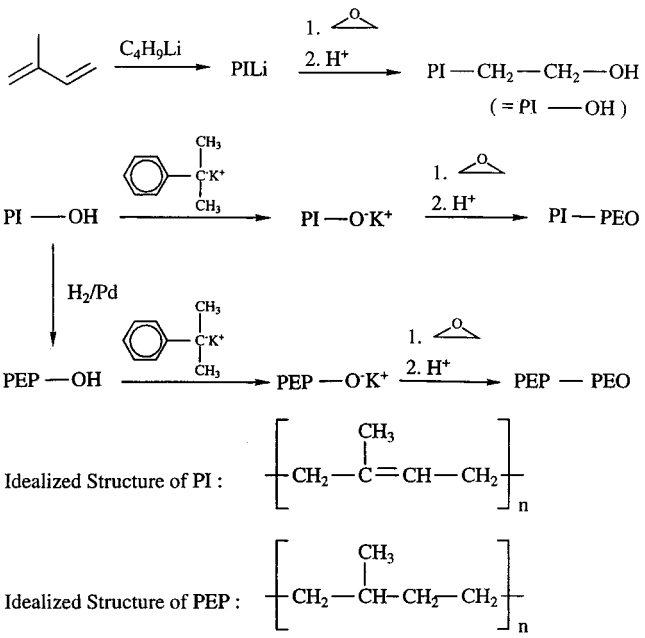

Table 1. Molecular Weight Characterization of the Precursors PI-OH and PEP-OH

	M_n		M_w/M_n	M_n	
sample	calcd	SEC	(SEC)	VPO	titration
PI5-OH	4500	4220[a]	1.03	4280	
PEP5-OH	4630	4860[b]	1.03	4480	4770
PI5′-OH	4600	4500[a]	1.03	4310	
PEP5′-OH	4740	5290[b]	1.03	4690	4720
PI22-OH	21 500	21 500[a]	1.02		20 900
PEP22-OH	22 100	22 000[b]	1.02		22 200

[a] Based on PS calibration, transformed into PI molecular weights. [b] Based on PS calibration, transformed into PEP molecular weights.

under reduced pressure, and the polymers were stirred under high vacuum for 1 day. In the case of PI-OH the stirring was carried out at room temperature. PEP-OH was heated to 100 °C because of its higher thermal stability. This measure increased the efficiency of the purification process. The complete procedure was repeated twice to remove all volatile protic impurities. It turned out that the high-vacuum technique, using all glass apparatus, is the ideal method for this procedure. Thus, the contamination of the polymers with air was excluded, since the reaction products of oxygen and cumylpotassium would also homopolymerize EO. The following titration of the polymers, as solution in THF, with the deeply red colored cumylpotassium was conducted likewise under high-vacuum conditions to avoid any contact of the reactants with air or moisture. Since the deprotonation of the hydroxyl polymer is a fast reaction, the decoloration of the added organometallic compound occurred immediately. At the end point of the titration the polymer solution turned slightly orange. This color disappeared after 1−2 h, indicating a slight excess of hydroxyl polymer in the system. Supplementary experiments proved that further addition of small traces of cumylpotassium resulted in a permanent coloration of the solution.

The titration can also be considered as end group analysis to determine M_n of the precursor polymers. The values, obtained by this method, are listed in Table 1. They agree very well with the calculated M_n and those obtained from VPO and SEC. The results for the PEP-OH also indicate that the terminal hydroxyl groups remain completely untouched during the hydrogenation reaction.

The resulting macroinitiators PI-OK and PEP-OK were used to polymerize EO. After consumption of all monomer, samples for the SEC analysis were taken directly from the reactor without purifying the polymer. The use of pure THF as eluant was already reported for the analysis of PS−PEO block copolymers.[1,3] For the analysis of the PI−PEO and PEP−PEO block copolymers, however, THF was not suitable. This is shown in Figure 1a. The SEC traces of a PEO homopolymer (M_n = 28 000, M_w/M_n = 1.03) and a PI−PEO block copolymer (total M_n = 35 400, M_w/M_n = 1.02, 41% PEO content) were obtained, using THF as eluant. The unusual shape of the signals is probably due to interactions between the polar PEO and the column material, which can be suppressed by polar solvents like DMA. The results, obtained with a mixture of 90% THF and 10% DMA, are given in Figure 1b. In this case the chromatograms show the characteristic shape for polymers with a narrow molecular weight distribution. Using the solvent mixture additional SEC experiments with PI and PEP homopolymers were performed. Although DMA is a nonsolvent for these polymers, the shape of the signal was identical with that in pure THF. Owing to these results the THF/DMA mixture was taken for all further SEC experiments.

The presence of homopolymer in the products was examined with block copolymers, having different relations of the block molecular weights. The SEC trace of PEP5−PEO2 (calculated block molecular weights M_n(PEP) = 4630, M_n(PEO) = 1500) is shown in Figure 2a. The absence of PEO homopolymer indicates that the purification process of the precursor is highly efficient. SEC details of the PEP5−PEO15 system (calculated molecular weights M_n(PEP) = 4630, M_n(PEO) = 14 600) are given in Figure 2b. Residues of the precursor,

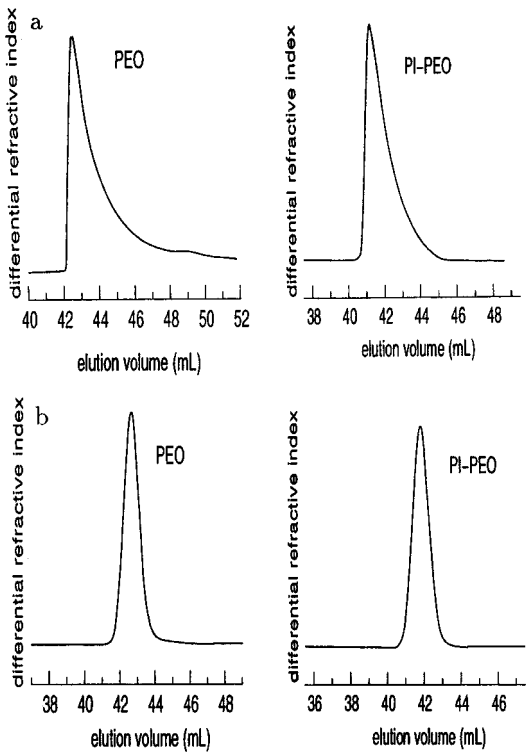

Figure 1. SEC traces of a PEO homopolymer (M_n = 28 000, M_w/M_n = 1.03) and a PI−PEO block copolymer (total M_n = 35 400, M_w/M_n = 1.02, 41% PEO content) using as eluant: (a) THF and (b) a mixture of 90% THF and 10% DMA (by vol).

arising from slight undertitration with cumylpotassium, are not visible. The fast proton exchange between the protonated and deprotonated chain ends compared to the slow propagation reaction allows a homogeneous growth of all chains.[3] The titration method is not limited to low molecular weights. Even block copolymers with PI and PEP molecular weights of M_n = 23 000 were synthesized without detectable amounts of homopolymer. Further evidence for the accuracy of the method is given in Table 2. The predicted molecular weights fit well with the M_n obtained from MO and combined NMR−VPO or NMR−end group titration measurements. The molecular weight distributions, obtained by SEC, are in the range usually obtainable by living anionic polymerization under high-vacuum conditions.

In order to study the aspect of undertitration polymer PI5−PEO15 was synthesized. Instead of titrating the precursor polymer, the molar amount of hydroxyl groups was calculated from M_n and the weight of the PI5-OH sample. Thereupon, the polymer was reacted with 50% of the stoichiometric requirement of cumylpotassium. After addition of EO the system was allowed to polymerize for 1 week to ensure complete conversion of all monomer. A SEC trace of the unpurified sample, taken directly from the reactor, is given in Figure 2c. No remaining PI5-OH homopolymer is visible; however, the block copolymer signal shows a small tailing toward the low molecular weight side. Nevertheless, the molecular weight analysis of PI5−PEO15 is in good agreement with the expected values (Table 2). These facts indicate that the proton exchange between protonated and deprotonated chain ends is fast enough to guarantee an almost homogeneous growth of all chains. Comparing the SEC results of PI5−PEO15 with the data obtained from polymers synthesized with the titration method, it is obvious that the latter procedure is the better one,

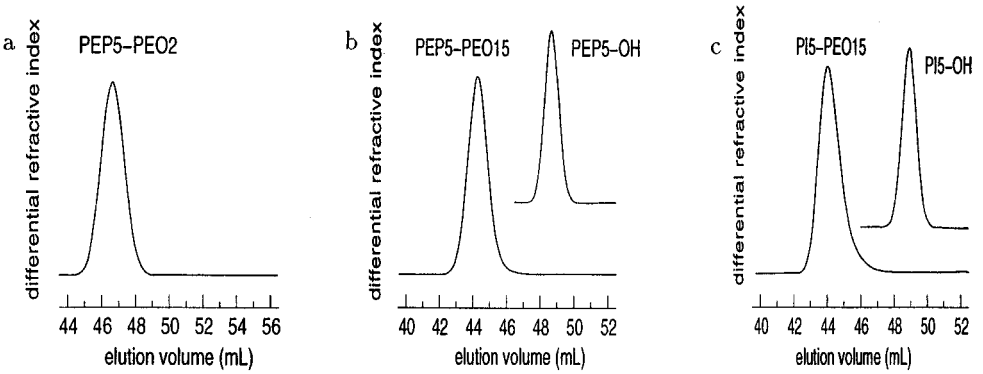

Figure 2. SEC traces of some block copolymers and the corresponding precursors.

Table 2. Molecular Weight Characterization of the Block Copolymers

sample	M_n(PEO block) calcd	M_n(PEO block) NMR	$M_{n(total)}$ calcd	$M_{n(total)}$ MO	$M_{n(total)}$ NMR	M_w/M_n (SEC)
PEP5−PEO2	1500	1200[a]	6130		5970[a]	1.04
PEP5′−PEO5	5780	5910[a]	10 500		10 600[a]	1.03
PEP5−PEO15	14 600	14 100[a]	19 200	19 200	18 900[a]	1.02
PI22−PEO15	15 500	14 500[a]	37 000	40 400	35 400[a]	1.02
PEP22−PEO11	11 000	10 600[a]	33 100	33 300	32 800[a]	1.02
PI5−PEO15	14 200	13 400[b]	18 700	20 600	17 700[b]	1.03

[a] Calculated from M_n(titration) of PI-OH and PEP-OH, respectively, and the composition by NMR. [b] Calculated from M_n(VPO) of PI-OH and the composition by NMR.

Table 3. Composition of the Block Copolymers and Their Solubility in Water and *n*-Decane

	composition by NMR		solubility	
sample	wt % PEO	wt % PI or PEP	in water	in *n*-decane
PEP5−PEO2	20	80	no	yes
PEP5′−PEO5	56	44	yes	yes
PEP5−PEO15	75	25	yes	yes
PI5−PEO15	76	24	yes	yes
PI22−PEO15	41	59	yes	yes
PEP22−PEO11	32	68	no	yes

but it seems possible that slight understoichiometric addition of cumylpotassium to the hydroxyl polymer yields products of a quality similar to those from the titration method. This measure would simplify the synthesis of the block copolymers.

In a further experiment an attempt was made to hydrogenate polymer PI22−PEO15 in order to obtain the corresponding PEP−PEO block copolymer. However, NMR analysis revealed that the PI block remained completely unsaturated. It is likely that interactions between the polar PEO and the palladium catalyst prevent the hydrogenation. No further experiments were done to examine the problem, since the direct hydrogenation of the PI-OH allows the synthesis of PEP−PEO block copolymers as well.

The purification of the products by precipitation was found to be a complex problem. In most common solvents either the hydrophilic or the hydrophobic block is soluble and causes the formation of micelles without precipitation of the polymer. Finally the use of acetone at low temperatures allowed the precipitation and elimination of initiator residues in the polymers.

First experiments were carried out to examine the solubility of the block copolymers. It was found that even the polymer, containing 41% PEO and having a total molecular weight of M_n = 35 400, forms soluble aggregates in water at room temperature (see Table 3). The polymers with a PEO content of 33% or less are insoluble in water. In contrast, PS−PEO block copolymers are water soluble, if the PEO content is higher than 50% and the PS block molecular weight is less than M_n = 5000. In order to obtain solubility at higher molecular weights, even higher PEO contents are required.[1,6] In *n*-decane all materials synthesized in this work form soluble aggregates, although the block copolymer with the smallest hydrophobic part contains only 24% PI, whereby M_n is 17 700. Detailed investigations are now in progress to examine the micellar behavior of the block copolymers.

Conclusion

In this work we have described the synthesis of well-defined block copolymers, having a hydrophobic poly-1,4-diene or corresponding hydrogenated polyolefin block and a hydrophilic PEO block. The two-step anionic polymerization process is demonstrated with PI−PEO and PEP−PEO systems. The characterization of the products by SEC shows narrow molecular weight distributions and the absence of homopolymer in the block copolymers. The calculated molecular weights and compositions are in good agreement with the results, obtained by MO, VPO, end group titration, and NMR. Comparing the materials with the broadly used PS−PEO block copolymers indicates that the latter ones are of minor quality since they usually contain homopolymer and show broader molecular weight distributions.

First solubility experiments indicate that micellar solutions are obtained in water and in *n*-decane even at relatively high contents of the nonsoluble block. Owing to their compatibility with water and aliphatic hydrocarbons and the fact that the hydrophilic lipophilic balance can be tailored easily by variation of the block length, the materials described here are potential candidates for applications as surfactants.

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