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Synthesis of Hydrophobic Poly(alkylene oxide)s and Amphiphilic Poly(alkylene oxide) Block Copolymers

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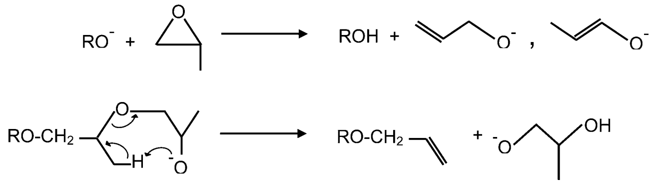
ABSTRACT: The anionic ring-opening polymerization of alkylene oxides, except ethylene oxide, is accompanied by strong side reactions, leading to high molecular weight and low molecular weight byproducts. In this work we investigated the anionic polymerization of hydrophobic alkylene oxides at different temperatures, solvents, and initiating systems. For polymers synthesized in the temperature range between 40 and 80 °C and employing potassium and cesium alcoholate initiators significant amounts of byproducts were found. With the help of crown ethers the temperature could be reduced to −23 °C without extending polymerization times too much. This measure allowed eliminating byproducts almost completely. The best results were obtained with potassium alcoholates and 18-crown-6 in toluene at −10 to −23 °C. Poly(1,2-butylene oxide), poly(1,2-hexylene oxide), and poly(1,2-octylene oxide) homopolymers were synthesized up to molecular weights in the range of 50 000−100 000 and $M_w/M_n < 1.1$. Furthermore, the method was employed to synthesize amphiphilic block copolymers of the hydrophobic poly(alkylene oxide)s with poly(ethylene oxide) as the hydrophilic moiety. Block molecular weights reached up to 50 000. Even at those high molecular weights the contents of homopolymer byproduct did not exceed 1%. The results indicate that side reactions usually involved in the anionic polymerization of alkylene oxides were largely suppressed using the employed polymerization technique.

Introduction

The lowest members of the poly(alkylene oxide) (PAO) family, poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), are known for a long time. The most widely employed technique for the polymerization of alkylene oxides is anionic ring-opening polymerization using sodium or potassium alcoholates as initiators. Alternatively, mixtures of alcoholate and alcohol can be used. The proton exchange between OH groups and alcoholate is much more rapid than the monomer addition step so that both species, alcohol and alcoholate, uniformly generate polymer chains. The anionic technique allows to polymerize ethylene oxide (EO) basically free of side reactions. For the polymerization of propylene oxide (PO) strong side reactions are present. The reason for the side reactions is the relatively high acidity of the methyl protons of PO leading to different types of termination and chain transfer reactions. As a result, high and low molecular weight byproducts are formed.[1,2] The details are given in Scheme 1. The rate constant for the PO propagation step is on the order of 100 times higher than the rate constants for the side reactions. If one translates the rate constant ratio into molecular weights, the result is that the highest possible molecular weight for monofunctional PPO is ∼5000. However, if the goal is to synthesize PPO with narrower molecular weight distribution (MWD) or block copolymers with low homopolymer content, the maximum molecular weight for the PPO segments is considerably lower.

Scheme 1. Side Reactions during the Anionic Polymerization of PO



The nature of the side reactions and methods to minimize them were studied intensively for PPO.[3−15] It was found that reduction of the polymerization temperature and reduction of the metal content in the alcoholate−alcohol initiator mixture reduced byproducts and sharpened the MWD. In addition, crown ethers and softer counterions such as rubidium, cesium, or different phosphonium ions instead of sodium and potassium were used successfully. These measures allowed synthesizing PPO with molecular weights of several thousand and $M_w/M_n <$ 1.1. In the older literature, there are reports dealing with the synthesis of the higher and more hydrophobic PAO than PPO. Poly(1,2-butylene oxide) (PBO), poly(1,2-hexylene oxide) (PHO), poly(1,2-octylene oxide) (POO), and even higher PAO were obtained by polymerizing the corresponding monomers with zinc organic catalysts.[16−18] This technique, however, yields polymers with broad MWD and does not allow producing block copolymers. Scheme 2 illustrates the chemical structures of some poly(alkylene oxide)s and the corresponding monomers.

Block copolymers from EO and 1,2-butylene oxide (BO) have been synthesized by Booth and co-workers using conventional anionic polymerization conditions and reaction temperatures

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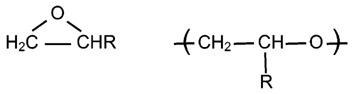
Scheme 2. Structures of Different Alkylene Oxide Monomers and Polymers



	monomer	polymer
R=H	ethylene oxide	polyethylene oxide (PEO)
R=CH_3	propylene oxide	polypropylene oxide (PPO)
R=CH_2-CH_3	1-butylene oxide	polybutylene oxide (PBO)
R=$(CH_2)_3$-CH_3	1-hexylene oxide	polyhexylene oxide (PHO)
R=$(CH_2)_5$-CH_3	1-octylene oxide	polyoctylene oxide (POO)

between 60 and 80 °C.[19−21] They also used crown ethers together with reaction temperatures between 60 and 110 °C.[22,23] Most of the polymers reported contained PBO blocks in the oligomeric range. Quirk and Ge described the synthesis of polystyrene−PBO block copolymers.[24] They used a polyiminophosphacene base for the polymerization of the PBO block. The molecular weights of the PBO blocks ranged up to several 10 000, but large quantities of PBO homopolymer were found in the block copolymer. Adachi and co-workers synthesized PBO homopolymers with molecular weights up to several 10 000. Despite the postfractionation, the MWD were broad.[25] In contrast to PPO, where side reactions were investigated intensively, there is little information about this subject for PBO and the higher PAO. Furthermore, the nature of side reactions during the anionic polymerization of BO is discussed controversially.[1,2] Because of the different chemical nature and acidity of the protons in the alkyl side chains of monomer and polymer, one cannot automatically assume the same types of side reactions being present in PPO and the higher PAO.

In contrast to the limited availability of the higher members, the poly(alkylene oxide) family offers interesting possibilities with respect to their physical properties. With increasing alkyl side chain R (see Scheme 2) the polymers get continuously more hydrophobic. PEO is water-soluble and used in a wide range of applications. PPO is soluble in cold water but insoluble in warm water. PEO−PPO block copolymers are widely used as surfactants despite the low amphiphilicity. PBO is the first member of the PAO family which is fully insoluble in water. By combining PEO with the other PAO, the amphiphilicity of the resulting block copolymers can be varied systematically. In addition to that, another aspect comes into play. PBO and its higher homologues are soluble in a large variety of nonpolar liquids including nonconventional oils like silicon oils.[26] These properties make the PAO block copolymers interesting candidates for the examination of interfacial properties, for example, at water−solid or water−oil interfaces. In those cases the compatibility of the hydrophobic moiety with the surface or its solubility in the oil is of crucial importance.[27] These parameters can be adjusted by changing the hydrophobicity of the nonpolar PAO block.

Beside the block copolymers also the PAO homopolymers are of interest because of the possibility to vary the side chain length and the low T_g values of about −70 °C,[18,28] which these materials exhibit. This allows continuously changing the polymer chain diameter, characterized by the packing length. This in turn influences dramatically the elastic properties defined by the plateau modulus because the plateau modulus scales with the inverse third power of the packing length.[29,30] In addition to that, all PAO except PEO have a dipole moment component parallel to the chain.[25] This allows a whole chain normal mode to be studied in addition to the single-monomer segmental mode. The two dielectric modes are the analogues of the mechanical terminal and glassy relaxation. Except polyisoprene, the PAO are the only common low-T_g polymers exhibiting this dielectric behavior. This scenario is interesting because it allows the combination of rheological investigations and dielectrical spectroscopy using the same materials.

In this work we report procedures for the anionic polymerization of BO, 1,2-hexylene oxide (HO), and 1,2-octylene oxide (OO) having molecular weights up to more than 50 000 and $M_w/M_n < 1.1$. The products are analyzed by SEC and NMR. In addition to that the synthesis of amphiphilic block copolymers with PEO as the hydrophilic moiety is described. By varying the hydrophobic part from PBO, PHO, and POO, this allows changing the amphiphilicity of the block copolymer systematically.

Experimental Section

Experimental Equipment. All manipulations were carried out at a high-vacuum line or in a glovebox filled with argon (M Braun, Unilab). The water level in the glovebox was usually below 1 ppm and the oxygen level below 0.1 ppm. The flasks for all manipulations were equipped with Teflon stopcocks that allowed to transfer materials between vacuum line and glovebox without contamination with air. The flasks that were exposed to overpressure were pressure tested to 4−12 bar, depending on the size of the flask.

Materials. Toluene (Merck, ≥99.9%) was degassed, distilled into another flask which contained sodium metal, and stirred over the sodium for at least 24 h before being degassed again and heated to 110−115 °C for 3−4 h. THF (KMF, ≥99.9%) was degassed, predried over CaH_2, and then distilled into a flask containing potassium metal and benzophenone. Dimethyl sulfoxide (DMSO) was degassed, distilled over CaH_2, and stirred for 2 weeks. After the drying process all solvents were distilled into other flasks and stored in the glovebox. Potassium metal (Fluka, >98%) and cesium metal (Riedel-deHaën, >99.5%) were used as received.

Potassium *tert*-butanolate (KOt-Bu) and cesium *tert*-butanolate (CsOt-Bu) were synthesized in the following way. *tert*-Butanol (Fluka, ≥99.7%) was degassed and reacted with potassium metal. After the metal had disappeared some *tert*-butanol was distilled into another flask and reacted with potassium metal or cesium metal. The molar ratio of alcohol to metal was about 5−7. After the metal had disappeared, the reaction mixture was frozen, and the excess alcohol was eliminated by sublimation. The sublimation was performed for 8 h at room temperature and then for 16 h at 80 °C. The crown ethers 18-crown-6 (18C6) (Aldrich, 99%), dibenzo-21-crown-7 (DB21C7) (Aldrich, 97%), dibenzo-24-crown-8 (DB24C8) (Merck, ≥99%), and 30-crown-10 (30C10) (Fluka, ≥97%) were freeze-dried under high-vacuum conditions with benzene, which was degassed and dried over *n*-butyllithium.

EO (Fluka, >99.8%) was condensed into a flask, degassed, and stirred over CaH_2 for 1−2 days. BO (Fluka, ≥99%) and part of the HO (Aldrich, 97%) were treated in the same way, except that the CaH_2 treatment was carried out twice for 3−7 days each. The rest of HO and OO (Aldrich, 96%) were first distilled using a distillation apparatus, equipped with a 50 cm Vigreux column. HO was distilled at normal pressure and OO under reduced pressure. For both monomers a middle fraction containing about 70% of the original material was degassed at the vacuum line and distilled over CaH_2. The mixture was stirred at room temperature for 1−2 weeks, and then the process was repeated. Finally, a third drying step over CaH_2 was carried out at 100 °C. In between each purification step the monomers were degassed to pump off the produced hydrogen gas. After the drying step all monomers were distilled in storage flasks and kept in the glovebox. EO was stored at −20 °C in a freezer, which was integrated in the glovebox. The other monomers were stored at room temperature.

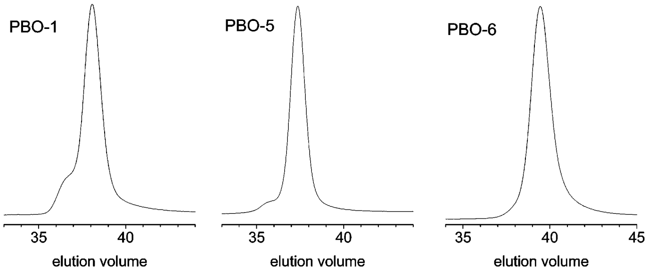


Figure 1. SEC refractive index signals of PBO samples with target molecular weights of 15 000, polymerized without crown ether at 80 °C in toluene (PBO-1), at 40 °C in toluene (PBO-5), and at 40 °C in THF/DMSO (PBO-6).

Polymerization Reactions. All polymerization reactions were carried out in 100 mL flasks, equipped with Teflon stopcocks. The flasks were pressure tested up to 12 bar. The flasks were filled inside the glovebox with KOt-Bu or CsOt-Bu and optionally with crown ether. Precise weight control was achieved by the use of an analytical balance which was installed in the glovebox. Then the solvent was added. Monomer was introduced also in the glovebox, or in the case of reaction temperatures below room temperature, the monomer was distilled into the reaction flask at low temperature. The weight ratio of monomer to solvent was 1.0, and in a typical polymerization run 20 g of monomer was polymerized. Polymerization reactions were carried out in a thermostated bath or in a freezer. The reactions were terminated with acetic acid. Monomer conversions were determined by distilling away the solvent and residual monomer at the vacuum line. The remaining viscous polymer liquid was stirred for another 1−2 days under high-vacuum conditions to eliminate all volatile materials. The precise knowledge of all weights allowed to calculate monomer conversions accurately. The homopolymers were purified by dissolution in freshly distilled heptane followed by washing with deionized water. Then the heptane was removed, and the polymer was dried under high-vacuum conditions.

If block copolymers with PEO as the second block were synthesized, samples of the first block were taken in the glovebox and treated as described before. Additional solvent was added for the polymerization of the EO block. The required amount of EO was distilled in at the vacuum line at dry ice temperature. The polymerization of EO was carried out slightly above room temperature for 2−4 days. The additional amount of toluene was chosen so the final polymer concentration was 20−25%. This measure was necessary because the high incompatibility of the hydrophobic PAO with PEO lead to highly viscous solutions at higher polymer concentrations. After termination with acetic acid the solvent was removed, and the block copolymers were dissolved in warm acetone. The solutions were then cooled to −10 to −15 °C. The precipitated polymer was isolated by centrifugation followed by two washing cycles with cold acetone and high-vacuum drying.

After purification some polymers were analyzed with regard to residues of potassium and crown ether residues. No potassium or crown ether could be found. The detection limit was 0.0005 wt % for potassium and 0.08 wt % for the crown ether. In the case of a polymer with a molecular weight of 5000 this corresponds to 0.06% of the potassium, and 1.0% of the crown ether initially used in the synthesis. Finally, it should be pointed out that the use of crown ethers accelerates alkylene oxide polymerizations strongly. In the case of too low heat dissipation this can lead to the explosion of the polymerization reactor. This is especially important for EO. Therefore, such reactions should be carried out only by experienced personnel and using adequate equipment.

Polymer Characterization. SEC experiments for the characterization of PAO homopolymers were carried out using a Waters 150-CV plus instrument together with five Styragel columns with a porosity range from 10^5 to 500 Å at 30 °C. For the signal detection a Viscotec model TDA 300 triple detector with a differential refractometer, a differential viscometer, and a right angle laser light scattering detector were used at 35 °C. The solvent was THF at a flow rate of 1 mL/min, which was degassed using a Viscotec model VE 7510 instrument. Molecular weights were calculated using the Viscotec TriSEC 3.0 GPC software. Block copolymers were characterized using a Polymer Laboratories PL 220 SEC instrument together with five Styragel columns with a porosity range from 10^5 to 500 Å at 30 °C. The solvent was a mixture of THF and *N*,*N*-dimethylacetamide (DMA) (90:10 by volume) at a flow rate of 1 mL/min. The NMR spectra were obtained on a Varian Inova 400 MHz. All samples were measured at 295 K in $CDCl_3$ with a 5 mm PFG AutoX DB Probe.

Results

1. Optimization of BO Homopolymerization. 1.1. Variation of Counterions, Temperature, and Solvent. In a first series of experiments the target molecular weight, defined by the amounts of monomer and initiator introduced into the reactor, was 15 000. The temperature was 80 °C, and toluene was chosen as an inert solvent. The SEC trace of sample PBO-1, where KOt-Bu was used as initiator, is given in Figure 1. Beside the main peak the signal contains a low molecular weight tailing and a high molecular weight shoulder. In agreement with this result, the MWD is elevated and the measured molecular weight is visibly smaller than the calculated molecular weight, obtained from the amounts of initiator and polymerized monomer (Table 1). For sample PBO-2 KOt-Bu was replaced by its cesium analogue CsOt-Bu. This measure allowed to cut in half the polymerization time needed to obtain almost quantitative monomer conversion. The amounts of high and low molecular weight byproducts were reduced slightly. This is reflected in a better comparison of the calculated and measured molecular weights and the narrower MWD compared to PBO-1 (see Table 1). In the next step CsOt-Bu was replaced by an equimolar mixture of CsOt-Bu and *tert*-butanol (sample PBO-3). The reduction of the metalation degree increased polymerization time without changing the byproduct fraction.

Using again fully metalated CsOt-Bu, the reaction temperature was reduced to 60 °C (PBO-4) and 40 °C (PBO-5). This measure slowed down the polymerization and considerably reduced the amount of byproduct. The calculated and the measured molecular weights, given in Table 1, coincide reasonably well, and the MWD is narrower than for the experiments before. Figure 1 shows the SEC trace of PBO5. Only small quantities of high and low molecular weight material are visible. For sample PBO-6 toluene was replaced by a mixture of 66 wt % THF and 34 wt % DMSO. The temperature was kept at 40 °C. From Table 1 it is visible that this measure increases the reactivity and allowed almost full monomer conversion in 37 h. However, the disagreement between calculated and measured molecular weights as well as the MWD indicates again increasing amounts of byproducts. The SEC trace of PBO-6 clearly shows a shift of the peak position to the longer retention time and a broader peak with a pronounced low molecular weight tailing (Figure 1).

1.2. Use of Crown Ethers in Combination with Different Counterions. In all the experiments of this series toluene was the solvent and crown ethers were added. To ensure that the cations were complexed quantitatively, the molar ratio of crown ether to metal was 3. The polymerization temperature was held constant at 20 °C. In order to more visualize the byproducts, the target molecular weight was increased to about 50 000. PBO-7 represents the sample where 18C6 was used together with KOt-Bu. Figure 2 shows the SEC chromatogram of PBO-7. On the high molecular weight side the shoulder has disappeared completely, but there still is a low molecular weight

Table 1. Reaction Conditions and Characterization of PBO Synthesized under Different Reaction Conditions without Crown Ether

	counterion/ metalation degree	polymerization temp (°C)	solvent	reaction time (h)	monomer conv (%)	calcd M_n[a]	measd M_n[b]	M_w/M_n[c]
PBO-1	K/100%	80	toluene	40	96	14 700	11 200	1.15
PBO-2	Cs/100%	80	toluene	18	97	14 800	11 700	1.11
PBO-3	Cs/50%	80	toluene	38	95	14 600	11 700	1.11
PBO-4	Cs/100%	60	toluene	38	94	13 800	14 400	1.06
PBO-5	Cs/100%	40	toluene	168	97	14 500	13 600	1.08
PBO-6	Cs/100%	40	THF/DMSO[d]	37	95	16 400	7 800	1.12

[a] Calculated from the amounts of initiator and polymerized monomer. [b] From GPC coupled with triple detection. [c] From GPC, PS calibration. [d] 34 wt % DMSO, 66 wt % THF.

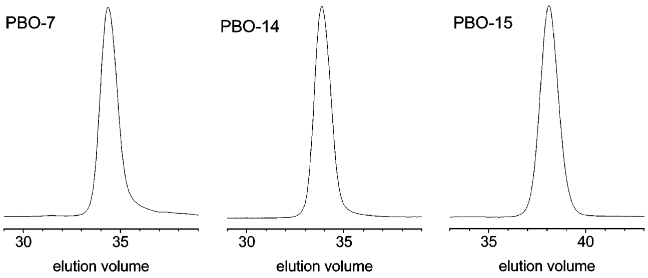


Figure 2. SEC refractive index signals of PBO samples polymerized with crown ether: at 20 °C and target molecular weight 50 000 (PBO-7), at −23 °C and target molecular weight 50 000 (PBO-14), and at −20 °C and target molecular weight 10 000 (PBO-15).

tailing. This result is reflected in the molecular weight characterization given in Table 2. In addition, the crown ether caused a considerable increase in polymerization rate although the temperature was lowered compared with the experiments without crown ether. In the next experiment (PBO-8) an equimolar mixture of KOt-Bu and *tert*-butanol was used as initiator system. The SEC results showed no substantial change, but the polymerization time increased dramatically. Samples PBO-9 to PBO-12 represent experiments where CsOt-Bu was used as initiator together with the crown ethers 18C6, DB21C7, DB24C8, and 30C10. In all these experiments polymerizations were slower than for the system KOt-Bu/18C6. Except for the system CsOt-Bu/18C6, the polymerization rates were so low that the experiments were stopped at low conversion and the products were not analyzed. For PBO-9, obtained with CsOt-Bu/18C6, the molecular weight analysis given in Table 2 shows again no improvement.

In a further series of experiments the reaction conditions from PBO-7 were taken as starting point. For the samples PBO-13 and PBO-14 the temperature was reduced to 0 and −23 °C, respectively. Accordingly, the polymerization times increased (Table 3). The comparison of the molecular weight analysis results for samples PBO-7, PBO-13, and PBO-14 shows that the lower the temperature, the better the calculated and the measured molecular weights coincide and the MWD gets narrower. These results are confirmed by the inspection of the SEC trace of PBO-14, given in Figure 2. The signal shape is almost symmetrical, and there is only a minor low molecular weight tailing. PBO-15 represents an example where the target molecular weight was reduced to 10 000. Otherwise, the polymerization conditions were comparable with sample PBO-14. The results shown in Figure 2 and Table 3 demonstrate that the material is perfectly polymerized. For sample 16 toluene was replaced by a mixture containing 33 wt % DMSO and 67 wt % THF. Although the reaction temperature was −10 °C, monomer conversion was small, so that this experiment was not continued.

2. Optimization of HO and OO Homopolymerization. First HO was polymerized under the same conditions as used for PBO-7 at room temperature and using KOt-Bu/18C6 as initiating system. The target molecular weight was 70 000 to obtain the same polymerization degree for PHO and PBO. The results for this polymerization experiment (PHO-1) are summarized in Table 4. It is clearly visible that the polymerization of HO took place much slower than the case of BO. The calculated and measured molecular weights differ significantly, and the MWD is relatively broad. In the SEC trace a small high molecular weight shoulder and a strong low molecular weight tailing were visible.

For both monomers, BO and the HO used in experiment PHO-1, the purification included two drying cycles over CaH_2 at room temperature. For further experiments with HO the monomer purification was carried out more rigorously. The details are described in the Experimental Section. This measure reduced the polymerization time. The MWD remained broad (PHO-2, Table 4), although in the SEC diagram the high molecular weight shoulder disappeared. In the next step the temperature was reduced to −23 °C (PHO-3). The results are summarized in Figure 3 and Table 4. Despite a small low molecular weight tailing, the MWD remained relatively narrow and the calculated and measured molecular weights agree well.

The polymerization experiments with OO were carried out from the beginning with rigorously purified monomer. The polymerization conditions for POO-1 were identical to PBO-14 and PHO-3, except that the target molecular weight was 85 000 in order to obtain the same polymerization degree as for PBO-14 and PHO-3. In this case the polymerization reaction was not terminated after a given time, but several samples were taken at different times. For the first sample after 189 h the monomer conversion was 73% (see Table 4). The SEC diagram showed an almost symmetrical signal having a small low molecular weight tailing and a narrow MWD. The next sample was taken after 356 h, where the monomer conversion was 89%. However, M_w/M_n increased from 1.06 to 1.10, and the low molecular weight tailing got more prominent. The result was even worse after 600 h where the conversion was 93%. The GPC results revealed a strong low molecular tailing together with $M_w/M_n = 1.43$. In agreement with that the measured molecular weight is considerably below the calculated value; it is even lower than the one from the sample before. POO-2 represents an example where the polymerization conditions were slightly varied compared to POO-1. The target molecular weight was reduced to 53 000, and the reaction temperature was −14 °C. After 187 h the monomer was almost completely converted into the polymer. The SEC signal shown in Figure 3 indicates that the MWD is narrow; no low molecular weight byproduct is visible. The calculated and measured molecular weights coincide well.

PHO-4 and POO-3 represent polymers where the target molecular weight was reduced to 10 000. The polymerization temperature was −15 °C. At lower temperatures solid material in the polymerization reactors indicated only partially solubilized initiator or crown ether. The molar ratio of crown ether to

Table 2. Reaction Conditions and Characterization of PBO Synthesized with the Help of Crown Ethers at Room Temperature

	counterion/ metalation degree	crown ether	polymerization temp (°C)	reaction time (h)	monomer conv (%)	calcd M_n[a]	measd M_n[b]	M_w/M_n[c]
PBO-7	K/100%	18C6	20	19	92	47 000	43 600	1.11
PBO-8	K/50%	18C6	20	1018	94	47 700	40 400	1.08
PBO-9	Cs/100%	18C6	20	68	81	39 600	28 000	1.13
PBO-10	Cs/100%	DB21C7	20	22	2			
PBO-11	Cs/100%	DB24C8	20	22	2			
PBO-12	Cs/100%	30C10	20	474	11			

[a] Calculated from the amounts of initiator and polymerized monomer. [b] From GPC coupled with triple detection. [c] From GPC, PS calibration.

Table 3. Reaction Conditions and Characterization of PBO Synthesized with the Help of Crown Ethers at Low Temperatures

	counterion/ metalation degree	crown ether	polymerization temp (°C)	reaction time (h)	monomer conv (%)	calcd M_n[a]	measd M_n[b]	M_w/M_n[c]
PBO-7	K/100%	18C6	20	19	92	47 000	43 600	1.11
PBO-13	K/100%	18C6	0	41	91	45 600	44 400	1.08
PBO-14	K/100%	18C6	−23	187	97	49 400	49 600	1.07
PBO-15	K/100%	18C6[d]	−20	39	97	9790	10 200	1.04
PBO-16[e]	K/100%	18C6	−10	40	8			

[a] Calculated from the amounts of initiator and polymerized monomer. [b] From GPC coupled with triple detection. [c] From GPC, PS calibration. [d] Molar ratio 18C6/K = 1.5, instead of 3 for the other samples. [e] Solvent: 33 wt % DMSO, 67 wt % THF.

Table 4. Reaction Conditions and Characterization of PHO and POO Synthesized with the Help of Crown Ethers at Low Temperatures

	counterion/ metalation degree	crown ether	polymerization temp (°C)	reaction time (h)	monomer conv (%)	calcd M_n[a]	measd M_n[b]	M_w/M_n[c]
PHO-1	K/100%	18C6	20	307	91	64 400	45 800	1.17
PHO-2	K/100%	18C6	20	92	99	67 800	52 500	1.18
PHO-3	K/100%	18C6	−23	187	84	56 500	52 700	1.09
POO-1	K/100%	18C6	−23	189	73	61 600	50 000	1.06
				356	89	75 800	64 000	1.10
				600	93	79 200	55 100	1.43
POO-2	K/100%	18C6	−14	187	98	51 300	48 900	1.05
PHO-4	K/100%	18C6[d]	−15	70	97	9 840	9 380	1.03
POO-3	K/100%	18C6[d]	−15	70	98	10 000	9 570	1.05

[a] Calculated from the amounts of initiator and polymerized monomer. [b] From GPC coupled with triple detection. [c] From GPC, PS calibration. [d] Molar ratio 18C6/K = 0.75, instead of 3 for the other samples.

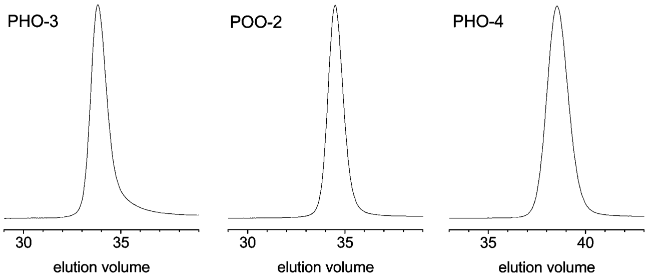


Figure 3. SEC refractive index signals of PHO and POO samples polymerized with crown ether: at −23 °C and target molecular weight 70 000 (PHO-3), at −14 °C and target molecular weight 53 000 (POO-2), and at −15 °C and target molecular weight 10 000 (PHO-4).

potassium was lowered to 0.75 compared to a value of 3 for the higher molecular weight samples. This measure also was necessary to limit the amount of crown ether in the polymerization experiment. Despite the low crown ether to potassium ratio after 70 h, monomer conversions were almost complete (Table 4). The SEC traces showed narrowly distributed polymers and the absence of low and high molecular weight byproducts (see Figure 3, sample PHO-4). For both polymers there is good agreement between calculated and measured molecular weights.

3. Block Copolymers. A−B block copolymers containing PBO, PHO, and POO as hydrophobic blocks and PEO as hydrophilic block were produced using the polymerization techniques described before. The samples PBO15-PEO, PHO4-PEO, and POO3-PEO represent block copolymers where the target molecular weights for the hydrophobic as well as the hydrophilic blocks were 10 000. The synthesis of the corresponding hydrophobic blocks was described before. Block copolymers were synthesized by adding more toluene and the required amount of EO into the reactor containing the living hydrophobic chains. The details are given in the synthetic part. The characterization results are summarized in Table 5. ^{1}H NMR was used to determine the block composition. Within experimental error the calculated compositions and the measured ones are similar. The small values of M_w/M_n indicate narrowly distributed polymers. As an example, the SEC trace of PBO15-PEO raw material before purification is given in Figure 4. It shows a symmetrical signal. At higher elution times there is no hint for homopolymer.

Sample PBO17-PEO represents a block copolymer where the target molecular weight for both blocks was 50 000. The synthetic procedures were the same as described before for the other block copolymers. Analytical results are given in Table 5. They show no significant difference with respect to product quality to the values obtained for the lower molecular weight block copolymers. The SEC chromatogram of the block copolymer after termination given in Figure 4 indicates a narrowly distributed polymer; there is only a small low molecular weight tailing visible.

Discussion

1. PBO. In this work tertiary alcoholates were used as initiators because of their higher solubility in nonpolar solvents compared to primary and secondary alcoholates. Generally, the reactivity order for the initiation step of alcoholates with alkylene oxides is primary > secondary > tertiary. The reactive chain end after the initiation is a secondary alcoholate, except for EO where a primary alcoholate is formed. Therefore, the initiation

Table 5. Characterization of PAO Block Copolymers

	hydrophobic block		block copolymer			
	M_n[a]	M_w/M_n[b]	mass % PEO calcd[c]	mass % PEO measd[d]	M_n[e]	M_w/M_n[b]
PBO15-PEO	10 200	1.04	50	53	21 700	1.04
PHO4-PEO	9 380	1.03	51	53	20 000	1.07
POO3-PEO	9 570	1.05	50	52	20 300	1.09
PBO17-PEO	50 600	1.06	51	52	105 000	1.06

[a] From GPC coupled with triple detection. [b] From GPC, PS calibration. [c] Calculated from the amounts of living first block and EO monomer added. [d] From ^{1}H NMR. [e] From M_n (hydrophobic block) and composition by ^{1}H NMR.

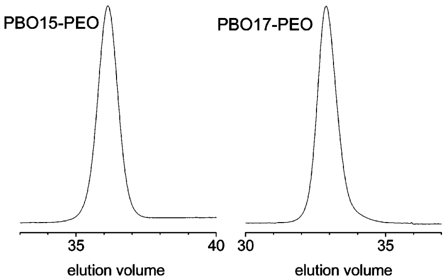


Figure 4. SEC refractive index signals of PAO block copolymer samples with block molecular weights of ∼10 000 (PBO15-PEO) and with block molecular weights of ∼50 000 (PBO17-PEO).

rate is slower than the propagation rate if tertiary alcoholates are used as initiators. However, our own experiments, not reported here, have shown that it is possible to obtain narrowly distributed PEO with molecular weights on the order of 1000 using KOt-Bu as initiator. For this reason the tertiary alcoholate initiators cannot be a reason for broader MWD of polymers synthesized in this work.

From the polymerization experiments PBO-1 to PBO-5 several conclusions can be drawn. First, the simultaneous appearance of high and low molecular weight byproducts suggests that the underlying mechanisms of the side reactions are similar for PBO and PPO. The first reaction shown in Scheme 1 for PO yields new monofunctional initiator molecules, and the second reaction leads to terminated polymer chains. As a result, both processes cause low molecular weight byproducts. The difunctional initiator being created together with the terminated chains is responsible for the production of polymer molecules having different chain lengths. Difunctional chains which grow from early reaction times have molecular weights higher than the chains being regularly initiated. Difunctional chains created at later polymerization stages contribute to the low molecular weight tailing. The expected SEC scenario from the sum of all these processes corresponds qualitatively with the SEC traces shown in Figure 1. The second result from the first series of PBO polymerization experiments is that the measured polymerization degrees are between 150 and 200 and are not too different from the calculated values, assuming no side reactions. In the case of PPO synthesized under the same conditions the strong side reactions limit the maximum polymerization degree to ∼100. This clearly shows that side reactions are less vigorous for PBO than for PPO.

The polymerization experiments PBO-1 to PBO-5 also show that the softer counterion Cs increases the polymerization rate compared to K and allows reducing the polymerization temperature to 40 °C. This measure minimizes both low and high molecular weight byproducts, leading to a fairly narrow MWD in samples PBO-4 and PBO-5. This is in agreement with the findings for PPO. Because of the low polymerization rates, no experiments were carried out below 40 °C and without crown ether. The use of alcoholate/alcohol mixtures as initiator instead of the pure alcoholate was not successful. This measure lowered the polymerization rate but did not reduce the amount of byproducts as was reported for PPO.[4,7,13] The replacement of toluene by a mixture of THF and DMSO led to the wanted effect of increasing the polymerization rate but was negative with respect to byproduct level. More polar solvents or solvent mixtures than the one used could not be tested because of insolubility of PBO in these media.

Crown ethers are strong complexing agents for alkali metal ions. Especially in less polar solvents they increase the degree of ion-pair separation. In the case of alkylene oxide polymerization this leads to increasing reactivities and polymerization rates. For PPO most of the reports dealing with this subject found that crown ethers suppress side reactions relative to chain propagation;[5−7] however, there is also a report where crown ethers increased the amount of byproduct.[14] Crown ethers also were used as an additive in the polymerization of BO.[19,20] Because of the relatively low molecular weights, it is not clear from these reports whether crown ethers are useful in suppressing side reactions in the BO case, too.

In our work crown ethers were used to reduce the polymerization temperature considerably below room temperature. Because of the low level of byproducts already achieved in PBO-4 and PBO-5, the target molecular weight was increased from 15 000 to 50 000. This measure increases the relative fraction of byproducts and helps to get a clearer picture about improvements of the product quality. As a consequence of the increased reactivity, the initiator system KOt-Bu/18C6 allowed almost full monomer conversion at 20 °C within 19 h for sample PBO-7. Under these conditions the formation of high molecular weight byproduct is suppressed completely. The low molecular weight tailing still exists. The comparison of the SEC traces PBO-7 and PBO-5 shows that the amounts of low molecular byproduct are almost similar for these two experiments. However, as the target molecular weight of PBO-7 was more than 3 times as high as for sample PBO-5, the same absolute amount of byproduct means that the side reaction relative to chain propagation is more suppressed for PBO-7. In agreement with the experiments carried out without crown ether, the use of alcoholate/alcohol initiator mixtures (PBO-8) slowed down reactivity so much that these systems were regarded being useless for applications. The reduced reactivity cannot be explained only with the smaller concentration of active head groups. In the case of PPO qualitatively the same scenario was seen and explained with strong hydrogen bonds between OH and OK head groups.[4]

The replacement of KOt-Bu by CsOt-Bu had no positive influence on the byproduct level and reduced reactivity. This might be explained at first view by the fact that 18C6 forms a very strong complex with potassium ions because the cavity diameter of 18C6 is almost identical with the diameter of the potassium ion. The diameter of the cesium ion is larger leading to weaker complexes with 18C6. However, when CsOt-Bu was used in combination with crown ethers having larger cavities, the polymerization rate even decreased. The same qualitative scenario was seen before for the polymerization of PO using different alkali metal alcoholates and crown ethers.[14] On a closer examination of the complexing behavior of alkali metal ions with crown ethers it gets clear that these results cannot be explained by nonideal agreement of the diameters of the metal ion and the crown ether cavity. For all alkali metals from K to Cs in combination with all crown ethers from 18C6 to 30C10 the equilibrium constants are higher than 10^3.[31] This is valid even for polar solvents like methanol, where the equilibrium constants are smaller than in nonpolar solvents. This simply means that for all polymerization experiments carried out with crown ethers the equilibrium between complexed and free alkali metal ion was basically complete on the complex side. Knowing this, one would expect approximately the same polymerization rates for all crown ethers. But this is not the case. An explanation could be that initiator systems of CsOt-Bu with crown ethers more favor side reactions leading to byproducts with OH-end groups than the system 18C6/K does. This in turn would slow down polymerization rates. In fact, for the system 18C6/Cs (PBO-9) the polymerization proceeds slower than for the system 18C6/K (PBO-7), and for PBO-9 the SEC trace shows a stronger tailing on the low molecular weight side. It should be pointed out that this explanation assumes that the PBO side reactions are similar to PPO, where the low molecular weight byproduct molecules contain OH-end groups.

The high reactivity of the initiator system KOt-Bu/18C6 made it possible to lower the reaction temperature to −23 °C. Under these conditions the side reactions are suppressed almost completely. For a molecular weight of 50 000 a small low molecular weight tailing reveals a minor amount of byproduct (sample PBO-14). If the molecular weight is lowered to 10 000, no byproduct is visible from the SEC analysis (sample PBO-15). From the results obtained without crown ether it was assumed that polar solvents help to increase reactivity at low temperatures. However, in the presence of 18C6 the replacement of toluene by a mixture of 33 wt % DMSO and 67 wt % THF reduced the polymerization rate drastically already at −10 °C. As 18C6 very efficiently complexes K ions, it would make sense that the polar solvent mixture does not additionally increase the polymerization rate. The reduction can only be explained if one again assumes that in DMSO/THF mixtures side reactions are more favored than in toluene.

2. PHO and POO. In principle, one would expect that the results found for PBO can be transferred to the polymerization of the more hydrophobic alkylene oxides. However, the first experiment carried out with HO at room temperature (sample PHO-1) resulted in a much lower polymerization rate and broader MWD compared to the experiment with BO under similar conditions (PBO-7). It turned out that the monomer purification was the key step to improve the results for HO as well as OO polymerization experiments. Whereas the purity of the commercial low molecular weight alkylene oxides from EO to BO is typically 99.9%, the values for HO and OO used in this work were 98.8% and 98.7%, respectively. Therefore, additional fractional distillation and a more rigid drying procedure were necessary for HO and OO. These procedures minimized the impurity level, increased the rate of polymerization, and so permitted to carry out the polymerization reactions at low temperatures. Nevertheless, the polymerization rate decreased from PBO to POO. For samples PBO-14, PHO-3, and POO-1 the reaction conditions are similar, but the monomer conversion after 187 h decreases from 97% for PBO to 73% for POO. To understand this result, it is necessary to remind that these polymerization experiments were carried out always with the same mass ratio of monomer to solvent. This leads to decreasing initiator and monomer concentrations on a molar level from PBO to POO, associated with lower reactivities of the HO and OO systems and incomplete monomer consumption at −23 °C at the given reaction time. In the case of POO-2 a slight increase of the reaction temperature to −15 °C was enough to almost quantitatively polymerize the monomer and keep the MWD narrow. As expected at molecular weights of 10 000, perfectly polymerized products were obtained. In this context it is important to note that the increase of reaction time for the systems with low reactivity negatively influences the structural quality of the products. In the case of POO-1, where the target molecular weight was 85 000 and the polymerization temperature −23 °C, with increasing reaction time the monomer conversion could be elevated; however, the MWD simultaneously broadened strongly. Although the polymerization continued, the measured molecular weight after 600 h of polymerization time was smaller than the value found after 356 h. This can be explained if we assume that the increase in molecular weight of the already existing polymer chains is overcompensated by the generation of new chains via the side reaction. The strong increase of M_w/M_n from 356 to 600 h supports this assumption. The finding that very long polymerization times led to large values of M_w/M_n is not unique to this sample. It was seen frequently also for the other alkylene oxides if low polymerization rates required such long reaction times.

3. Block Copolymers. A−B block copolymers were synthesized by successively polymerizing the hydrophobic alkylene oxide and EO in a one-pot reaction. The only difficulty using this synthesis procedure results from the fact that EO is polymerized in the presence of crown ether and that the reaction cannot be carried out below room temperature. At those temperatures PEO gets insoluble in toluene. As the polymerization rate of EO is much higher than for the other alkylene oxides, the reaction might get out of control. However, in none of the polymerization experiments were such observations made in this work.

Copolymers having block molecular weights of about 10 000 and 50 000 were synthesized successfully. In the SEC analysis of the products no homopolymer was detectable in the products. To verify this, the soluble residues obtained after precipitation of the raw products in cold acetone were analyzed. For the copolymers having block molecular weights of 10 000 the SEC spectra of the acetone soluble residues were identical with the ones of the purified products. The result is slightly different for the sample PBO17-PEO, where the block molecular weights are about 50 000. Here the SEC signal of the acetone soluble residue showed a bimodal distribution. The peak at longer retention time corresponds to low molecular weight byproduct. First, it must be emphasized that the fraction of byproduct is extremely small; it represents only 1% of the total amount of product. The elution time of the byproduct corresponds almost exactly with the one from the PBO precursor. However, under the SEC experimental conditions, the molecular weight−elution time relation is more or less the same for PBO and PEO. Therefore, the location of the peak cannot be used to identify the byproduct. The signal shape contains more information. The byproduct peak is narrow. This would not be expected for the low molecular weight PBO byproduct. For this reason one must assume that the byproduct is predominantly PEO homopolymer, which was generated via protic contaminants introduced into the reactor together with EO.

Conclusions

The results show that hydrophobic PAO can be obtained by anionic ring-opening polymerization of the corresponding 1,2-

alkylene oxide monomers at low reaction temperatures. The use of crown ethers increases the reactivity of the alcoholate head groups in the growing polymer chains and so keeps polymerization times in an acceptable range. Simultaneously side reactions are strongly suppressed, which allows to synthesize PAO up to high molecular weights and almost free of byproducts. In contrast at high reaction temperatures side reactions cause relatively large amounts of high and low molecular byproducts. Besides homopolymers amphiphilic block copolymers with PEO are accessible in high structural quality.

From the analysis of the SEC results it seems reasonable that the byproducts being formed in the anionic polymerization of BO and the higher oxides are qualitatively similar to the byproducts found in PO. However, the results indicate that the side reactions are stronger for PO than for the other alkylene oxides. Interestingly, our attempts to polymerize PO failed if reaction conditions were applied successfully used for the other alkylene oxides. This discrepancy cannot only be explained with the more violent side reactions in the case of PO. Therefore, we now analyze the byproducts resulting from the polymerizations of PO, BO, and HO in more detail to find out if the side reactions are similar for all alkylene oxides. In addition, work is in progress to investigate PBO, PHO, and POO with respect to their viscoelastic behavior. Other investigations using amphiphilic block copolymers with PEO are on the way to examine their interfacial properties at oil−water and solid−water interfaces.

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