Synthesis of PB−PEO and PI−PEO Block Copolymers with Alkyllithium Initiators and the Phosphazene Base *t*-BuP_4

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Amphiphilic block copolymers are receiving increasing attention because of their rich lyotropic and thermotropic phase behavior which can be utilized for emulsification, pharmaceutical applications, and the synthesis of advanced materials.[1,2] In particular, block copolymers of the Pluronic type[3] (PEO−PPO−PEO block copolymers) have been studied intensely. However, because of their inherent polydispersity and specific properties of different batch-polymerization charges, a quantitative interpretation of experimental data with theoretical models is often difficult. Thus, there has arisen a need for water-soluble model amphiphilic block copolymers with narrow molecular weight distributions, controllable block lengths, and high purity. These requirements are met by polystyrene−poly(ethylene oxide) (PS−PEO), polybutadiene−poly(ethylene oxide) (PB−PEO), and polyisoprene−poly(ethylene oxide) (PI−PEO) block copolymers, which can be synthesized by living anionic polymerization. Of these block copolymers, PB−PEO and PI−PEO are particularly suitable for experimental investigations of aqueous phase behavior, because they are directly soluble in water even at large hydrophobic block lengths. This is in contrast to PS−PEO, where the high glass-transition temperature of the PS block mostly prevents direct dissolution in water.

The currently employed synthesis of PB−PEO and PI−PEO block copolymers proceeds in two steps:[4,5] (1) the polymerization of the PB or PI block with Li^+ as the counterion and (2) the polymerization of the PEO block with K^+ as counterion. The cross-step involves end-capping with ethylene oxide, purification of the polymer, and reinitiation with organo-potassium compounds such as cumyl potassium or potassium naphthalide. The reason for this two-step procedure is the tendency of living PEO chain ends to strongly associate with Li^+, forming ion pairs that terminate chain propagation. This prevents polymerization of the second block by addition of ethylene oxide to the living PB or PI block. Association is less pronounced for larger alkali metal cations such as K^+.

A way to overcome the problem of Li^+ association would allow the synthesis of PB−PEO and PI−PEO block copolymers in a one-step procedure via a direct cross-step from butadiene or isoprene to ethylene oxide. Crown ethers or cryptands that could encapsulate cations have been found to shift the free-end/cation equilibrium toward the reactive free anions, but no efficient polymerization has been observed.[6] Recently, Esswein and Möller showed that ethylene oxide could be efficiently polymerized with alkyllithium compounds in the presence of the phosphazene base *t*-BuP_4[7,8] (Figure 1). This extremely strong base can efficiently complex lithium ions, thereby suppressing ion pair association and facilitating polymerization of ethylene oxide through the formation of lithium alkoxides. Homopolymerization of ethylene oxide in THF with BuLi/

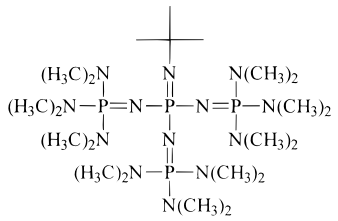

Figure 1. Chemical structure of the phosphazene base *t*-BuP_4.

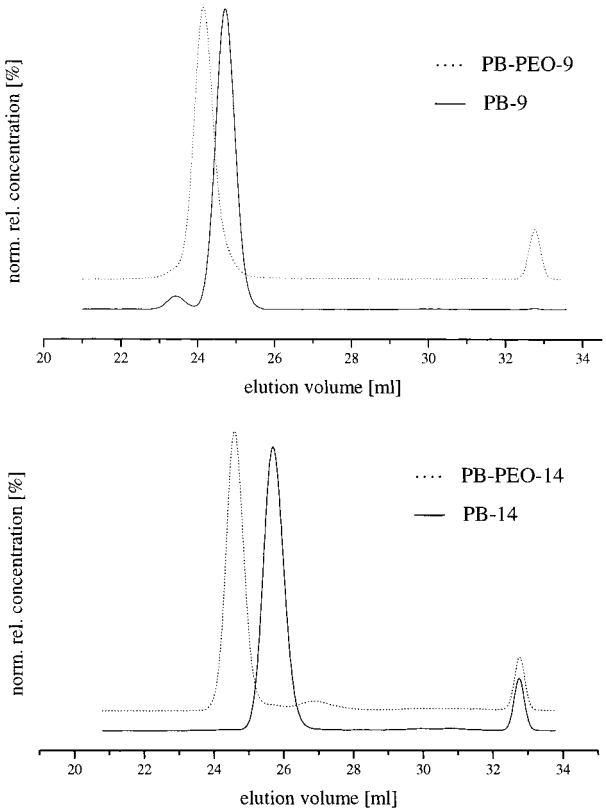

Figure 2. GPC elugrams of (a) PB-9 and PB−PEO-9 and (b) PB-14 and PB−PEO-14 in chloroform. The peak positions of the PB−PEO block copolymers are shifted to smaller elution volumes compared to the PB precursors. The peak widths remain unchanged.

Table 1. Molecular Weights and Polydispersities of the PB or PI Precursors and the Respective PB−PEO or PI−PEO Diblock Copolymers Synthesized in the Present Study[a]

sample ID	N_{calc} (PB or PI)	N_{GPC} (PB or PI)	N_{calc} (PEO)	N_{GPC} (PEO)	M_w/M_n (PB or PI)	M_w/M_n (PB−PEO or PI−PEO)	f_{PB} or f_{PI}
PB−PEO-8	200	202	250	360	1.02	1.06	0.36
PB−PEO-9	200	212	100	112	1.02	1.03	0.65
PB−PEO-11	400	432	400	484	1.02	1.02	0.47
PB−PEO-12	800	797	800	893	1.02	1.04	0.47
PB−PEO-13	15	16	100	102	1.12	1.05	0.14
PB−PEO-14	100	125	100	155	1.02	1.02	0.45
PI−PEO-1	400	(631)	800	(1110)	1.03	1.04	0.36

[a] N_{calc} is the degree of polymerization calculated from the monomer/initiator ratio. The degree of polymerization N_{GPC} of the PB and PI precursors is determined by GPC in chloroform and calibrated with narrow PB standards. N_{GPC} of the PEO block is calculated from the PB/PEO and PI/PEO peak ratios in the ^1H NMR spectra. $f_{PB} = N_{PB}/(N_{PB} + N_{PEO})$ Is the relative molar amount of the hydrophobic block (PB or PI) in the block copolymers.

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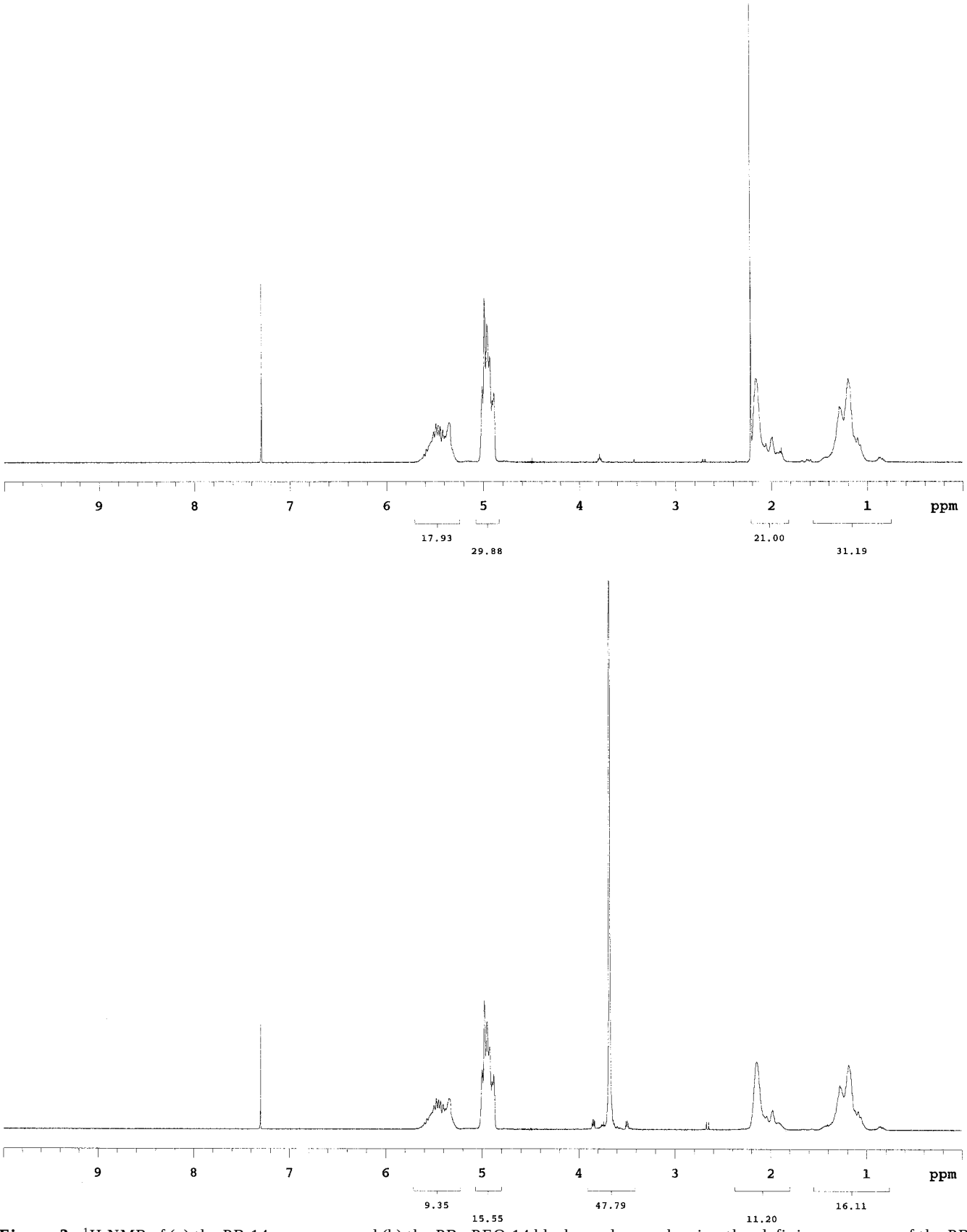

Figure 3. ^{1}H NMR of (a) the PB-14 precursor and (b) the PB−PEO-14 block copolymer showing the olefinic resonances of the PB block at 5.3−5.6 (−CH═C) and 4.9−5.0 ppm (terminal C═CH_2). From the peak ratio, one calculates 89% 1,2- and 11% 1,4-addition. The PEO resonance (−CH_2−O−) of the PB−PEO block copolymer is apparent at 3.7 ppm.

t-BuP_4 as the initiator led to good yields of PEO with low polydispersity ($1.08 \leq M_w/M_n \leq 1.28$) in the molecular weight range 2000−20 000. Furthermore, the use of the phosphazene base allowed the synthesis of a poly(styrene-*b*-ethylene oxide) (PS−PEO) block copolymer in toluene at room temperature.

In this communication, we report the synthesis of PB−PEO and PI−PEO block copolymers using the

alkyllithium/*t*-BuP_4 system in THF. Several PB−PEO and one PI−PEO were synthesized, covering a wide range of molecular weights. Butadiene and isoprene were purified by cryo-distillation from *n*-Bu_2Mg and *n*-BuLi, and THF was purified by distillation from a sodium/potassium alloy and a benzophenone/potassium complex. Ethylene oxide was purified successively by distillation from CaH_2, sodium mirror, and *n*-BuLi. *t*-BuP_4 (Fluka, 1.00 ± 0.02 molar in hexane) was used as received. Prior to polymerization, *t*-BuP_4 (1.05:1.00 ratio to *s*-BuLi) was introduced into the reactor, the solvent was distilled off, and the solid base was dried overnight under vacuum. THF and butadiene or isoprene were condensed into the reactor. The calculated amount of *s*-BuLi (Aldrich, 1.3 molar in hexane) was added at −110 °C, the temperature of a just molten THF/monomer mixture. This ensures that chain propagation is slow compared to the initiation reaction and routinely yields narrow disperse polymers ($M_w/M_n \leq 1.03$). After completion of the polymerization (4−6 h) at −78 °C, a precursor is drawn from the reactor for analysis of molecular weight by gel permeation chromatography (GPC). Afterward, a small amount of ethylene oxide is added at −40 °C to cap the living PB or PI chain ends. After 1 h at −40 °C, the remaining ethylene oxide is added, and the reaction solution is heated to 40 °C to start chain propagation. After 1 day, a deep blue color develops. The polymerization is quenched with acetic acid after 2 days. The polymer is precipitated in cold (−20 °C) acetone and dried under vacuum to constant weight.

GPC of the PB and PI precursors as well as the PB−PEO and PI−PEO block copolymers was performed in chloroform. Three columns (10^3, 10^5, 10^6 Å pore size SDV-Gel from Polymer Standards Service) at a flow rate of 1 mL/min were used. Signals were detected with a Shodex RI-71 detector. As examples, elugrams of PB-9 and PB−PEO-9 (Figure 2a) and PB-14 and PB−PEO-14 (Figure 2b) are shown. The block copolymer peaks are shifted to smaller elution volumes compared to the respective PB precursors,[9] and the peak widths remain unchanged. This indicates complete conversion at the cross-step from butadiene to ethylene oxide. The GPC was calibrated with PB standards (Polymer Standards Service) that had been synthesized under the same conditions (*s*-BuLi/THF) as the blocks in the present communication and thus had the same microstructure (rel amount of 1,4- vs 1,2-addition). The degree of polymerization of the PEO block was calculated from the molar ratios of PB/PI and PEO from ^{1}H NMR. The characteristic data of the block copolymers are summarized in Table 1. Over a broad range of molecular weights ($5000 < M_n < 100\,000$) the phosphazene method yields narrow disperse polymers ($1.02 < M_w/M_n < 1.06$) with good control of block lengths. The PB precursor of PB−PEO-13 has a higher polydispersity following the Poisson distribution typical for living polymerization mechanisms. For PB−PEO, the molecular weights as determined by GPC are slightly higher than values calculated from the monomer/initiator ratio, indicating slight deactivation of the initiator solution (*s*-BuLi in hexane) upon storage. The values for the PI−PEO block are overestimated because of calibration with PB standards.

From ^{1}H NMR, the stereochemistry of the PB block was determined to be 89% 1,2- and 11% 1,4-addition (Figure 3). This is identical to the values reported for butadiene in THF without *t*-BuP_4.[10] This indicates that the phosphazene base does not influence the stereochemistry of the butadiene addition. In addition, in the case of isoprene (28% 1,2-, 61% 3,4-, and 11% 1,4-addition), there are no observable differences with or without the phosphazene base.

To obtain narrow disperse block copolymers, we found it necessary to use the exact stoichiometric amount of *t*-BuP_4 and *s*-BuLi. In our first attempts to synthesize PB−PEO block copolymers with phosphazene bases, we observed that an excess of *t*-BuP_4 leads to the formation of PEO homopolymer. This probably occurs through a nucleophilic attack of noncomplexed *t*-BuP_4 at the oxirane ring. Ring opening of the oxirane subsequently leads to polymerization of ethylene oxide. This side reaction can lead to considerable amounts of PEO because of the long reaction times (2 days) at elevated temperatures (40 °C). The less nucleophilic Li^+-*t*-BuP_4 complex does not undergo this side reaction. The small peak at $V_e = 27$ mL in the GPC trace of PB−PEO-14 in Figure 2 is due to traces of the PEO homopolymer.[11] For all other samples listed in Table 1, a slight (5%) excess of *s*-BuLi versus *t*-BuP_4 routinely lead to the formation of polymers with narrow molecular weight distribution without contamination by PEO homopolymer. Except PB−PEO-9, which has the largest hydrophobic content ($f_{PB} = 0.65$), all block copolymers listed in Table 1 are directly soluble in water. Their lyotropic phase behavior is currently being investigated.[12]

In conclusion, we have found that the phosphazene base *t*-BuP_4 allows the synthesis of PB−PEO and PI−PEO block copolymers in THF by simply adding ethylene oxide to the living PB or PI chain ends. Narrow disperse polymers over a broad range of molecular weights with good control of block lengths can be obtained for an exact 1:1 stoichiometry of *t*-BuP_4/*s*-BuLi.

References and Notes

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