Controlled Anionic Homo- and Copolymerization of Ethylene Oxide and Propylene Oxide by Monomer Activation

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Received February 21, 2007; Revised Manuscript Received July 2, 2007

ABSTRACT: The anionic polymerization of ethylene oxide initiated by alkali metal-based initiators suffers from low polymerization rates even in polar media. We found that the addition of triisobutylaluminum to initiators like alkali metal alkoxides or tetraalkylammonium salts strongly enhances the ethylene oxide polymerization rate, while keeping its living character. At ratio [i-Bu$_3$Al]/[initiator] = 1.5, the controlled synthesis of poly(ethylene oxide) of relatively high molar masses is achieved in short time at room temperature in dichloromethane or toluene. Beside the formation of an aluminate 1:1 complex involving i-Bu$_3$Al and the initiator, a second complex between the trialkylaluminum and the oxirane is formed, which strongly increases the reactivity of the epoxide monomer. Gradient di- and triblock ethylene oxide/propylene oxide copolymers of high molar mass are readily prepared with this system.

Introduction

The anionic polymerization of ethylene oxide (EO) has been studied for many years, and a large number of anionic initiators have been investigated to improve both the polymerization control and kinetics. Conventional sodium- and potassium-based initiators yield in ether solvent, such as tetrahydrofuran (THF), or in polar media, such as dimethyl sulfoxide (DMSO), a controlled polymerization allowing the synthesis of end-functional PEO,[1,2] PEO-based block copolymers[3−5] as well as PEO chains with more complex architectures like stars[6,7] or dendrimers.[8] Several days are generally required at room temperature to get high monomer conversions and polyethers with high molar mass.[9] Besides, systems based on Li derivatives are inactive in similar conditions[10] due both to the more covalent character of the lithium−alkoxide bond and strong aggregation phenomena.[11] However, Esswein and Möller showed that the addition of strong Lewis base, for example the phosphazene base tBu-P$_4$, can strongly complex the Li$^+$ counterion and allows EO polymerization in THF.[12−14]

We have shown recently that the association of organoaluminic derivatives (AlR$_y$X$_{3-y}$) to alkali metal salts yield the formation of "ate" complexes which are active initiators both for the retarded anionic polymerization of styrenic monomers and dienes[15,16] and for the anionic polymerization of propylene oxide (POx).[17,18] For the oxirane, in contrast to ethylenic monomers, a slight excess of the aluminum derivative with respect to the alkali metal is needed to trigger the polymerization. This is explained by the necessary formation of a second complex between the aluminum derivative in excess and the monomer. The latter is strongly activated toward nucleophiles and polymerizes rapidly. This strategy was recently applied to polymerization systems based on the association of tetraalkylammonium salt initiators with trialkylaluminum.[18,19] In the present article we have extended this approach to ethylene oxide and investigated its polymerization as well as its random and block copolymerizations with propylene oxide.

Experimental Section

Materials. Triisobutylaluminum (i-Bu$_3$Al) (1 mol/L in toluene, Aldrich) was used without further purification. Ethylene oxide (99.8%, Fluka) was purified under vacuum over sodium metal for 1 h, distilled under vacuum, and stored at room temperature (RT) in high-pressure graduated glass tubes. Propylene oxide (POx) (99%, Fluka) was purified over CaH$_2$, distilled under vacuum, and stored for 15 min in a glass flask equipped with PTFE stopcocks in the presence of *i*-Bu$_3$Al to remove traces of impurities. POx was finally distilled under vacuum and stored under vacuum at RT in graduated glass tubes until use. Toluene (98%, J.T. Baker) was purified with polystyryllithium seeds, and dichloromethane (98%, J.T. Baker) was purified over CaH$_2$. Both were distilled under vacuum and then stored in graduated glass tubes under vacuum.

i-PrONa was synthesized by reaction of *i*-PrOH (99.5% anhydrous, Aldrich), previously dried, and distilled over CaH$_2$, with sodium metal (99.95%, cubes in mineral oil, Aldrich) dispersed in toluene. The mixture was reacted at 50 °C for one night and stored over a small excess of sodium metal. NBu$_4$Cl (98%, Aldrich) and NOct$_4$Br (98%, Aldrich) were purified first by solubilization in methanol followed by MeOH evaporation under vacuum until dryness. Then they were solubilized into dried toluene followed again by a complete drying under dynamic vacuum. Tetraalkylammonium salts solutions of known concentration were then prepared in dried toluene and stored in graduated glass tubes fitted with PTFE stopcocks.

Procedures. All (co)polymerizations were performed between −30 and 25 °C under argon in a high-pressure glass reactor equipped with a magnetic stirrer and fitted with PTFE stopcocks. The reactor was flamed under vacuum and cooled prior to introduction of solvent and monomer(s) through connected glass tubes. Then a toluene solution of initiator and finally the trialkylaluminum catalyst were added via a syringe under argon. For the block copolymerizations, the second and third monomers were introduced after the desired reaction time. A small amount of ethanol was then added to stop the reaction, and the remaining monomer and solvent were stripped off under vacuum. Polymer conversions were determined gravimetrically after complete drying of the polymer under vacuum at 50 °C.

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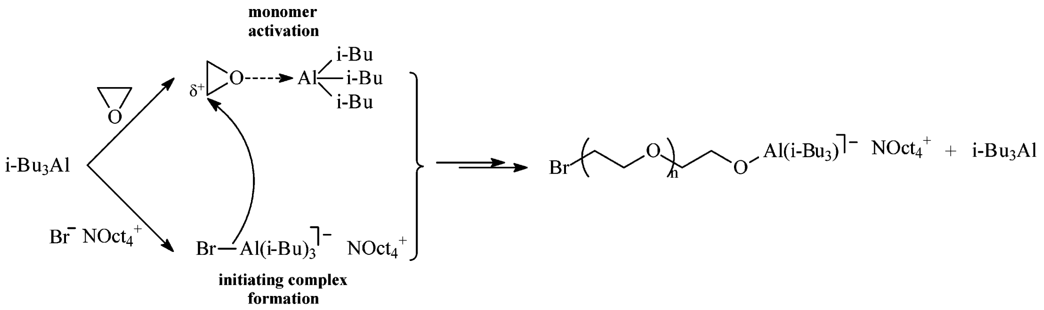
10.1021/ma070450c CCC: $37.00

Table 1. Ethylene Oxide (EO) Polymerization Initiated by i-PrONa or NR_4X (I) in the Presence of Triisobutylaluminum (Dichloromethane, [EO] = 4 M)

run	initiator	[I] (mol L^{-1})	$[i\text{-}Bu_3Al]/[I]$	T (°C)	time (h)	conv (%)	$t_{1/2}$ (h)	$\bar{M}_n(\text{th})^a$ (g/mol)	$\bar{M}_n(\text{exp})^b$ (g/mol)	I_p^c
1	*i*-PrONa	1.06×10^{-2}	1.5	25	6	30	10.0	5 000	4 400	1.12
2	NBu_4Cl	8.81×10^{-3}	1.5	25	6	57	5.26	11 400	11 500	1.14
3	$NOct_4Br$	8.81×10^{-3}	1.5	0	6	17	17.6	3400	7100	1.28
4	$NOct_4Br$	8.81×10^{-3}	3	0	6	80		16 000	11 600	1.41
5	$NOct_4Br$	9.12×10^{-3}	1.5	25	4	100		19 300	17 300	1.15
6	$NOct_4Br$	8.81×10^{-3}	1.5	25	2	100	0.87	20 000	19 000	1.16
7	$NOct_4Br$	3.52×10^{-3}	1.5	25	4	93		46 500	36 000	1.20

[a] Number-average molar mass calculated by ([monomer]/[initiator]) × conversion. [b] Number-average molar mass measured by SEC. [c] Polydispersity index given by SEC.

Scheme 1. Reaction Mechanism Involving Monomer Activation Prior Insertion into the Growing "ate" Complex



Typically for a block copolymerization, in a 100 mL high-pressure glass reactor equipped with a magnetic stirring bar, 10 mL of toluene and 2.00 mL of POx (28.60 mmol), both stored in graduated tubes, were introduced under vacuum through glass connectors to the reactor. Then, 0.38 mL (0.08 mmol) of a solution of $NOct_4Br$ in toluene (0.22 mol/L) followed by 0.12 mL (0.12 mmol) of triisobutylaluminum (1.00 mol/L in toluene) were added by a syringe under argon to start the polymerization. The reactor was maintained at 0 °C for 4 h, and then 2.00 mL of EO (39.10 mmol) was distilled directly into the reactor. The system was kept for an additional 12 h under stirring at the same temperature. Ethanol was finally added for deactivation. The polymer was recovered by solvent evaporation under vacuum.

Kinetic studies were followed either by sample withdrawing or by dilatometry. For the first method, conversion was determined by SEC (size exclusion chromatography) from the peak area ratios of the polymer and of an added reference (known amount of polystyrene with a number-average molar mass ($\bar{M}_n$) equal to 214 000 g/mol). Dilatometry measurements were performed in a glass dilatometer previously flamed. The initiator solution was first added using a syringe, and the system was thermostated at the desired temperature. Then the solvent, the monomer, and finally triisobutylaluminum were successively added. Monitoring of the reaction was immediately followed by recording the volume level of the solution in the capillary tube attached to the reactor.

Analysis. PEO molar masses were determined by SEC at 20 °C using THF as eluant on a Jasco apparatus equipped with a Varian 2510 HPLC pump and a refractive index Jasco detector and fitted with four TSK gels HXL columns (2000, 3000, 4000 and 5000), at an elution rate of 0.8 mL/min. Poly(ethylene oxide) was used as standard.

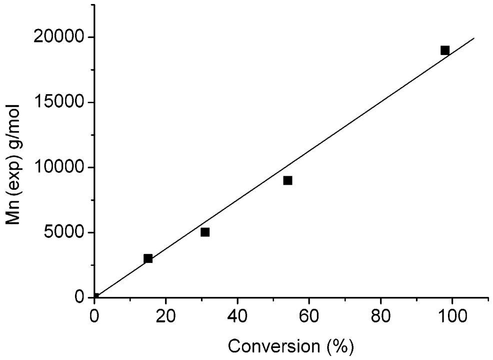


Figure 1. Variation of the number-average molar mass ($\bar{M}_n$(exp)) vs conversion in ethylene oxide polymerization initiated by $NOct_4Br{:}iBu_3Al$ (1:1.5) at 25 °C in CH_2Cl_2.

^1H (400 MHz) and ^{13}C (100 MHz) NMR measurements of PEO and PEO-*co*-PPOx were performed on a Brüker Avance 400 spectrometer, in $CDCl_3$ at room temperature.

Differential scanning calorimetry (DSC) measurements were performed on a DSC Q100 apparatus from TA Instruments. Data were recorded during the second run for temperatures ranging from −90 to 70 °C at a heating rate of 5 °C min^{-1}. The cooling rate between the first and second runs was also equal to 5 °C min^{-1}. The glass transition temperature (T_g) was given by the inflection point of the transition. The melting temperature (T_m) was taken at the maximum of the endothermic peak and the enthalpy variation calculated from the peak area. The DSC instrument was calibrated with indium ($T_m = 156$ °C, $\Delta H = 28.71$ J/g).

Results and Discussion

Homopolymerization of Ethylene Oxide. As previously reported for propylene oxide,[17−19] ethylene oxide polymerization readily takes place in the presence of alkali metal alkoxides or tetraalkylammonium salts in toluene at 20 °C when a slight excess of trialkylaluminum ([Al]/[initiator] > 1) is added to the system. However, since high molar mass poly(ethylene oxide)s are not soluble in hydrocarbons, dichloromethane was chosen as reaction medium in this study to keep the system homogeneous during the whole polymerization. A first set of polymerization data obtained for different initiators (I) and reaction conditions are collected in Table 1. Both sodium and tetraalkylammonium salts behave as efficient polymerization initiators independently of the nature of the associated anion (RO^-, Cl^-, Br^-), which is directly involved in the initiation step as proved by Maldi-Tof analysis of the polymer ends. The time for half monomer conversion at 25 °C indicates a rate of polymerization twice faster with tetrabutylammonium chloride as compared to sodium isopropoxide initiation. In the ammonium salts series the reactivity strongly increases with the size of the alkylammonium cation: $NBu_4 < NOct_4$. As shown in Table 1, in most cases, the PEO experimental molar masses are in good agreement with calculated values assuming one chain formed per initiator molecule and polydispersities are

Table 2. Statistical Copolymerization of Ethylene Oxide (EO) and Propylene Oxide (POx) Initiated by NOct$_4$Br(I) in the Presence of Triisobutylaluminum (Solvent Toluene; [EO + POx] = 4 M)

run	[EO]/[POx] in comonomer feed	[I] × 10^3 (mol/L)	[i-Bu$_3$Al]/[I]	T (°C)	time (h)	conv (%)	$\bar{M}_n$(th)^a (g/mol)	$\bar{M}_n$(exp)^b (g/mol)	I_p^{c}
1	0.33	9.20	1.5	−30	6	100	10 000	10 000	1.11
2	0.66	6.41	1.4	−30	6	100	30 000	27 000	1.11
3	0.50	8.32	5.6	0	6	100	20 000	26 200	1.48
4	0.50	8.32	1.5	25	1.5	90	18 000	18 400	1.22
5	0.50	1.67	1.5	25	4	71	63 300	71 000	1.23

[a] Number-average molar mass calculated by ([monomer]/[initiator]) × conversion. [b] Number-average molar mass measured by SEC. [c] Polydispersity index given by SEC.

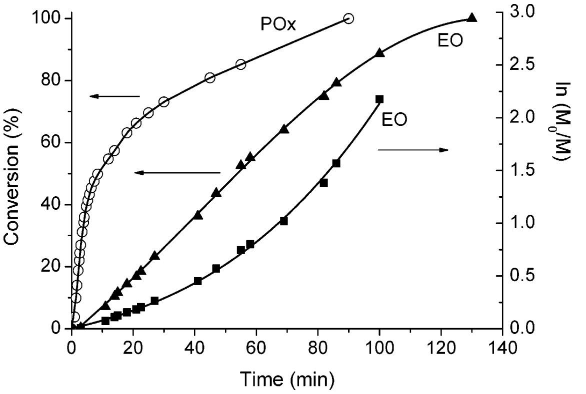


Figure 2. Monomer conversion vs time and ln([M]$_0$/[M]) vs time curves for ethylene oxide and propylene oxide homopolymerizations in CH$_2$Cl$_2$ in the presence of NOct$_4$Br:iBu$_3$Al (1:1.5) as initiator at 25 °C; [M]$_0$ = 4 M; [I] = 8.81 × 10^{-3} M.

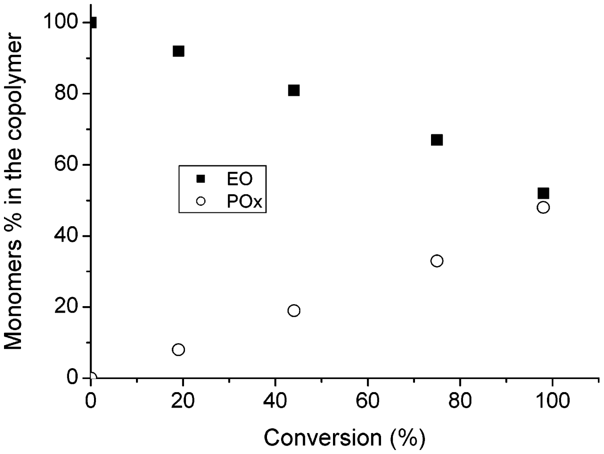


Figure 3. Evolution of the ethylene oxide and propylene oxide copolymer composition with conversion starting from a 50/50 molar comonomer feed (toluene, t = 25 °C, [i-Bu$_3$Al]/[NOct$_4$Br] = 1.5, [OE] = [POx] = 1.45 M, [I] = 8.81 × 10^{-3} M).

narrow. The evolution of the PEO molar masses with monomer conversion for a polymerization initiated by NOct$_4$Br ([iBu$_3$Al]/[I] = 1.5) is shown in Figure 1: the linear variation observed, in direct relation with the equation $\bar{M}_n = [EO]_{consumed}/[NOct_4Br]$, and the narrow polydispersity of the final PEO (I_p = 1.17) are consistent with a living polymerization process.

As already reported for POx activated polymerization,[17] an excess of triisobutylaluminum with respect to the initiator is needed to trigger the polymerization. Although 1.5 equiv is enough to get a quantitative EO polymerization in a few hours at 25 °C, with NOct$_4$Br, the polymerization can be speed up by increasing the [iBu$_3$Al]/[initiator] ratio. These results are consistent with the monomer activation process described for POx polymerization and illustrated in Scheme 1 for EO. In the proposed mechanism one iBu$_3$Al molecule is involved in the formation of an aluminate-type complex (1:1) with the initiator, while the excess of trialkylaluminum coordinates with the epoxide monomer, increasing its electrophilic character and therefore its reactivity toward nucleophiles: the higher the amount of trialkylaluminum, the higher the concentration of complexed monomer and the higher the polymerization rate. At elevated [R$_3$Al]/[I] ratios a loss of polymerization control is observed, and some care should be taken to avoid overheating due to very fast polymerization that can generate high EO pressure in the reactor.

Kinetics of EO polymerization were further investigated at 25 °C in CH$_2$Cl$_2$ in the presence of different initiators (I) associated with i-Bu$_3$Al with [R$_3$Al]/[I] = 1.5. The polymerization rate strongly varies with the nature and size of the associated cation and the polymerization kinetics exhibit different profiles. Reactions initiated by i-PrONa are characterized by an induction period that can be attributed to aggregation of the active species in the first stage of the reaction, as reported for propylene oxide.[17] In contrast with the tetraalkylammonium salts, monomer conversion increases linearly with time from the very beginning. A typical variation of EO conversion ([EO]$_0$ − [EO]$_t$/[EO]$_0$) vs time, using NOct$_4$Br as initiator, is presented in Figure 2. It shows a linear dependence of the monomer consumption with time, up to high conversion (≈80%), which fits with a monomer order for the polymerization close to zero, in good agreement with the proposed monomer activation mechanism. In support to this conclusion, the ln([EO]$_0$/[EO]$_t$) vs time plot, also shown in Figure 2, presents a strong curvature, indicating that the first-order monomer dependence does not apply. The slight deviation from linearity of the EO conversion vs time curve at high monomer conversion could be attributed to the competitive complexation of the oxygen of the PEO chain with trialkylaluminum, which lowers the concentration of the activate monomer/trialkylaluminum complex. The POx conversion vs time plot obtained in similar polymerization conditions is also shown in Figure 2 for comparison. Kinetics also fits with a zero monomer order dependence of the polymerization and shows a similar deviation, even more pronounced, at high monomer conversion (>50%). The EO propagation rate constant $k_{p,EO}$, calculated considering the rate law $R_p = k_p[NOct_4Br]^1[M]^0$, gives at 25 °C in dichloromethane a $k_{p,EO}$ value of 410 min^{-1}. For comparison with propylene oxide, the $k_{p,POx}$ value is equal to 3470 min^{-1}, indicating a higher reactivity of the POx monomer. A similar reactivity order was observed in toluene ($k_{p,POx} > k_{p,EO}$).

Simultaneous Copolymerization of Ethylene Oxide and Propylene Oxide. Since EO and POx activated anionic polymerizations proceed in very similar experimental conditions and are both nearly free of transfer and termination reactions, the synthesis of statistical EO/POx copolymers of controlled molar masses having an identical distribution of comonomer units in all chains was investigated. A first series of copolymerization experiments were implemented in toluene using NOct$_4$-

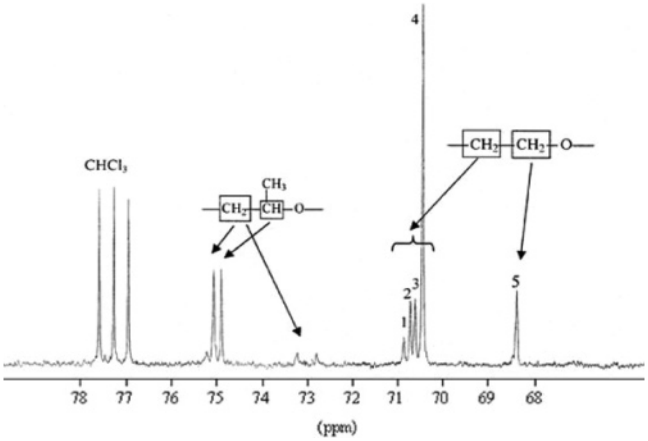


Figure 4. 100 MHz ^{13}C NMR spectrum of a statistical poly(ethylene oxide)-*co*-poly(propylene oxide) copolymer (run 4, Table 2) in $CDCl_3$ (zoom on methylene and methine regions).

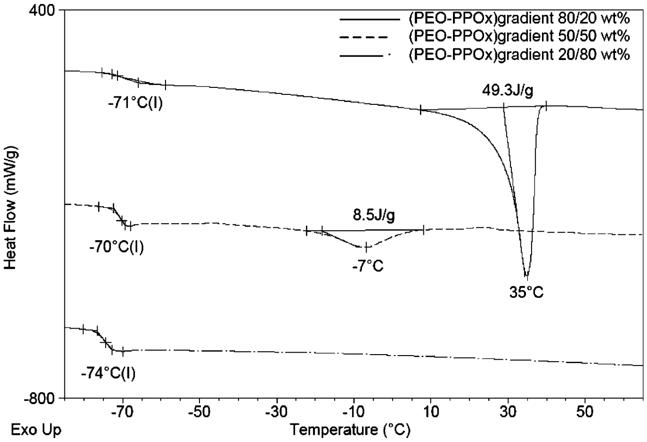


Figure 5. DSC analysis of poly(ethylene oxide)-*co*-poly(propylene oxide) gradient copolymers: influence of composition.

Br as initiator, at temperatures ranging from −30 to 25 °C. The main characteristics of the EO/POx copolymers obtained from various comonomer feeds are given in Table 2. When using low [Al]/[I] ratio (1.5), the good agreement between experimental and calculated copolymer molar masses and the observed narrow polydispersities support the formation, by living polymerization, of EO/POx copolymers with controlled structure and composition over a broad range of molar masses. The evolution of the copolymer composition with the conversion, starting from a 50/50 molar composition feed (Figure 3), shows that EO incorporates much faster than POx in the growing chains, in contrast with its lower propagation rate in homopolymerization. The EO/POx reactivity ratios were determined in a set of copolymerization experiments using various comonomer feeds. To limit the influence of the comonomer composition drift with conversion, all the experiments were stopped at low monomer conversion (<10%). Reactivity ratios calculated by the Kelen−Tüdos method,[20,21] at 25 °C in toluene ([i-Bu_3Al]/[$NOct_4Br$] = 1.5), are $r_{EO} = k_{EOEO}/k_{EOPOx} = 2.05$ and $r_{POx} = k_{POxPOx}/k_{POxEO} = 0.013$. This is consistent with both a higher reactivity of the EO monomer and of the POx active ends. Despite the major contribution of the monomer complexation step in the reactivity enhancement, the copolymerization ratios are close to those reported for conventional anionic copolymerization, $r_{EO} = 3.1$ and $r_{POx} = 0.3$.[22] The main difference concerns the relative reactivity of POx active ends toward POx and EO monomers, cross-addition being significantly favored in respect to the formation of POx−POx diads. This may be due to larger steric hindrance of POx, considering that monomer addition proceeds into bulky aluminum complexes.

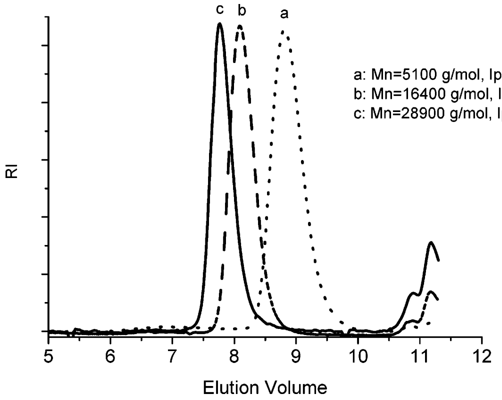


Figure 6. SEC traces corresponding to the different stages of the synthesis of a PEO−PPOx−PEO triblock copolymer (run 3, Table 3): (a) PEO first block; (b) PEO−PPOx diblock; (c) final triblock.

Figure 4 shows the ^{13}C NMR spectrum of a poly(EO-*co*-POx) copolymer (run 4, Table 2). Four distinct methylene peaks corresponding to EO-centered triads are observed between 70 and 71 ppm (peaks 1−4). They are attributed[22,23] to POx−EO_b−POx (1), POx−EO_b−EO (2), EO−EO_b−POx (3), and EO−EO_a−POx + EO−EO_{a+b}−EO (4), where a and b correspond respectively to the first and second CH_2 groups of the central EO unit (R−O−CH_{2a}−CH_{2b}−O−R). Peak 5 at 68.5 ppm corresponds to POx−EO_a−EO and POx−EO_a−POx sequences. As shown in Figure 4, the high intensity of peak 4 indicates the presence of a significant fraction of EO−EO−EO sequences, which likely form at the beginning of the polymerization, in agreement with a tapered structure for the copolymers.

DSC analysis carried out on PEO−PPOx copolymers with different PEO weight percentage (20, 50, and 80%) are shown in Figure 5. For each sample, a glass transition is observed at −70 °C in agreement with PPOx-rich sequences containing very few EO units. Besides, a melting peak is observed at 35 and −10 °C respectively for the 80 and 50 wt % EO compositions, while no melting peak is observed for the 20% PEO sample,

Table 3. Block Copolymerization of Ethylene Oxide (EO) and Propylene Oxide (POx) Initiated by $NOct_4Br$(I) in the Presence of Triisobutylaluminum (Solvent Toluene, [EO + POx] = 7 M; Sequential Addition Order: POx−EO (Runs 1 and 2); POx−EO−POx (Run 3); EO−POx−EO (Run 4))

run	[I] × 10^4 (mol/L)	[i-Bu_3Al]/[I]	time (h)	*T* (°C)	conv (%)	$\bar{M}_n$ (th)[a] (g/mol) × 10^{-3} first block	second block	third block	$\bar{M}_n$(exp)[b] (g/mol)× 10^{-3} (SEC)	I_p[c]
1	0.415	1.5	2 + 4	0	100	20	10		33.8	1.28
2	0.58	1.4	12 + 12	0	100	20	20		39.0	1.06
3	1.24	1.5	2 + 2 + 2	0	100	10	5	10	22.4	1.29
4	1.66	1.3	4 + 8 + 12	20	100	5.3	10	12	28.9	1.10

[a] Number-average molar mass calculated by ([monomer]/[initiator]) × conversion. [b] Number-average molar mass measured by SEC. [c] Polydispersity index given by SEC.

likely because of too short PEO sequences. The presence of both a T_g close to that of homo-PPOx and a T_m which increases when increasing the EO fraction in the copolymers are consistent with the formation of gradient copolymers.

Block Copolymerization of Ethylene Oxide and Propylene Oxide. Low molar mass POx/EO diblocks and triblocks found important applications as amphiphilic copolymers.[24−27] On the basis of the living character for both EO and POx anionic activated polymerizations, the synthesis by sequential monomer addition of diblock and triblock copolymers with various compositions and lengths was investigated. Results obtained with i-$Bu_3Al/NOct_4Br$ systems ([Al]/[I] = 1.3−1.5) as initiating system are collected in Table 3. In toluene, when EO is used as first monomer, a short PEO block ($\bar{M}_n$ = 5300 g/mol) was prepared to avoid precipitation. Upon addition of POx, the formation of a second block, with a molar mass in agreement with the calculated value, was readily obtained in a short period of time, yielding PEO-*b*-PPOx diblock copolymers. Addition of a new EO feed yields a triblock copolymer, with narrow molar mass distribution, constituted by two external water-soluble PEO blocks and a central poorly hydrophilic and thermosensitive PPOx block (see Figure 6). The reverse addition order of the two monomers yields narrow polydisperse poly(POx-*b*-EO-*b*-POx) triblocks, with the more hydrophilic block in between the two thermoresponsive ones. In the two cases the achieved copolymers have molar masses significantly higher than those obtained by conventional anionic polymerization, especially regarding the PPOx block length.

Conclusion

“Living” high speed anionic polymerization of ethylene oxide and copolymerization with propylene oxide can be readily achieved in hydrocarbon or in methylene dichloride at temperatures ranging from −30 to about 25 °C, using conventional sodium alkoxide or tetraalkylammonium salts as initiators and triisobutylaluminum as an activator. PEO and PPOx homopolymers as well as PEO−PPOx tapered and di- and triblock copolymers of controlled molar masses can be prepared directly, without termination step, and in short reaction times, while polymerizations using other initiating systems are generally limited by important transfer reaction during POx polymerization.

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MA070450C