

Controlled Oxyanionic Polymerization of Propylene Oxide: Unlocking the Molecular-Weight Limitation by a Soft Nucleophilic Catalysis

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The oxyanionic ring-opening polymerization of propylene oxide (PO) from an exogenous alcohol activated with benign (complexed) metal-alkali carboxylates is described. The equimolar mixture of potassium acetate (KOAc) and 18-crown-6 ether (18C6) is demonstrated to be the complex of choice for preparing poly(propylene oxide) (PPO) in a controlled manner. In the presence of 18C6/KOAc, hydrogen-bonded alcohols act as soft nucleophiles promoting the PO S_N2 process at room temperature and in solvent-free conditions while drastically limiting the occurrence of parasitic hydrogen abstraction generally observed during the anionic ROP of PO. The resulting PPO displays predictable and unprecedented molar masses (up to 20 kg mol⁻¹) with low dispersities ($\bar{M}_w < 1.1$), rendering the 18C6/KOAc complex the most performing activator for the oxyanionic polymerization of PO reported to date. Preliminary studies on the preparation of block and statistical copolyethers are also reported.

growth rate (CARG) of 5.25% through 2030. The oxyanionic polymerization of epoxides represents the classical technique for the synthesis of polyethers and it is the one preferentially exploited industrially.^[2] As far as PPO is concerned, the most frequently used process involves the bulk ROP of PO at high temperatures (105–125 °C) and pressures (0.3–0.5 MPa) from an initiating system composed of a mixture of KOH and 1,2-propylene glycol (Scheme 1).^[2b]

A major complication during the oxyanionic S_N2 of PO is the occurrence of E2 reaction intervening and serving as a chain-transfer process, owing to the high nucleophilicity of the initiating/propagating alkoxides (Scheme 2).^[3]

The alkoxide ion formed by elimination is also capable of initiating a new chain, now capped at one end by an allyl ether group or a *cis*-propyleneoxy function, possibly obtained by isomerization.^[4] As a consequence of this so-called transfer reaction, the number-average molecular weight of the PPO is limited to a relatively low value (<6000 g mol⁻¹), the molecular weight distribution is broadened and the synthesis of block copolymers is challenging.^[1b,5] In addition to the fact that other PO polymerization mechanisms—mainly coordinative—may lead to much higher molar masses by drastically limiting the proportion of elimination reactions,^[1a,6] several methods have also been developed to minimize the extent of hydrogen abstraction from the monomer during the oxyanionic process of PO. However today none of those has been sufficiently performant to drastically diminish such “inescapable” side reactions. Those methods consist on limiting the temperature of the reaction,^[3b,7] increasing the size of the counter-ion (replacing K⁺ by Cs⁺ or Rb⁺),^[1a] adding complexing crown-ethers,^[2b,8] adjusting the ratio alcohol-to-alkoxide, or by modifying the nature of the initiating alcohol.^[2b] Nevertheless, and to the best of our knowledge, the molecular weight of PPO produced by an oxyanionic polymerization has never exceeded 13 000 g mol⁻¹ (as determined by size exclusion chromatography [SEC]),^[8b,9] limiting de facto the possible applications.

Catalysis employing hydrogen bonding for substrate activation has been shown to be an effective and versatile strategy in a wide variety of transformations, analogous to many enzymatic pathways.^[10] Metal- and organo-based carboxylates have already been exploited for activating various carboxylic acid and

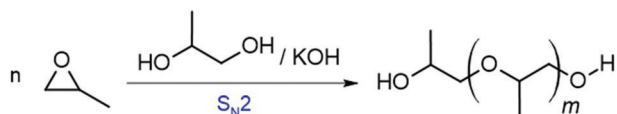
1. Introduction

Aliphatic polyethers generated by Ring-Opening Polymerization (ROP) of cyclic ether monomers represent an important class of materials employed today in a large variety of applications.^[1] Among the different classes of cyclic ethers, epoxides, mainly represented by ethylene oxide (EO) and propylene oxide (PO), are by far the most studied monomers due to their readily commercial availability and their ability to be polymerized by different mechanisms. Both poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) are estimated to be produced worldwide in several millions of tons per year with a market still anticipated to grow. As an example, the global PPO market witnessed a demand of 1.64 million of tons in 2020 with a compound annual

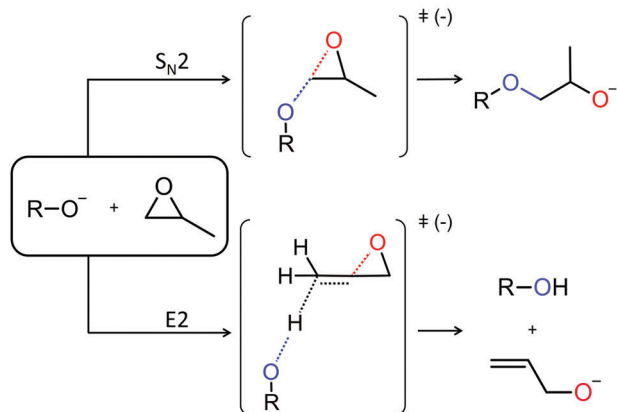
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Scheme 1. Synthesis of PPO by oxanionic S_N2 -based ROP of PO.

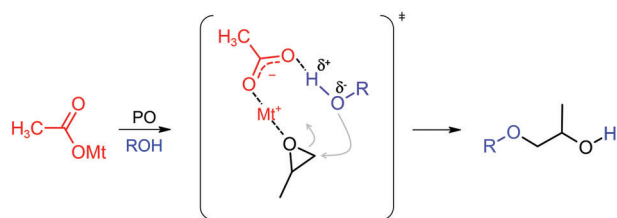


Scheme 2. S_N2 and E2 pathways for reactants $RO^- + PO$.

alcohol groups involved in bimolecular nucleophilic substitution processes.^[11] Recently, alkali metal carboxylates,^[12] eventually complexed by crown-ethers^[13] were also demonstrated to be efficient in producing polyesters and polycarbonates, enriching the catalytic toolbox for ROP. It was demonstrated that these catalysts activate the protic initiating/propagating sites during the ROP process.^[14] While the catalyst motif is versatile in design as the hydrogen bond activation of the polymer propagating site can be tailored (mainly by the size of the cation catalyst), its ability to be used in bulk, its low toxicity, and its low cost render such activation mode very promising. Bimolecular nucleophilic substitution and base-induced elimination reactions are known to be both accelerated when the electron-donating capability of a nucleophile increases, but the E2 pathway benefits more and it becomes favored.^[15] We anticipated that in presence of metal alkali carboxylates, hydrogen-bonded alcohols would act as soft nucleophiles promoting then the PO S_N2 process while limiting the occurrence of parasitic hydrogen abstraction (**Scheme 3**).

2. Results and Discussion

To establish the competence of metal alkali carboxylates to activate an exogenous alcohol toward a propylene oxide S_N2 process, we first investigated the single-turnover reaction of PO



Scheme 3. Proposed S_N2 activation mode when PO is reacted with metal alkali carboxylate and ROH exogenous alcohol.

Table 1. Conversion of propylene oxide (PO) opening at 110 °C after 2 h in presence of benzyl alcohol (BnOH) and metal alkali carboxylates (Cata).

Entry	$[PO]_0/[BnOH]_0/[Cata]_0$	Type of catalyst	Conversion [%] ^{a)}
1	1/1/0	-	0
2	1/0/1	KOAc	0
3	1/0/1	CsOAc	0
4	1/1/1	KOAc	89
5	1/1/1	CsOAc	98
6	1/1/1	18C6/KOAc	99

^{a)} As determined by 1H NMR analysis.

and benzyl alcohol (BnOH) at 110 °C for 2 h in presence of cesium acetate (CsOAc), potassium acetate (KOAc), and an equimolar mixture of KOAc and 18-crown-6 ether (18C6/KOAc) ($[PO]_0/[BnOH]_0/[catalyst]_0 = 1/1/1$, **Table 1**, entries 4–6).

The necessity to use those catalysts for performing the PO opening was also evaluated by comparing those reactions to systems in which either BnOH or the catalyst itself were excluded (**Table 1**, entries 1–3). As anticipated, the presence of the metal alkali carboxylate appears as a prerequisite to sufficiently activate the primary alcohol and open the PO synthon via a S_N2 process at 110 °C (entry 1, **Figure S1**, Supporting Information). As compared to the recent work of Wang and Luo,^[16] who demonstrated that KOAc is an efficient initiator to mediate the ring-opening alternating copolymerization of PO and phthalate anhydride, no reaction was here observed in the absence of BnOH either from pristine KOAc or CsOAc (entries 2 and 3, **Figure S1**, Supporting Information). Such an inability to open the epoxide by using pristine metal alkali carboxylates could hypothetically be explained by a synergistic effect of the phthalate monomer improving either the extremely low solubility of KOAc in PO, or enhancing the PO electrophilicity by a possible coactivation driven by polar interactions between the carbonyl groups of the anhydride and the oxygen atom of the PO oxirane.^[17]

As expected, both CsOAc and 18C6/KOAc complex appear more efficient than KOAc to catalyze the PO S_N2 with BnOH (entries 4–6, **Figures S2–S4**, Supporting Information). Limiting the reaction to a few minutes allows for the further refinement of the results. When 18C6/KOAc is used as catalyst, PO is consumed completely in 5 min (**Figure 1A**), which is ≈ 6.5 times faster than with CsOAc (**Figure 1B**). 1H NMR analyses of both final products reveal a very low content of E2-based contamination (0.4 to 0.5 mol%) when the reaction is performed with CsOAc while no sign of hydrogen abstraction has been observed from 18C6/KOAc (**Figures S5 and S6**, Supporting Information). Such observations prompted us to select the 18C6/KOAc complex as activator for the rest of our investigations.

It is industrial practice to polymerize PO at temperatures in excess of 100 °C. As the selection of the catalyst was performed at 110 °C, we first selected that thermal condition to promote the PO ROP from BnOH by targeting an initial polymerization degree ($DP = [PO]_0/[BnOH]_0$) of 50 and using the 18C6/KOAc complex as activator ($[BnOH]_0/[18C6/KOAc]_0 = 1$). Polymerization proceeded in a near quantitative monomer conversion in 2 h to give a PPO with a number-average molar mass (M_n) of

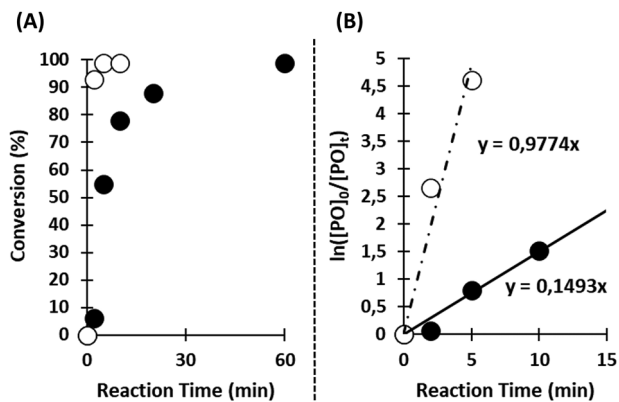


Figure 1. A) Kinetics of PO S_N2 reaction with BnOH at 110 °C, activated by CsOAc (●) and 18C6/KOAc complex (○) ($[PO]_0/[BnOH]_0/[Cata]_0 = 1$). B) Associated semilogarithmic plots ($[PO]_t$ measured by 1H NMR)

2500 $g\ mol^{-1}$ and a dispersity value ($D_M = M_w/M_n$) of 1.25, as determined by SEC. By reference to a polystyrene (PS) standard calibration, using the Mark–Houwink relationship $[\eta] = KM^a$ for PS and PPO ($K_{PS} = 1.25 \times 10^{-4}\ dL\ g^{-1}$, $a_{PS} = 0.707$, $K_{PPO} = 6.2 \times 10^{-4}\ dL\ g^{-1}$, $a_{PPO} = 0.585$), an absolute molecular weight of 1700 was calculated. The discrepancy between experimental and theoretical ($M_{n,th} = 2900\ g\ mol^{-1}$) molar masses is explained by the intervention of the E2 process as supported by the presence of allyl ether functions observed by 1H NMR analysis. By integration of the methylene protons of the α -phenyloxy PPO end-group ($C_6H_5C(H)2OCH_2-\dots$), obtained by S_N2 reaction between the initiating BnOH and a single PO monomer unit, $\approx 36\ mol\%$ of the polyether chains are end-capped by an allyl function. To avoid, or at least limit, the extent of E2-based hydrogen abstraction, further polymerizations were carried out at lower temperatures (30 to 90 °C), while maintaining all other experimental conditions as identical. After 2 h of reaction, crude reaction mixtures were analyzed by 1H NMR spectroscopy allowing for both conversions and E2 molar proportions to be calculated (Figure S7, Supporting Information). While the evolution of the E2-to-conversion ratio demonstrates, as expected, that the proportion of hydrogen abstraction diminishes by lowering the temperature, an important modification of the S_N2 -to-E2 proportion is observed at $\approx 50\ ^\circ C$ (Figure 2A). This suggests that polymerizing PO at temperature $\leq 50\ ^\circ C$ significantly increases the polymerization control while minimizing the energy investment costs. Interestingly, at 50 °C, two main observations can be drawn from the kinetic plot expressed in semilogarithmic coordinates (Figure 2B).

The first is the occurrence of an induction time, before actual chain growth can be observed ($DP = 3$ after 1 h). This could suggest a modification of the initial 18C6/KOAc/BnOH supramolecular organization by PO molecule(s) leading to an induction period. In a second time, while limited to roughly 13 mol% (as compared to the methylene phenyloxy protons), the E2 proportion linearly increases during the whole process (Figure S8, Supporting Information). The proton abstraction is then not limited to the initiation step but increases with time and presents features associated with a transfer reaction accelerating the overall polymerization kinetics, as highlighted by the slight upward curvature of the semilogarithmic curve. This indicates a very fast ex-

change between the 18C6/KOAc activator and the propagating alcohol suggesting that the complexed metal alkali carboxylate could also be used in default, that is, $[ROH]_0/[18C6/KOAc]_0 > 1$, while maintaining an efficient overall polymerization activity. By comparing to two polymerizations performed to quantitative conversion ($[PO]_0/[BnOH]_0 = 50$; $0.5 \leq [BnOH]_0/[18C6/KOAc]_0 \leq 2$), the E2-to- S_N2 proportion is also drastically impacted and appears to be minimal for an initial $[BnOH]_0/[18C6/KOAc]_0$ ratio of 2, limiting the occurrence of proton abstraction to 1.3 mol% (Figure 3 and Figure S9, Supporting Information).

With these data in hand, and in order to finally unlock the molecular weight limitation associated to the oxyanionic polymerization of PO, final experiments were performed at 21 °C for an initial $[OH]_0$ -to- $[18C6/KOAc]_0$ ratio of 2. Eager to replicate the industrially produced polymer, the polymerization was performed from a propylene glycol (PG) initiator and for a PO-to-PG ratio of 265 ($M_{n,th} = 15\ 400\ g\ mol^{-1}$ at 100% conv.). Due to the very rapid increase of the viscosity, 4 days were needed to reach a conversion of 70% while 15 days were necessary to push the polymerization to completion. As presented by the Figure 4, a plot of the absolute molecular weight (obtained by SEC after application of the Mark–Houwink parameters) and dispersity versus conversion was linear attesting a good polymerization control. It is important to note that the reliability of the corrective Mark–Houwink parameters, for such high DPs, was confirmed by confronting (from time to time) the corrected M_n SEC to the molecular weights obtained by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF MS) analysis.

The living character of the oxyanionic polymerization was then confirmed by a chain extension reaction consisting on a subsequent addition of PO monomer ($13.8 \times 10^{-3}\ mol$). After an additional 10 days of reaction, the M_n SEC of the sample increased to 21 600 $g\ mol^{-1}$ ($D_M = 1.07$, Figure S10, Supporting Information) while the matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF MS) analysis revealed a monomodal distribution centered on a molecular weight of 18 300 $g\ mol^{-1}$ (Figure 5). The primary population is formed with molecular ions with a mass corresponding to the potassium ion PPO initiated with a PG molecule.

To demonstrate the versatility of the 18C6/KOAc complex for the production of high value-added PPOs, the oxyanionic ROP of PO was conducted from an α,ω -hydroxy-terminated poly(ethylene glycol) (PEG₃₀₀, $M_n \approx 300\ g\ mol^{-1}$) macroinitiator. The polymerization was performed for an initial PO-to-PEG ratio of 100 ($M_{n,th} = 6100\ g\ mol^{-1}$ at 100% conv.), all other experimental conditions unchanged. All along the polymerization course, relative SEC chromatograms vary linearly with time and dispersities remaining low (Figure S11, Supporting Information). After 7 days of reaction, the medium was quenched and the final polymer was isolated by precipitation. While a conversion of 80% was determined by 1H NMR analysis (Figure S11, Supporting Information), the formation of a PPO-*b*-PEG-*b*-PPO triblock copolymer was attested by a clear shift of its SEC trace to the higher molar masses, compared to that of the parent PEG (M_n SEC = 6500 $g\ mol^{-1}$, $D_M = 1.15$, Figure 6).

Combining this new controlled epoxide polymerization technique with a highly efficient coupling chemistry is certainly of interest for the macromolecular engineering of polyethers.

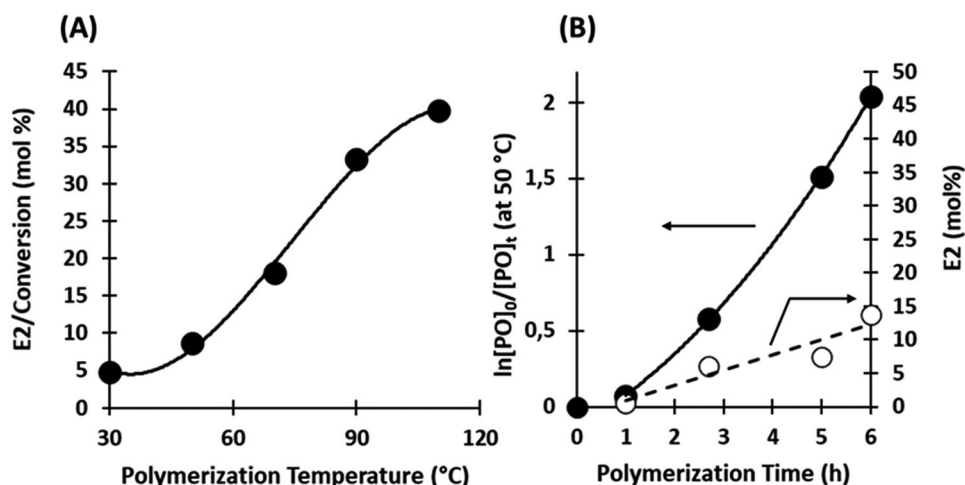


Figure 2. A) Evolution of the E2 proportion for a PO polymerization performed at different temperatures. B) Kinetic plot in the semilogarithmic coordinates (●) and the associated E2 proportion evolution (○) for the polymerization of PO initiated with BnOH and activated by the 18C6/KOAc complex at 50 °C. Conditions: $[PO]_0/[BnOH]_0/[18C6/KOAc]_0 = 50/1/1$.

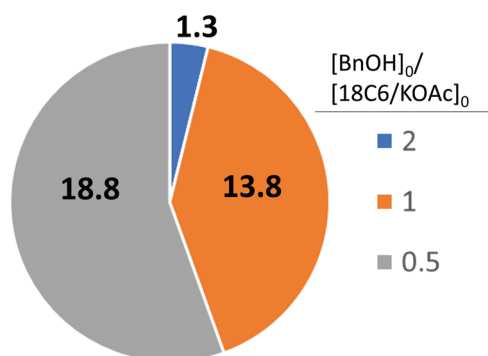


Figure 3. Relative percentage of PPO chains end-capped by an allyl ether function when PO polymerization is initiated at 50 °C from BnOH and different BnOH-to-18C6/KOAc ratios. Conditions: $[PO]_0/[BnOH]_0 = 50$, $0.5 \leq [BnOH]_0/[18C6/KOAc]_0 \leq 2$, conv. ≈ 85 –90%.

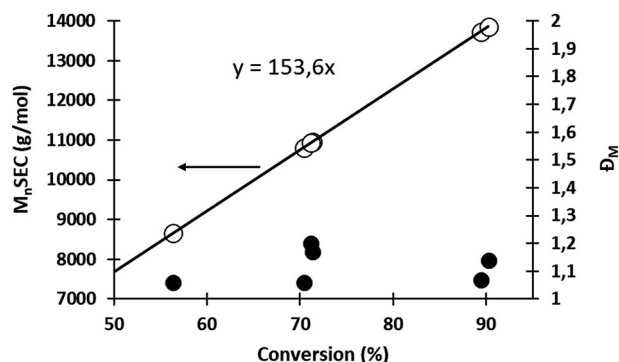


Figure 4. Evolution of the corrected molecular weight (○), as determined by SEC, and \bar{D}_M (●) versus conversion for the polymerization of PO from PG and activated by the 18C6/KOAc complex ($[PO]_0/[PG]_0/[18C6/KOAc]_0 = 265/1/1$).

Since in terms of polymeric conjugation chemistry, the so-called “thiol-ene” reaction appears as one of the most straightforward approaches,^[18] the alkene group tolerance of the 18C6/KOAc complex has been evaluated by (co)polymerizing the allyl glycidyl ether (AGE) monomer. Not subjected to proton abstraction,^[19] the AGE homopolymerization has been carried out in bulk at 21 °C from a PEG₃₀₀ macroinitiator and for an initial [OH]₀-to-[18C6/KOAc]₀ ratio of 1 ($[AGE]_0/[PEG_{300}]_0 = 100$, $M_n,th \approx 12\,000$ g mol⁻¹ at 100% conv.). As attested by ¹H NMR analysis (Figure S12, Supporting Information), polymerization of AGE proceeded with near quantitative monomer conversion in 72 h to give PAGE-*b*-PEG-*b*-PAGE triblock copolymer composed by two PAGE segments characterized by a degree of polymerization of 45. Assuming an inherent experimental error close to 10%, a good agreement thus exists between theoretical and experimental molecular weights.

As expected, the SEC trace of PAGE-*b*-PEG-*b*-PAGE triblock copolymer is also quantitatively shifted to a lower retention volume compared to the PEG used as macroinitiator ($M_{n,SEC} =$

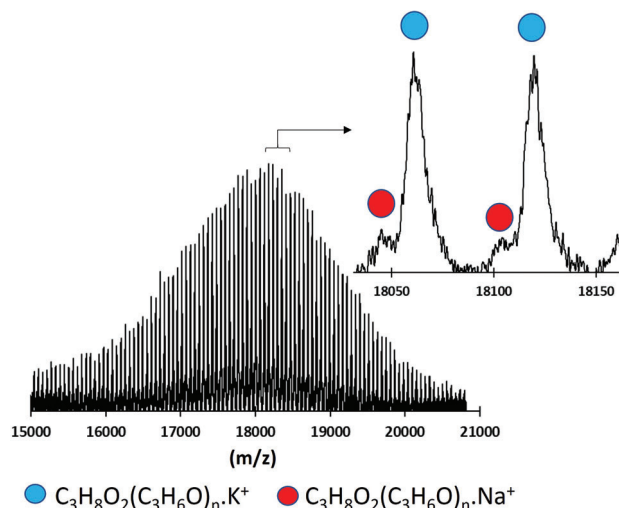


Figure 5. MALDI-ToF MS of PPO obtained after chain extension of PPO prepared by PO ROP as initiated with PG and activated by the 18C6/KOAc complex (see main text for information).

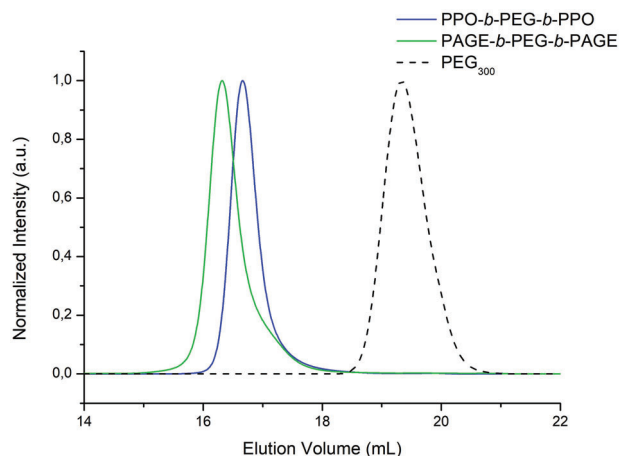


Figure 6. SEC traces of PEG precursor (dash line) and corresponding PPO-*b*-PEG-*b*-PPO (blue line) and PAGE-*b*-PEG-*b*-PAGE (green line) triblock copolymers.

9000 g mol⁻¹, $D_M = 1.25$, Figure 6). Significantly, analysis of the polymer after 4 additional days revealed no discernable change in the molecular weight and dispersity value (Figure S12, Supporting Information), thus suggesting the inherent chemical stability of the pendant allyl groups toward the 18C6/KOAc complex.

As controlled synthesis of PPO and PAGE was established, this prompted us to prepare P(PO-*co*-AGE) statistical copolymers. In our preliminary study, the copolymerization was performed under the same conditions described above for the homopolymerization of PO from PG initiator and using the following molar mass ratios: $[PO]_0/[AGE]_0/[PG]_0/[18C6/KOAc]_0 = 265/335/1/1$. Monitoring the reaction by ¹H NMR revealed that comonomers were both inserted into the copolymer chain with a slight preference for AGE; after 14 days, ≈99% of AGE had been converted while 98% of PO had been consumed (Figure S13, Supporting Information). The extreme viscosity of the medium necessitates 12 additional days to fully consume the remaining PO monomer with no detrimental effect on the control of the process as evidenced by the linear evolution of the SEC chromatograms with time and the narrow associated dispersity values ($M_n, SEC = 19\,630\text{ g mol}^{-1}$ at 100% conversion, $D_M = 1.20$, Figure S13, Supporting Information).

A detailed investigation into this 18C6/KOAc-mediated copolymerization process, including the determination of reactivity ratios will be the topic of a forthcoming publication.

3. Conclusion

This work addresses a challenging topic in oxyanionic polymerization of propylene oxide (PO), which suffers from chain transfer reaction due to the high nucleophilicity of the initiating/propagating alkoxides. This side process leads to poly(propylene oxide) (PPO) chains with low molecular weight and unsaturated end groups. In this contribution, we demonstrated the potential of potassium acetate (KOAc) complexed by 18-crown-6 ether (18C6) as an environmentally benign, inexpensive and soft catalyst system for the controlled ROP of PO, in which benzyl alcohol (BnOH), propylene glycol (PG) or

poly(ethylene glycol) (PEG) act as the initiators. The 18C6/KOAc complex exhibited a better performance than pristine cesium acetate (CsOAc) and KOAc, which is comparable to those of the metal-based catalysts and organocatalysts. The methodology has unique advantages over existing ones; good catalytic activity, readily achieved high-molar mass and narrow dispersity PPO, simplicity and commercial availability of the catalyst, and feasibility for bulk and room temperature reaction. Very interestingly, the developed ROP catalytic system is compatible not only with various initiators but also with other functional monomers, such as allyl glycidyl ether (AGE), enabling the design of triblock copolymers and statistical P(PO-*co*-AGE) structures. Such studies thus expand the understanding of the mechanism of oxyanionic ROP of PO and will serve as a springboard for the preparation not only of high valuable homopolymers and copolymers, but also more complex polymer architectures for potential applications in a wide range of technological areas.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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