Abstract: A metal-free phosphonium bisborane Lewis pair (PBB-Br) was demonstrated to realize the immortal ring-opening polymerization (iROP) of propylene oxide (PO) under mild conditions with alcohols as chain transfer agents (CTAs). Narrow dispersed poly(propylene oxide) (PPO) with controllable molar mass was obtained in quantitative conversion. These indicated the iROP feature of PBB-Br-catalysed PO polymerization. The rapid, reversible and quantitative chain transfer assured the iROP characteristic of intramolecular Lewis pair catalyst PBB-Br, so various well-defined heterofunctionalized PPOs were easily produced. All the α,ω-difunctionalized PPOs were characterized. Density functional theory (DFT) calculations reveal the chain transfer to CTA process is almost barrierless (0.8 kcal mol⁻¹) and thermodynamically favorable as compared to chain propagation. Moreover, PPO-based block copolyethers were easily obtained in one-pot using epoxide mixtures. This research demonstrated that the delicately designed intramolecular synergistic Lewis pair offered a powerful and controllable method to prepare various heterofunctionalized PPO samples with high values.

Introduction

The precise control of polymer structures, e.g. their molecular weight, dispersion (Đ), chain-end groups and monomer sequences, is vital importance in controlling the physical properties and potential applications of polymers. Such precise control highly depends on the advances of polymerization methods and new catalysts. Living polymerization, characterized with fast initiation, free of chain transfer and termination, has been developed to prepare well-defined polymers and copolymers.[1-2] In 1985, Inoue found aluminum porphyrin catalysed ring-opening polymerization (ROP) of epoxides featuring a living characteristic in the presence of MeOH due to the rapid and reversible chain transfer reaction between the active species and MeOH. These merits allowed a unimodal, narrow dispersity and controlled molecular weights of generated polymers. Based on the above characteristics, he defined such polymerization process as iROP.[3] Conventional living polymerization allowed one polymer chain to grow from one active metal center. In contrast, iROP offered the possibility to generate more polymer chains from one active metal center, thus significantly reduced the catalyst loading. Therefore, iROP received considerable attention from academia and industry. To establish a successful iROP, the transfer reaction between active species and CTAs must be rapid, reversible and quantitative.

Poly(propylene oxide) (PPO), an important aliphatic polyether, is widely used in polyurethane (PU) industry.[4] PPO was usually prepared via anionic ROP of propylene oxide (PO).[5-6] Conventionally, the catalytic systems included alkali metal derivatives,[7] homogeneous[8-9] and heterogeneous metal-based complexes.[10-12] Strategies including addition of crown ethers,[13-14]onium salts[15-16] and monomer activation reagents[17-19] were adopted to realize the controllable polymerization of PO. However, metal-residue contamination, limited access to α,ω-difunctionalized PPOs and high molecular weight samples required more efficient and environmentally friendly catalysts. In particular, the replacement of metal-based catalysts by organocatalysts is highly desirable. A series of metal-free systems, including phosphazene-type organic bases,[20] N-heterocyclic carbenes (NHCs),[21-22] N-heterocyclic olefins (NHOs)[23-24] and monomer activation reagents[25] had been developed to achieve controlled/living polymerization of PO. However, these reported catalytic systems did not afford α,ω-difunctionalized PPO products with high efficiency, controllability or high molecular weight at the same time.

Over the past decade, Lewis pairs mediated polymerization had attracted considerable attention.[26-30] Since the seminal work of copolymerization of epoxides and CO₂ using triethylborane (BE₃) and sodium binary system reported by Gnanou et al.,[31] several binary Lewis pairs had been developed and utilized in the ROP of PO. Phosphazene/BE₃ binary system showed a living characteristic for the ROP of ethylene oxide (EO)[32-33] and PO.[34] However, the synthesis of functionalized polyethers with diverse end-groups were limited.[35] Moreover, the high moisture sensitivity of BE₃ caused a practical problem of handling it. PPNCl/triphenylboroxin[36] and DMAP/BE₃[37] were also applied as Lewis pairs however having low catalytic activities. The Wu group reported bifunctional ammonium borane Lewis pairs as initiators/catalysts, which allowed living ROP of PO and EO, selectively generating α-halide/ω-CH₃ or α-OH/ω-CH₃ polyethers (Figure 1).[38-39] Feng and coworkers reported a series of bifunctional ammonium borane-based catalysts that enable the living ROP of PO and EO with an unprecedented activity (TOF ≥ 1.8 x 10⁵ h⁻¹) and a molar mass up to 10⁶ g/mol under mild conditions (Figure 1).[40] Very recently, we developed the first example of an intramolecular phosphonium bisborane Lewis pair,
which served as dual initiator and catalyst to achieve high activity and living characteristic in PO polymerization. In particular, well-defined α-OH/ω-OH PPO was generated using water as CTAs.\(^{[1]}\) Moreover, our previous observation indicated that the precise control of \(M_n\) of the resultant polymer with relatively low \(D_n\) was ascribed to the rapid, quantitative and reversible characteristics of the chain transfer reaction between the active species and water molecules. These results promoted us to take advantage of synergistic effects of PBB-Br and to attempt the iROP of PO using functionalized CTAs with different \(pK_a\)s (Table S1). In this way, we are able to diversify functionalities of generated PPOs using iROP of PO for the first time. Herein, we employed PBB-Br as the organocatalyst in combination with different alcohols as CTAs to attempt the iROP of PO (Figure 1). By this means, α,ω-difunctionalized PPOs become accessible in a versatile manner combining excellent control of molecular weights, dispersity, quantitative chain-end functionalization, and absence of metallic residues. The organocatalyzed synthetic pathway to α,ω-difunctionalized PPOs in an immortal manner not only significantly broadens the architectures of PPOs, but also appears as a promising and more advantageous methodology than previous reports.

\[\text{α,ω-difunctionalized PPOs in a living/controlled metal-free manner}\]

Figure 1. iROP of PO using PBB-Br with various CTAs in a living/controlled metal-free manner

Results and Discussion

iROP of PO catalysed by PBB-Br with different CTAs. Firstly, 1,4-benzenedimethanol (BDM) was used as the CTAs. In a molar ratio of [PO]/[BDM]/[PBB-Br] = 90/0/0.1, PBB-Br could catalyse the PO polymerization in quantitative conversion at -20 °C within 4 h (Table 1, run 1). The number averaged molecular weight \((M_n)\) determined from GPC was 4.4 kg/mol with \(D = 1.05\), consistent with \(M_n^{\text{NMR}}\) (4.6 kg/mol, Figure S12), albeit slightly lower than \(M_n^{\text{theo}}\) (4.9 kg/mol). Upon increasing the ratio of [BDM]/[PBB-Br] to 20/1, \(M_n^{\text{GPC}}\) was reduced to almost half with \(D = 1.05\) (Table 1, run 2). On the other hand, increasing the ratio of [BDM]/[PBB-Br] from 20/1 to 100/1 while having fixed [PO]/[BDM] ratio did not alter the \(M_n\) and \(D\) of resulting PPO products much (Table 1, runs 3-4), indicating that the \(M_n\) of PPO was predominately determined by the molar ratio of [PO]/[BDM]; given that PBB-Br was in trace amount (1 mol% ~ 5 mol% relative to CTA). These results demonstrated the characteristic of iROP by using a combination of PBB-Br and BDM. Considering that the PBB-Br could be less than 1 mol%, predominant α/ω-di-hydroxyl PPO with \(M_n\) in the range of 1.7-4.6 kg/mol could be obtained in this way. The \(^1\)H NMR spectra and GPC curves of obtained PPOs were presented in Figures S12-S15 and Figures S63-S66. The end groups of the resultant PPOs (Table 1, run 1) were defined by matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS). Only one population of α-OH/ω-OH PPO was observed (Figure 2). Moreover, the presence of BDM moiety in the PPO backbone was confirmed by \(^1\)H NMR spectroscopy, in which the resonances at 7.30 ppm (4 H) and 4.53 ppm (4 H) can be assigned to aryl protons and -CH₂-O, respectively. The methine attached to -OH showed typical resonance at 3.92 ppm (Figure S25). These observations indicated chain transfer to both -OH groups in BDM occurred given the identical environment, so the generated alkoxide propagated from both sides, thus affording α-OH/ω-OH PPO.

We then investigated the temperature effects on iROP of PO. Given the [PO]/[BDM]/[PBB-Br] ratio between 100/1/0.1 and 200/2/0.1, all polymerizations exhibited good control on both \(M_n\) and \(D\) at 25 and 45 °C (Table 1, runs 5-10), although the dispersities became slightly broader at 45 °C, which might be caused by the attenuated noncovalent interaction between boron and PO at elevated temperature, thus resulting in a less controlled manner. All the obtained PPOs featured well-defined α-OH/ω-OH structure with BDM moiety in the PPO backbone, which were verified by \(^1\)H NMR spectroscopy (Figures S16-S21). In all cases, no proton signals of allyloxyl group were observed in \(^1\)H NMR spectra (Figures S16-S21), indicating negligible chain transfer to PO thus negligible epimerization. Apparently, the precise control of \(M_n\) of the resultant PPOs with relatively low \(D_n\) was ascribed to the rapid, quantitative and reversible chain transfer reaction between the limiting active species and large excess BDM. To examine the effects of catalyst concentrations, we performed the iROP at [PO]/[BDM]/[PBB-Br] = 100/1/0.01, and found that the conversion was only 35% at 25 °C after 72 h (Table 1, run 12). In contrast, 97% conversion was observed at -20 °C after 41 h (Table 1, run 13). It is worth noting that the ROP with high BDM loading can apparently slow down the polymerization because the control experiment without adding BDM finished within 6 min, however, yielding PPO with much higher \(M_n\) (Table 1, run 14). These indicated that the amount of CTAs had significant influences on the catalytic activity of iROP, which was frequently observed in immortal polymerization.\(^{[2]}\)

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Table 1. Bulk polymerization of PO using PBB-Br in the presence of BDM at different molar ratios and temperatures.
BA was chosen as CTA because the benzyl group can be easily identified by $^1$H NMR.\[^{[2]}\] For the PBB-Br/BA system, the conversion was up to 98% at -20 °C in 1.5 h, which was comparable to that of BDM under identical conditions (Table 1, run 11). The $M_{n}^{NMR}$ coincided with $M_{n}^{GPC}$ (Table 2, run 6), and the $\omega$-benzyl/ω-OH end-groups were well characterized by MALDI-TOF-MS (Figure S5) and $^1$H NMR spectroscopy (Figure S31). For the PBB-Br/AA system, the allyl group was designed for thiol–ene coupling or hydrosilation to introduce additional functionalities. In this case, the polymerization went to complete at 25 °C within 1 h. The $M_{n}^{NMR}$ of produced PPO was close to $M_{n}^{GPC}$ (Table 2, run 7). The terminal α-allyloxy and ω-OH groups were confirmed by MALDI-TOF-MS (Figure 4a) and $^1$H NMR spectroscopy (Figure S32). The amino functionalized PPOs is rather challenging and has not been achieved directly by using iROP. Here we tried to use EA as CTA. Unfortunately, PBB-Br/EA system, even with addition of BEt$_3$ as a masking reagent, was inactive to the ROP of PO (Table S2, runs 1-2). This might be ascribed to that the formation of stable five-membered alkoxide intermediates with reduced nucleophilicity caused invalidity of the propagation and restricted further chain transfer process. In contrast, PBB-Br/ABO system gave a full conversion of PO at 25 °C. There is good match among $M_{n}^{Thes}$, $M_{n}^{NMR}$ and $M_{n}^{GPC}$ (Table 2, run 8). Therefore, the aromatic amino group on the PPO $\omega$-chain end was successfully installed via a non-protected amino manner, thus providing a pathway for a direct synthesis of aromatic $\alpha$-amino/ω-OH PPO (Figures S6 and S33). Tertiary amine based heterotelechelic PPO was successfully prepared by using DBAE as CTA. The good agreements of $M_{n}^{Thes}$, $M_{n}^{GPC}$ and $M_{n}^{NMR}$ indicated a controlled characterization of such system (Table 2, run 9). Detailed characterizations were provided in Figures 4b and S34.

The $\alpha$-alkyne group offers a highly efficient conjugation platform for the powerful Huisgen 1,3-dipolar cycloaddition (“click chemistry”).\[^{[43-45]}\] Here, we applied PBB-Br/TMS-PO pair to...
preapre alkyne functionalized PPO. The SiMe₃ group can be readily removed by fluoride ion to generate an α-alkyne group. For [PO]₀[Br][PO]₀/[PBB-Br]₀ = 1000/10/1, the polymerization took 4 h to reach full conversion (Table 1, run 10). Low M₈ of α-3-trimethylsilyl)-2-propargyl-1-oxyl/u-OH PPO was produced (Figure 4c and Figure S35), in which the α-3-trimethylsilyl)-2-propargyl-1-oxyl moiety exhibited characteristic peaks at 4.17 (SiCC₂H₂O) and 0.17 ppm (SiMe₃). The signals at 91.3, 101.7 ppm in ¹³C[¹H] NMR confirmed the presence of SiC bond (Figure S36). ²⁹Si[¹H] NMR showed characteristic resonance at -17.9 ppm (Figure S37). On the other hand, furfuryl group is subject to [4+2] cycloaddition reaction. The α-furfuryl/u-OH PPO was prepared using FuG as CTAs (Table 2, run 11) and further characterized by MALDI-TOF-MS (Figure 4d) and ¹H NMR spectroscopy (Figure S38). The furfuryl group showed peaks at 4.47, 6.30 and 7.39 ppm with relative integrals of these peaks in a ratio of 2:2:1.

(Meth)acrylate is versatile functional group for Michael addition or radical polymerizations. To our delight, α-acrylamide/u-OH PPO was achieved by using N-(2-hydroxyethyl)acrylamide as CTA. The GPC curves of obtained PPO showed bimodal distributions (Table 2, run 12, Figure S88). Further characterizations were provided in SI (Figure S7 and Figure S39). Interestingly, α-acrylate/u-OH PPO and α-methacrylate/u-OH PPO were successfully synthesized using 2-HEA and 2-HEMA, respectively (Table 2, runs 13-14). The GPC curves of obtained PPOs exhibited monomodal characteristic (Figures S89 and S90). 2-Ethoxyl acrylate capped-PPO exhibited characteristic signals at 6.40, 6.15, 5.84 ppm corresponding to acrylate protons and those at 4.29 ppm and 3.72 ppm belong to protons of COOCH₂CH₂O moiety (Figure S40). 2-Ethoxyl methacrylate terminated-PPO showed characteristic peaks at 6.13, 5.56, 1.95 ppm ascribing to methacrylate protons, while protons of COOCH₂CH₂O moiety showed resonances at 4.29 and 3.72 ppm (Figure S41). The end group fidelity of α-acrylate/u-OH PPO and α-methacrylate/u-OH PPOs were further characterized by MALDI-TOF-MS, respectively (Figure S8 and Figure 4e).

Organic azides are indispensable precursors for click chemistry, a versatile method of creating C-N bonds under mild experimental conditions, combining tolerance of functional groups and high yields. The α-azide/u-OH PPO was previously obtained by NHCl initiated PO polymerization using N₃SiMe₃ as nucleophile.[22] In our case, α-azide/u-OH PPO was successfully generated using 2-azide ethanol (2-EA) as CTAs. The N₃CH₂CH₂O moiety showed resonances at 2.42, 2.74, 2.98, 3.41 ppm in the ¹H NMR spectrum (Figure S42). The carbon atom of N₃CH₂ showed typical peak at 50.9 ppm in the ¹³C[¹H] NMR spectrum (Figure S43). α-Azide/u-OH PPO was further characterized by MALDI-TOF-MS (Figure 4f). Assuming the presence of one azido terminal group at every PPO chain, the predicted M₉[θ][HO] (5.4 kg/mol) is very close to M₉[GPC] (5.3 kg/mol) and M₉[NMR] (4.6 kg/mol). The presence of the -N₃ group was further verified by IR spectroscopy with a characteristic band at 2103 cm⁻¹.[46]

To obtain carboxyl or amino group functionalized PPO, functional group protecting strategy was utilized to prepare alliphatic α-carboxyl/u-hydroxyl or α-amin/o-hydroxyl PPO. 2-BG and 2-BAE were attempted to explore the efficiency of introducing protected carboxylic and amino groups.[33, 47-48] For PBB-Br/2-BG and PBB-Br/2-BAE systems, the excellent agreements between M₉[GPC] and M₉[NMR] were found (Table 2, runs 16 and 17). The 2-tert-butyl glycolate end capped-PPO showed peaks at 4.00 ppm (OCH₂O) and 1.47 ppm (BuCOO) in the ¹H NMR spectrum (Figure S44). The 2-(Boc-amino)ethoxyl terminated-PPO exhibited characteristic signals at 5.00 ppm (NH) and peaks at 3.30 ppm and 3.15 ppm (NHCH₂CH₂O). The Bu group showed peaks at 1.43 ppm (Figure S46). Both PPOs were further confirmed by MALDI-TOF-MS (Figures S9-S10). Subsequently, the acid-catalyzed hydrolysis of α-2-tert-butyl glycolate/u-OH PPO and α-2-(Boc-amino)ethoxyl/u-OH PPO offered a convenient way to produce α-carboxyl/u-hydroxyl PPO and α-amin/o-hydroxyl PPO, respectively (SI, hydrolysis experiments). Both samples were characterized by ¹H NMR spectra shown in Figure S45 and Figure S47.

![Figure 3. Functionalized mono alcohols as CTAs employed for the preparation of heterotelechelic PPOs.](image)

Table 2. iROP of PO using PBB-Br in the presence of other CTAs
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[a] The polymerizations were performed using catalyst PBB-Br (10 μmol) in neat PO with different feed ratios of PO/CTAs. [b] Conversion% of the PO was determined by $^1$H NMR spectroscopy. [c] $M_n^\text{NMR} = 58.08 \times (PO/(PBB-Br+CTAs)) \times \text{Conv.} \times M_n(\text{CTAs}).$ [d] $M_n^\text{GPC} = 58.08 \times \{A(3.55+3.41)/3\}/[A(\text{typical peaks of CTAs})/\text{actual number of typical protons of CTAs}].$ [e] $M_n(\text{CTAs})$ means the molecular weight of chain transfer agents. [f] Determined by GPC in THF, calibrated with PPO as standards.

The photosensitive protecting group, 4,5-dimethoxy-2-nitrobenzyl alcohol (DMNA)[48], is stable to a variety of chemical treatments and can be cleaved readily by irradiation, thus could be applied in many areas of synthetic chemistry. Finally, α,4,5-dimethoxy-2-nitrobenzyl/ω-OH PPO was synthesized by PBB-Br/DMA system, which indicated PBB-Br had good tolerance to nitro group. A good agreement of $M_n^\text{NMR}$ and $M_n^\text{NMR}$, as well as low $\eta$ of obtained PPO were observed (Table 2, run 18). In addition, characteristic protons of 4,5-dimethoxy-2-nitrobenzyl group were clearly identified at 7.69, 7.32 ppm (C9H2), 4.93 ppm (C1H2-C1H2O) and 3.96, 3.93 ppm (two OCH3) (Figure S48). The end group fidelity of α,4,5-dimethoxy-2-nitrobenzyl/ω-OH PPO was further confirmed by MALDI-TOF-MS (Figure S11). The inefficiency of TBSOH as CTAs might be ascribed to the low Lewis acidity of Si-H bond (Table S2, run 3). Addition of acetic acid or phenol as CTAs led to deactivation of catalyst PBB-Br (Table S2, runs 4-5), which might be due to their higher Lewis acidity, resulting in less nucleophilic species to initiate the ROP of PO.
Density Function Theory (DFT) Calculations and Proposed Mechanism. The fast and reversible chain transfer assured the immortal polymerization of PBB-Br in the presence of alcohols. To better understand the reaction process, we selected benzyl alcohol (BA) as the model CTAs in the DFT calculations for Gibbs energy changes of important elementary steps.

In the absence of CTAs, the catalytic pathway proceeded via catalytic cycle 1.\(^{[41]}\) In the initiation step, the nucleophilic attack of the Br\(^{-}\) to the activated PO leads to the formation of IN2 featuring an alkoxide-involved tetracoordinated boron. The lower Gibbs energy than the initial state indicated the formation of IN2 is thermodynamically favorable. The relative Gibbs energy barrier in the initiation step is 16.3 kcal mol\(^{-1}\). In the presence of excess BA, IN2 preferentially coordinates with BA than PO because the formation of IN3 is thermodynamically favorable with Gibbs energy decrease to -23.4 kcal mol\(^{-1}\). Chain transfer from Br-capped alkoxide to the activated BA results in the formation of IN4 via transition state TS2 with an energy barrier of 0.8 kcal mol\(^{-1}\) relative to IN3. The small Gibbs energy barrier between IN3 and IN4 indicates the chain transfer process is almost barrierless. Competitive coordination of PO to B2 results in the formation of IN5 with the liberation of Br-capped alcohol. This process causes an increase of Gibbs energy of 5.6 kcal mol\(^{-1}\). In the propagation step, the nucleophilic attack of the benzyloxide to the activated PO leads to the formation of IN6 via transition state TS3 with an energy barrier of 22.2 kcal mol\(^{-1}\) relative to IN4 (Figure 5). The higher Gibbs energy barrier of propagation (22.2 kcal mol\(^{-1}\)) compared to initiation step (16.3 kcal mol\(^{-1}\)) indicates initiation is much easier than propagation. The formation of the new coordinate O-B2 bond in IN6 indicates the completion of the catalytic cycle 2. IN6 repeatedly adds PO via Sn2 ring-opening addition into the alkoxide-boron bond to propagate into polymeric alkoxide boron species. The lower relative Gibbs energy of TS3 (-0.6 kcal mol\(^{-1}\)) than TS2 (1.8 kcal mol\(^{-1}\)) indicates catalytic circle 2 dominates in the presence of BA. Rapid and reversible exchange reaction of benzyl alcohol with INT2 gives the benzyloxide propagating species (IN4\(^{1}\)), along with dormant Br-capped polymer. The dormant Br-capped polymer can reverse to the propagation cycle with the active alkoxide species. Moreover, the unimodal and narrow molecular weight distribution (\(\Delta M=1.1\)) of the isolated PPO implies the CTAs, benzyl-ended active chain and Br-capped active chain are reversible and much more rapid than the propagation steps, ensuring that the rapid growing/dormant interconversion goes on over the entire lifetime of the polymerization process (Scheme 1).
Figure 5. DFT-calculated Gibbs energy profiles with the key intermediates and transition states for PBB-Br-mediated ROP of PO both in the presence and absence of CTAs.

Scheme 1. Proposed reaction mechanism of iROP of PO catalysed by PBB-Br in the presence of BA.

Synthesis of Block Copolyethers. We previously demonstrated that PBB-Br was effective for the ROP of butylene oxide (BO) and allyl glycidyl ether (AGE). Moreover, we
observed the polymerization rate of BO and AGE initiated by PBB-Br are less active than PO. Therefore, we assume PBB-Br could be a suitable catalyst/initiator for one-pot sequence-controlled diblock polymer synthesis with PO/BO or PO/AGE mixtures. The kinetic bias of polymerization rate ($k_v$) would allow precise control of the PPO based block copolymers, which would expand scope and potential application of these polymers. Mixing $[\text{PO}]_0/[\text{BO}]_0/[\text{PBB-Br}]_0 = 50/50/1$ in one-pot, the polymerization finished at 0 °C within 3 h (Table 3, run 1). GPC revealed a monomodal distribution of the generated PPO$_{20}$-b-PBO$_{50}$ with relatively narrow dispersity. For comparison, PPO$_{50}$ was obtained by PBB-Br initiated polymerization of PO at 0 °C under $[\text{PO}]_0/[\text{PBB-Br}]_0 = 50/1$ condition, which showed much lower molecular weight than PPO$_{20}$-b-PBO$_{50}$ (Figure 6a). The PPO$_{20}$-b-PBO$_{50}$ diblock copolyether was characterized by $^1$H NMR and $^{13}$C($^1$H) NMR spectra, respectively (Figures S50 and S51). In the $^1$H NMR spectrum, ethyl protons attributed to PBO showed peaks at 1.53 and 0.92 ppm, while methyl group ascribed to PPO showed peaks at 1.13 ppm. Moreover, the ratio of integral of ethyl to methyl was 5:3, which indicated the generated diblock copolyether possessed the same molar amount of PBO and PPO. Moreover, the precise formation of PPO$_{20}$-b-PBO$_{50}$ was monitored by $^1$H NMR spectroscopy, which showed that no BO was consumed before the depletion of PO (Figure S54).

Diblock copolyether with pendant allyl group can also be easily introduced by using PBB-Br initiated PO/AGE copolymerization. In $[\text{PO}]_0/[\text{AGE}]_0/[\text{PBB-Br}]_0 = 50/50/1$, both monomers were consumed at 0 °C within 2 h (Table 3, run 2). The obtained PPO$_{20}$-b-PAGE$_{50}$ was measured by GPC (Figure 6b) and NMR spectroscopy (Figure S55). PAGE exhibited typical peaks at 5.88, 5.26, 5.15 ppm. The integral ratio of allyl group of PAGE to methyl group of PPO was 3:3, which reflected formation of an equal amount of PAG and PPO in the PPO$_{20}$-b-PAGE$_{50}$. A good control of the PPO$_{20}$-b-PAGE$_{50}$ was further confirmed by $^1$H NMR, which indicated that no AGE was consumed before the full consumption of PO (Figure S58).

Finally, well-defined PPO$_{20}$-b-PBO$_{50}$-b-PPO$_{20}$-b-PBO$_{50}$ and PPO$_{20}$-b-PAGE$_{50}$-b-PPO$_{20}$-b-PAGE$_{50}$-b-PPO$_{50}$-b-PAGE$_{50}$ were successfully prepared using sequential addition of three portions of PO/BO mixture and PO/AGE mixture, respectively. Runs 1 and 2 in Table S3 were performed at 25 °C to ensure full conversion of the first portion before addition of the second portion. The complete consumption of each portion were tracked by $^1$H NMR spectra (Table S3, Figures S60 and S62). GPC curves revealed a linear increase of molecular weight after each addition of monomer mixture (Figure 6c and 6d). The ratio of integrals of typical peaks at 1.14 ppm (PPO) relative to typical peaks at 0.92 ppm (PBO) was almost to 1:1, which indicated a precise control of obtained PPO$_{20}$-b-PBO$_{50}$-b-PPO$_{20}$-b-PBO$_{50}$-b-PPO$_{50}$-b-PAGE$_{50}$ (Figure S59). Furthermore, in the $^1$H NMR spectrum (Figure S61), the molar ratio of typical peaks of PAGE to that of PPO revealed a perfect 1:1 molar composition of AGE and PO in the obtained PPO$_{20}$-b-PAGE$_{50}$-b-PPO$_{20}$-b-PAGE$_{50}$-b-PPO$_{50}$-b-PAGE$_{50}$. To the best of our knowledge, well-defined multi-block copolymers composed of PPO, PBO, PAGE have not been reported before.

![Figure 6](image-url) (a) GPC analysis of PPO$_{20}$-b-PBO$_{50}$ (Table 3, run 1), (b) PPO$_{20}$-b-PAGE$_{50}$ (Table 3, run 2), (c) PPO$_{20}$-b-PBO$_{50}$-b-PPO$_{20}$-b-PBO$_{50}$-b-PPO$_{50}$-b-PAGE$_{50}$ (Table S3, run 1), (d) PPO$_{20}$-b-PAGE$_{50}$-b-PPO$_{20}$-b-PAGE$_{50}$-b-PPO$_{50}$-b-PAGE$_{50}$ (Table S3, run 2).

Table 3. Copolymerization results of PO with BO and AGE catalysed by PBB-Br

<table>
<thead>
<tr>
<th>Run</th>
<th>Epoxide</th>
<th>[PO]/Epoxide/PBB-Br</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Conversion%</th>
<th>$M_v$ (kg/mol)</th>
<th>$M_M$ (kg/mol)</th>
<th>$D$</th>
</tr>
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<tr>
<td>1</td>
<td>BO</td>
<td>50/50/1</td>
<td>0</td>
<td>3</td>
<td>99/99</td>
<td>6.4</td>
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</tr>
<tr>
<td>2</td>
<td>AGE</td>
<td>50/50/1</td>
<td>0</td>
<td>2</td>
<td>99/99</td>
<td>8.5</td>
<td>7.4</td>
<td>1.13</td>
</tr>
</tbody>
</table>

[a] The polymerizations were performed using catalyst PBB-Br (10 μmol, 5.9 mg) at 0 °C in an equal molar amount of PO and other epoxides (5 mmol). [b] $M_v$: $50 \times M_v$(PO) $\times$Conv. + $50 \times M_v$(epoxide) $\times$Conversion% $\times$ $M_v$(Br). [c] Determined by GPC in THF, calibrated with commercially available PPO as standards. [d]
Conflict of Interest

The authors declare no conflict of interest.

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References

Immortal polymerization of PO in a metal-free and controlled manner

- CTAx: FG\xrightarrow{\text{CTA}} OH

- CTAx catalyst is up to 100/1, catalyst/PO loading is minimalized to 0.01 mol%
- ABABAB block polyether is accessible

Phosphonium Lewis pair organocatalyst P608r