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Phosphazene-Promoted Metal-Free Ring-Opening Polymerization of Ethylene Oxide Initiated by Carboxylic Acid

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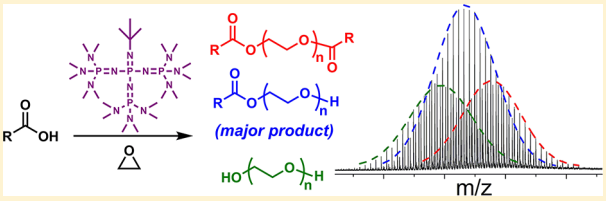
Supporting Information

ABSTRACT: The effectiveness of carboxylic acid as initiator for the anionic ring-opening polymerization of ethylene oxide was investigated with a strong phosphazene base (*t*-BuP_4) used as promoter. Kinetic study showed an induction period, i.e., transformation of carboxylic acid to hydroxyl ester, followed by slow chain growth together with simultaneous and fast end-group transesterification, which led to poly(ethylene oxide) (PEO) consisting of monoester (monohydroxyl), diester, and dihydroxyl species. An appropriate *t*-BuP_4/acid ratio was proven to be essential to achieve better control over the polymerization and low dispersity of PEO. This work provides important information and enriches the toolbox for macromolecular and biomolecular engineering with protic initiating sites.



INTRODUCTION

In the recent surge for metal-free polymerization techniques,[1−3] a family of organic superbases, the phosphazenes, have shown their remarkable potential as promoter/catalyst for the anionic polymerization of various types of monomers,[4] including epoxides,[5−8] cyclosiloxanes,[9−13] lactams,[14,15] cyclopropane derivatives,[16−18] (meth)acrylates,[19−22] cyclic esters,[23−25] and cyclic carbonates.[26−28] Generally, phosphazene bases improve the nucleophilicity of the initiator/chain-end significantly by complexation with the counterion (e.g., proton or lithium cation), resulting in a rapid and usually controlled anionic polymerization. Phosphazene-promoted polymerization techniques appeal to us not only for its metal-free feature or the enhanced polymerization rate but also for the powerful synthetic toolbox they provide for sophisticated macromolecular engineering.[4] Through the activation of initiating sites from a designated substrate and subsequent *in situ* polymerization, different macromolecular architectures have been achieved, including end-functionalized,[29−31] bioconjugate,[32] graft,[33−35] star-shaped,[36−38] and hyperbranched polymers.[39,40]

Similarly to other metal-free ring-opening polymerization systems developed so far, hydroxyls have been the most commonly employed initiating sites in association with phosphazene bases. Some recent reports have demonstrated that other protic functionalities, e.g., thiol[16−18] and (primary or secondary) amide,[41,42] can also be activated by phosphazene bases, allowing effective initiation and polymerization. Expanding the diversity of potential initiating functionalities provides new pathways toward facile macromolecular engineering on desirable substrates such as biomolecules, polymeric, or all-carbon materials.

So far, the use of carboxylic initiators has scarcely been reported probably due to their high acidity and the seemingly low nucleophilicity. The only case found in the literature is the phosphazene-promoted polymerization of highly reactive *β*-lactone derivatives, where both the initiator and growing chain end are carboxylate species.[43,44] Reaction between carboxylic acid and epoxide catalyzed by weak bases has been long-known for the synthesis of esters;[45−47] however, the highly basic alkoxide abstracts the proton from the catalyst, thus preventing the polymerization to occur. In this article we aim to investigate whether the use of a strong phosphazene base, *t*-BuP_4 (Figure 1), can trigger initiation and subsequent polymerization of

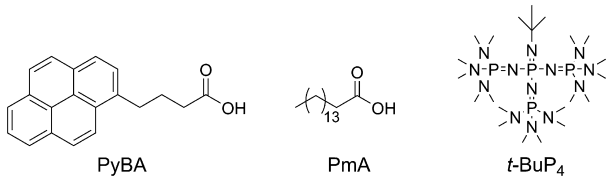


Figure 1. Formula of 1-pyrenebutyric acid (PyBA), palmitic acid (PA), and the strong phosphazene base (*t*-BuP_4).

ethylene oxide (EO) from carboxylic acid. We assume that [*t*-BuP_4H]$^+$ could retain the proton trapped and thus preserve nucleophilicity after the carboxylate turns into alkoxide. To confirm such an assumption, we have used 1-pyrenebutyric acid (PyBA) and palmitic acid (PmA) as model carboxylic compounds and conducted anionic ring-opening polymerization (AROP) of EO in the presence of *t*-BuP_4.

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Table 1. Experimental Conditions and Molecular Characteristics of PEO Samples Initiated by Carboxylic Acids in the Presence of *t*-BuP$_4$

entry[a]	$[t\text{-BuP}_4]_0/[\text{COOH}]_0$[b]	time (h)	$M_{n,theo}$[c] (g mol^{-1})	$M_{n,NMR}$[d] (g mol^{-1})	$M_{n,SEC}$[e] (g mol^{-1})	M_w/M_n[e]
PyBAEO1	0.1	48	2080	2340	2270	1.05
PyBAEO2	0.1	24	2080	1770	1740	1.05
PyBAEO3[f]	0.01	48	2080			
PyBAEO4	0.5	48	4990	5060	4570	1.10
PmAEO1	0.1	48	2080	2180	2460	1.04
PyBAEO5[g]	0.1	30	2080	2310	2060	1.04
PyBAEO6[g]	0.5	6	2080	2140	1950	1.13

[a]PyBAEO and PmAEO denote respectively PEO samples from 1-pyrenebutyric acid and palmitic acid. [b]Molar ratio of *t*-BuP$_4$ to carboxylic acid. [c]Theoretical number-average molecular weight calculated from the feed ratio of EO to carboxylic acid. [d]Determined by ^{1}H NMR ($CDCl_3$). [e]Determined by SEC (DMF, 70 °C, PEO standards). [f]No polymer is formed as indicated by SEC and ^{1}H NMR. [g]Kinetic studies are performed for these two entries.

EXPERIMENTAL SECTION

Chemicals. All chemicals were purchased from Sigma-Aldrich. Ethylene oxide (EO, 99.5%) was dried successively by calcium hydride and *n*-butyllithium (*n*-BuLi) prior to polymerizations. 1-Pyrenebutyric acid (PyBA, 97%), palmitic acid (99%), phosphazene base (*t*-BuP$_4$, 1 M solution in *n*-hexane), and acetic acid (99%) were used as received. Tetrahydrofuran (THF) was dried successively over Na and *n*-BuLi.

Instrumentation. Size exclusion chromatography (SEC) coupled with UV (λ = 270 nm) and RI detectors was carried out in *N*,*N*-dimethylformamide (DMF, with 0.05 M LiBr) at 70 °C using two identical PLgel columns (5 μm, MIXED-C) at a flow rate of 1.5 mL/min. Calibration was done with poly(ethylene oxide) standards. Nuclear magnetic resonance (NMR) measurements were carried out at room temperature using a Bruker AVANCE III 400 spectrometer operating at 400 MHz; $CDCl_3$ (Aldrich) was used as solvent. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed on a Bruker Ultraflex III MALDI-TOF mass spectrometer (Bruker Daltonik, Bremen, Germany). Samples were dissolved in THF (10 mg mL^{-1}) and mixed with a solution of potassium/sodium trifluoroacetate in THF (10 mg mL^{-1}) in volume ratio of 5:1. This solution was then mixed with a solution of matrix, 2,5-dihdroxybenzoic acid in THF (20 mg mL^{-1}), in volume ratio of 1:10. Then, 0.4 μL of the final solution was spotted on the target plate (dried-droplet method). The reflective positive ion mode was used to acquire the mass spectra of the samples. The calibration was made externally with the poly(methyl methacrylate) standards using the nearest-neighbor positions.

Polymer Synthesis. Typical procedure for PyBAEO1: 0.673 g of PyBA (2.33 mmol) was dissolved in ca. 20 mL of dry THF and filtered (through 1 μm glass fiber filter) into the reaction flask. THF was removed slowly by cryo-evaporation followed by condensation of dry THF into the reactor to dissolve PyBA and cryo-evaporation of the THF again. After repeating this step twice, PyBA was dried on vacuum line for 1 h with constant pumping. Then, 40 mL of dry THF was condensed into the reactor as the polymerization solvent. After complete dissolution of PyBA, 0.23 mL of *t*-BuP$_4$ solution (0.23 mmol) was added dropwise with an argon flow. The solution was stirred for 30 min, and temperature was brought down to −30 °C, after which 5.5 mL of purified EO (4.8 g, 110 mmol) was condensed slowly into the reactor. Then the reactor was sealed by a stopcock, and temperature was slowly elevated to 45 °C. The color of the solution turned slowly from brownish yellow to dark green. After heating and stirring for 48 h, the polymerization was quenched by addition of 0.1 mL of acetic acid, upon which the color turned back to brownish yellow. The product was isolated by precipitation in *n*-hexane followed by drying thoroughly in vacuum. $M_{n,theo}$ = 2080 g mol^{-1}; $M_{n,SEC}$ = 2270 g mol^{-1}, M_w/M_n = 1.05. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 8.35−7.82 (aromatic protons on pyrenyl end group), 4.28−4.21 ($-COOCH_2-$), 3.85−3.43 ($-CH_2CH_2O-$), 3.42−3.35 (pyrenyl$CH_2CH_2CH_2-$), 2.54−2.43 ($-CH_2COOCH_2-$), 2.26−2.12 (pyrenyl$CH_2CH_2CH_2-$).

Kinetic Study. A reaction flask equipped with a ground joint (male) was used for kinetic study. The joint was stopped by a rubber septum, through which the aliquots (ca. 0.2 mL each) were withdrawn by syringes at different reaction time. The aliquot was injected immediately into 2 mL of THF with a few drops of acetic acid, dried extensively by vacuum, and dissolved in $CDCl_3$ for ^{1}H NMR analysis.

RESULTS AND DISCUSSION

Most of the experiments are performed with PyBA, as its aromatic functionality facilitates the structural and compositional analysis of the products. For PyBAEO1 (Table 1), 0.1 equiv of *t*-BuP$_4$ with regard to PyBA is used. The polymerization is allowed to proceed for 48 h at 45 °C to ensure complete conversion, and the product is analyzed by SEC, NMR, and MALDI-TOF MS.

Both RI and UV signals are shown in SEC traces (Figure 2, left), manifesting the incorporation of pyrenyl group in the polymer chain. The calculation based on PEO standards calibration gives a low dispersity (M_w/M_n = 1.05) and a number-average molecular weight ($M_{n,SEC}$) close to the theoretical value ($M_{n,theo}$). ^{1}H NMR spectrum (Figure 2, right) presents clearly all the characteristic signals from both PEO and PyBA components. The triplet centered at 4.25 ppm indicates the existence of ester groups, and the number of protons fits very well with other signals from PyBA moiety. The molecular weight ($M_{n,NMR}$) of PEO calculated based on the peak integrals of the ester protons and PEO ether protons also fits with $M_{n,theo}$ (Table 1). These results confirm that the polymerization is initiated by the carboxyl group, with practically 100% initiation efficiency and full conversion of EO.

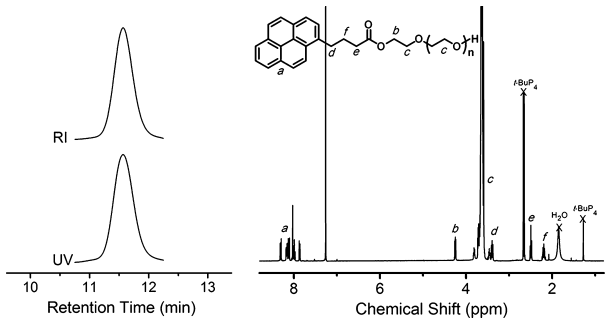

Figure 2. SEC traces (left) and ^{1}H NMR spectrum (right) of a representative poly(ethylene oxide), PyBAEO1 (Table 1), initiated by 1-pyrenebutyric acid in the presence of *t*-BuP$_4$.

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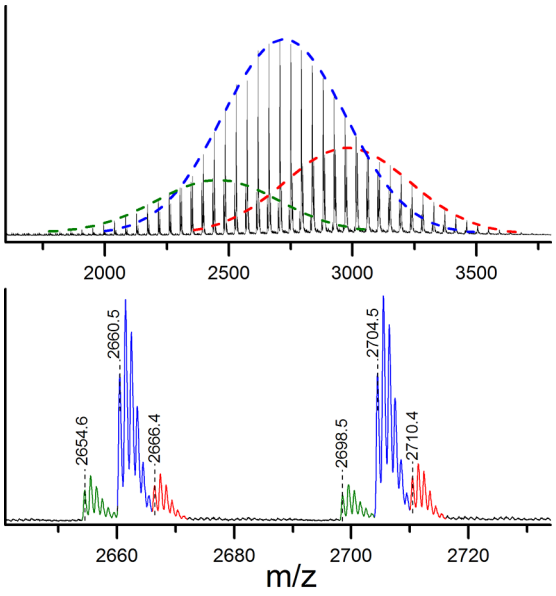
MALDI-TOF MS of PyBAEO1 (Figure 3) reveals that, while the main product is the expected species, bearing one ester and



DP	Calculated exact mass*	Structural formula
60	2698.7 Da	
54	2704.7 Da	
48	2710.6 Da	

Figure 3. MALDI-TOF MS of PyBAEO1 showing the three distributions (upper figure: full spectrum; lower figure: enlarged region). The measured values are presented in the lower figure, and the calculated exact masses for the different species ionized with potassium ion for the right signals are shown in the table.

one hydroxyl end group (monoester species, blue), there are two more distributions visible from the spectrum. Detailed analysis shows that the lower molecular weight distribution belongs to the species bearing no ester moiety at either end (dihydroxyl species, green), while the higher molecular weight distribution belongs to the species with ester moieties on both ends (diester species, red). However, the degree of polymerization for the apexes of all three distributions is the same (DP = 54). The difference of the apex positions is only due to the different numbers (0, 1, or 2) of pyrenyl ester moieties attached to the polymer chains. The uniform PEO length in the three species is further verified by reacting PyBAEO1 with large excess of ethyl acetate in the presence of *t*-BuP$_4$, which transforms the three species exclusively into diacetylated PEO giving a well-defined symmetric MALDI-TOF MS with the same DP (54) of the apex as the precursor (Figure S1).

The formation of these two extra species is considered to be caused by simultaneous chain-end transesterification during the polymerization. In this case the molar concentration of diester species should be half of monoester species and equal to dihydroxyl species. Actually, MALDI-TOF MS of PyBAEO1 shows a slightly higher intensity for the diester species (Figure 3). This is due to the presence of the pyrenyl groups, which absorb the laser light, thus improving the ablation of the polymer chains to which they are attached. This effect is even more pronounced for PyBAEO2 (Figure S2), which has a lower PEO molecular weight (higher pyrenyl content) as the reduced polymerization time (24 h) leads to 84% conversion of EO (calculated from $M_{n,NMR}$ and $M_{n,theo}$). The MALDI-TOF MS of the sample from palmitic acid (PmAEO1, Table 1) shows the expected ratio of three distributions (Figure 4) due to the absence of aromatic groups.

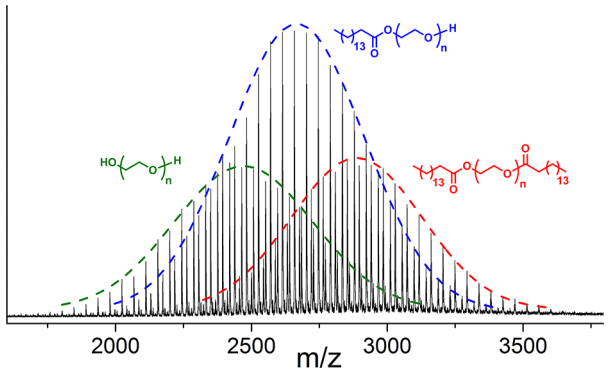


Figure 4. MALDI-TOF MS spectrum of PmAEO1 (Table 1) showing the three distributions (green: dihydroxyl; blue: monoester; red: diester species).

Scheme 1 shows the proposed reaction mechanism. Generally, the reaction consists of an induction period, i.e., the transformation of carboxylic acids into hydroxyl esters and alkoxides, followed by chain growth with simultaneous end-group transesterification and proton transfer. Kinetic studies are performed for PyBAEO5 and PyBAEO6 to confirm the proposed mechanism, by withdrawing and analyzing aliquots from the reaction solutions at different time. The aliquots are substantially dried to get rid of the solvent (THF), as its ^{1}H NMR signals overlap significantly with some of the products.

During the induction period, carboxylic acid is first deprotonated by *t*-BuP$_4$, followed by the esterification of carboxylate by EO. The formed alkoxide gets protonated by another carboxylic acid immediately due to its high basicity, generating a hydroxyl ester and another carboxylate. This step occurs repeatedly until all the carboxylic acids are consumed (Stage 1). For PyBAEO5, this stage takes ca. 7 h, during which (e.g., 3 and 5 h in Figure 5) the ^{1}H NMR spectra of the aliquots show only the remaining carboxylic acid and hydroxyl ester. As can be seen in the ^{1}H NMR spectra (Figure 5, 3 and 5 h), the pyrenyl methylene groups from both carboxylic acid and hydroxyl ester almost completely overlap (*c*). Signals *a* and *b* are assigned respectively to the methylenes next to ester group and hydroxyl group. The integrals of these signals show a decreasing amount of the carboxylic acid and an increasing amount of the hydroxyl ester. The conversion of carboxylic acid, calculated as a/c (here *a* and *c* denote the integrals of the corresponding signals), is ca. 38% at 3 h and 69% at 5 h.

At Stage 2 of the induction period, the remaining carboxylates keep turning into alkoxides, which now can remain due to the absence of carboxylic acid. ^{1}H NMR spectrum (Figure 5, 7 h) shows an extra singlet assigned to the methylene next to ester group (a'), which indicates the existence of diesters with a symmetric structure. An extra signal (c') next to the pyrenyl methylene signal (*c*) is also seen. Based on the integrals, i.e. $c' \approx a'$, c' should be assigned to the pyrenyl methylene signal on the diester. The conversion of carboxylic acid, in this case calculated by the integrals as $(a + a')/(c + c')$,

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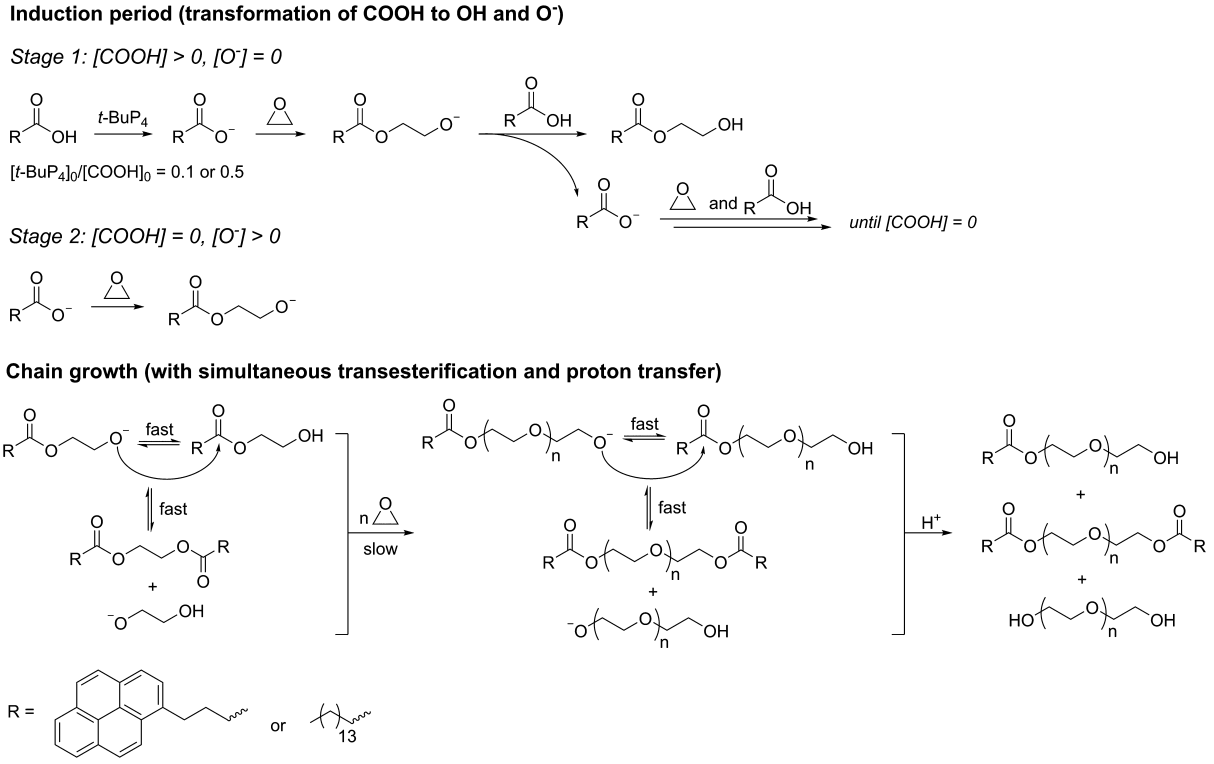
Scheme 1. Proposed Mechanism for the Ring-Opening Polymerization of Ethylene Oxide Initiated by Carboxylic Acid in the Presence of *t*-BuP$_4$, where COOH, OH, and O$^-$ Denote Respectively Carboxylic Acid, Hydroxyl Ester, and Alkoxide Species



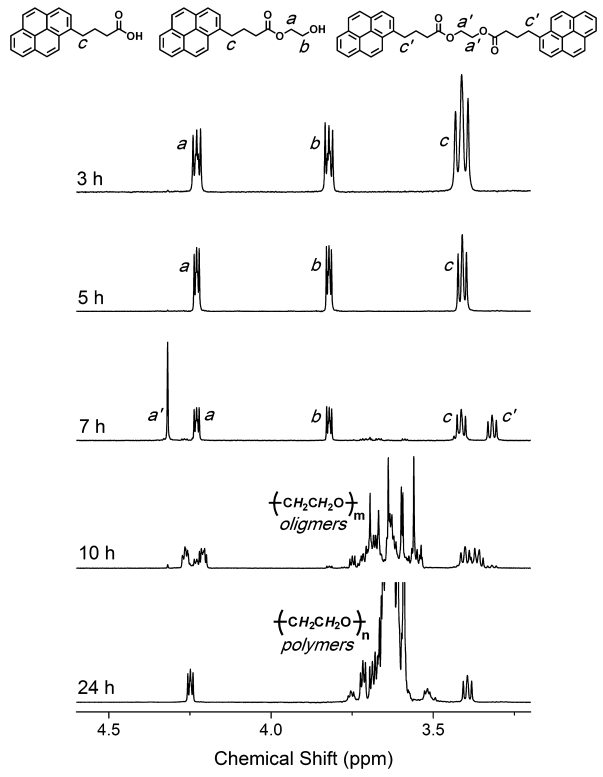


Figure 5. ^{1}H NMR spectra of the dried aliquots withdrawn at different time from the reaction solution of PyBAEO5 (Table 1).

is close to 90% (note that ca. 0.1 equiv of *t*-BuP$_4$ is used with regard to PyBA for this experiment), which means alkoxides have probably just started to remain in the system. At this point, chain growth has barely started; however, transesterification has already reached its equilibrium as indicated by a 1:2 ratio of diester to monoester. This confirms that transesterification is much more readily to occur compared to chain growth. Another product of transesterification, ethylene glycol, is not present in the ^{1}H NMR spectrum because of the removal during drying.

At 10 h, induction period is completed as indicated by the full conversion of carboxylic acid (calculated based on the integrals). Oligomers are already formed and the singlet representing the diesters (DP = 1) almost disappears due to the breakage of the structural symmetry. At 24 h, ^{1}H NMR integrals indicates a ca. 85% EO conversion, which is in good agreement with PyBAEO2. After 30 h, the ^{1}H NMR spectrum and SEC trace both stay constant, indicating the completion of polymerization.

In the case of PyBAEO4 and -6 (Table 1), for which 0.5 equiv of *t*-BuP$_4$ is used, higher dispersities are obtained (Table 1). Kinetic study on PyBAEO6 shows that stage 1 of the induction period takes ca. 30 min only, and the chain growth is completed after 6 h as indicated by ^{1}H NMR and SEC. The tailing in SEC trace (Figure S3) indicates a slow initiation−fast propagation mode, which is caused by the extensive overlap of the induction period (Stage 2) and chain growth. In the case of PyBAEO1, -2, and -5 (Table 1), for which 0.1 equiv of *t*-BuP$_4$ is used, the overlap period is significantly shorter, and thus low dispersities of PEO are obtained. In the case of PyBAEO3 for which 0.01 equiv of *t*-BuP$_4$ is used, no polymer is formed after heating at 45 °C for 48 h as indicated by SEC. The ^{1}H NMR spectrum of the dried product (Figure S4) shows the induction period is completed and transesterification equilibrium of the esterified PyBA (DP = 1) is already reached. Clearly, such a low amount of *t*-BuP$_4$ causes extremely slow chain growth.

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A relatively weaker phosphazene base, *t*-BuP$_2$, is used to conduct a polymerization (0.1 equiv of *t*-BuP$_2$). Similarly to PyBAEO3, no polymer is formed upon heating at 45 °C for 48 h as indicated by SEC. However, the ^{1}H NMR spectrum of the dried product indicates the induction period is completed and the transesterification equilibrium of esterified PyBA (DP = 1) is already reached (Figure S5).

CONCLUSIONS

We have demonstrated the effectiveness of carboxylic acid as initiator for the AROP of EO by the aid of a strong phosphazene base (*t*-BuP$_4$). The end-group transesterification, as well as the proton transfer between dormant (hydroxyl) and active (alkoxide) chain ends, occurs simultaneously with the chain growth in a much faster manner (Scheme 1), so that it does not influence the molecular weight and dispersity of the PEO chains. Because of the existence of an induction period and its inevitable overlap with the chain growth, it is essential to use appropriate amount of the base promoter in order to ensure low dispersity, targeted molecular weight, and a reasonable polymerization time scale. This work adds to the option of initiators for the AROP of epoxides and opens a new pathway toward controlled polymerization from protic initiating sites (more acidic than the growing chain end). Such information can be very useful for macromolecular and biomolecular engineering.

ASSOCIATED CONTENT

Supporting Information

Additional MALDI-TOF MS, SEC traces, ^{1}H NMR spectrum, and reaction schemes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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