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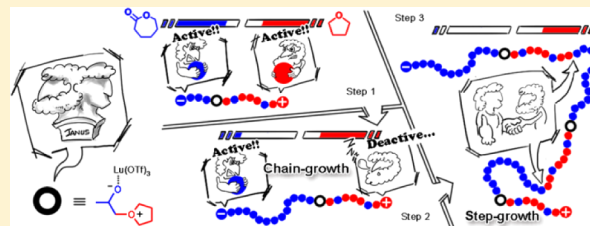
Janus Polymerization

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Supporting Information

ABSTRACT: Is it possible to combine cationic and (coordinated) anionic ring-opening polymerizations (CROP and AROP) into a unimolecular chain? In this work, we design polymerizations of ϵ -caprolactone (CL) and tetrahydrofuran (THF) using a single catalytic system of lutetium triflate/propylene oxide (Lu(OTf)₃/PO) in which a cationic copolymerization of THF with CL and an AROP of CL perform at two chain ends of a growing chain. Kinetic and mechanistic studies demonstrate that the two chain-growth ROPs which have no mutual interference up to 90% of CL conversion keep a living manner producing diblock copolymers of PCL-*b*-P(THF-*co*-CL) with narrow polydispersities below 1.2. Afterward, the depletion of CL triggers a final step-growth polymerization via intermolecular coupling reaction of cationic and anionic chain ends, developing multiblock polyester–polyether elastomers of [PCL-*b*-P(THF-*co*-CL)]_{*m*}. A concept of “Janus polymerization” is defined as a combination of cationic and anionic polymerizations on the two ends of a single growing chain, involving an initially living chain-growth polymerization and a subsequently self-triggered step-growth polycondensation.



INTRODUCTION

Can a polymer chain propagate on both ends simultaneously via different mechanisms? Early attempt goes back to half a century ago when Professor Michael Szwarc tried to transfer a radical anion to styrene from sodium naphthalene.¹ Instead of an anionic and a free radical polymerizations on the two ends of a polystyrene chain that he expected, a fast combination of free radicals and the same anionic polymerizations performed on the both ends, which brought forth “living polymers”.^{2,3} Some successful combinations of two polymerization mechanisms on a single compound include controlled radical polymerizations (nitroxide-mediated radical polymerization, atom transfer radical polymerization, and reversible addition–fragmentation chain transfer polymerization) and various ring-opening polymerizations (ROPs), such as cationic ROP,^{4–6} coordinated anionic ROP,^{7–9} activated monomer ROP,^{10,11} and enzymatic ROP.^{12,13} All the above simply combine two compatible mechanisms that do not interfere with each other theoretically.¹⁴ To the best of our knowledge, no successful attempt has been reported in combining cationic and anionic propagation species in a single polymerization mixture since they react with each other to be dead products.

In this work we develop a novel polymerization defined as “Janus polymerization” where the two ends of a polymer chain propagate via a cationic polymerization and an anionic one. “Janus” is the god with two faces looking to the past and the future in ancient Roman religion and myth. The word indicates something consisting of counter parts in scientific society, for instance, the term of “Janus nanoparticles”.¹⁵ Generally cation and anion pairs are known as close associated counterions. A zwitterionic polymerization involves both cation and anion on a single chain.^{16–20} However, only one ion, either cation or

anion, initiates polymerization while the other acts simply as an inert counterion.

Herein, a Janus polymerization composed of apparently two mechanisms of cationic ring-opening copolymerization (CROP) and (coordinated) anionic ring-opening polymerization (AROP) is generated by a simple lutetium triflate (Lu(OTf)₃)/propylene oxide (PO) catalytic system (**1**) as illustrated in Scheme 1. **1A** initiates AROP of ϵ -caprolactone (CL) while **1B** undergoes CROP of tetrahydrofuran (THF) with CL simultaneously in step I. When THF is consumed to a certain extent in step II, the CROP side deactivates. Meanwhile, side **1A** initiates the AROP of CL exclusively until CL conversion approaches over 90%. After the first two chain-growth living ROPs, a step-growth polymerization follows where the concentration of CL acts as a trigger to turn “on” or “off” the switch. Moreover, to the best of our knowledge, we are not aware of any one-pot protocol for the combination of chain growth and the subsequent step growth without any intermediate functionalization reactions despite some successful examples based on simultaneous chain- and step-growth polymerizations.^{21,22} A well-controlled combination is realized in the Janus polymerization from step II to step III in Scheme 1.

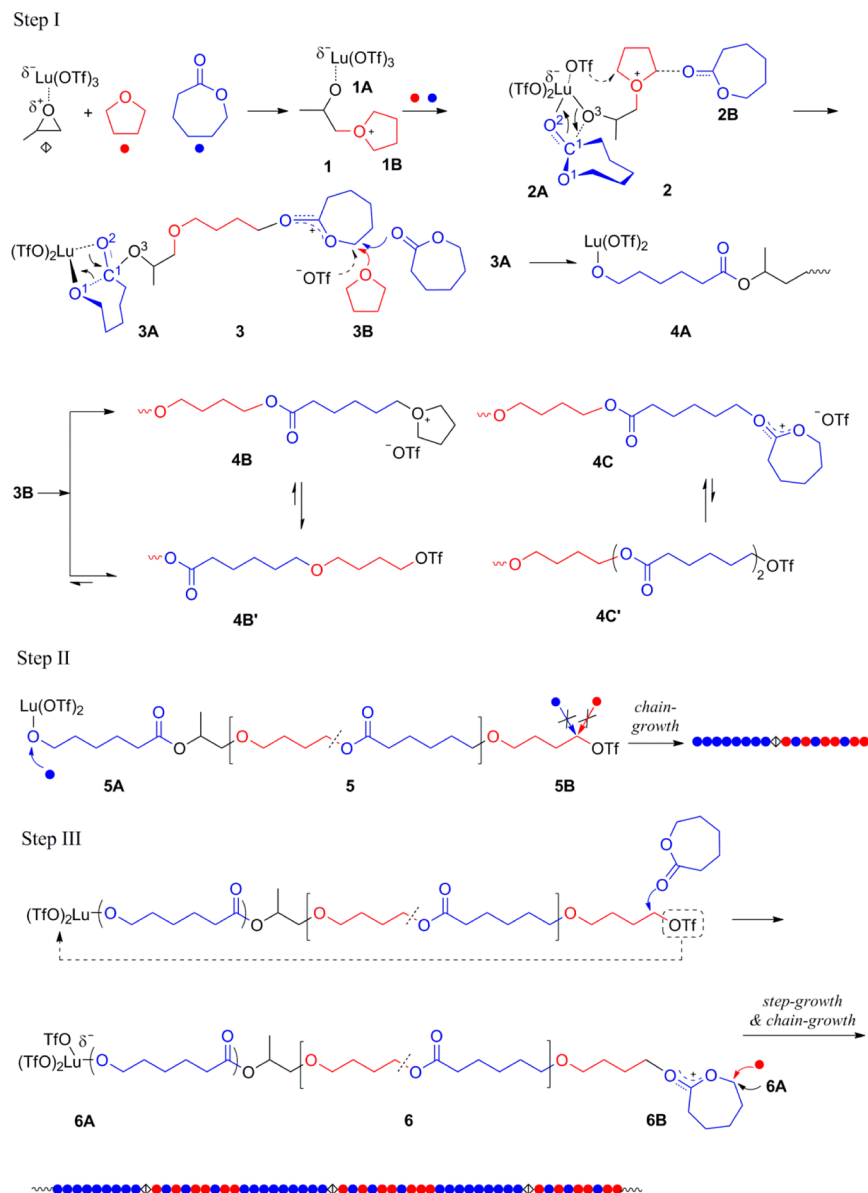
RESULTS AND DISCUSSION

Supported by our previous research on the rare earth triflates (RE(OTf)₃)/PO catalyzed controlled/living CROP of THF,²³ the negatively charged moiety of zwitterion-like compound **1** in Scheme 1 is analogous to rare earth alkoxides which effectively

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Scheme 1. Janus Polymerization of THF with CL Catalyzed by $\text{Lu}(\text{OTf})_3/\text{PO}$ 

initiate living AROP of CL.^{24–26} We choose $\text{RE}(\text{OTf})_3/\text{PO}$ to promote a model Janus polymerization, simultaneously initiating AROP of CL at 1A side and CROP of CL with THF at 1B side. Some interesting results are obtained (Table 1). All the $\text{RE}(\text{OTf})_3/\text{PO}$ ($\text{RE} = \text{Sc}, \text{Y}$, and Lu) catalytic systems initiate ROPs of THF with CL with distinguished polymerization features. In particular, $\text{Lu}(\text{OTf})_3/\text{PO}$ fulfills the concept of Janus polymerization. Activated by $\text{Lu}(\text{OTf})_3$, PO is attacked by THF and an alkyltetrahydrofuranium active center is formed (Scheme 1),²³ which initiates CROP of the two monomers. Previous researches concluded that THF was consumed a little faster than CL in CROP due to its relatively higher basicity.^{27,28} We find similar results at the early stage copolymerization for all the three rare earth metal catalysts (Table 1). However, at a certain point in the $\text{Lu}(\text{OTf})_3/\text{PO}$ case, THF propagation stops while CL keeps being consumed up to a high conversion over 90% (Table 1, run 10). On the contrary, with respect to Sc and Y (Table 1, runs 15–21), the final conversion of CL is far less than 90% and THF polymerizes continuously throughout the whole process.

$\text{Lu}(\text{OTf})_3/\text{PO}$ displays an unusual behavior in copolymerization of THF with CL. In a typical CROP of THF, PO is found at the chain end since methine and methyl signals are observed at $\delta \sim 3.95$ and 1.12 ppm, respectively. After esterification by trifluoroacetic anhydride (TFA), the above signals shift down to 5.28 and 1.33 ppm.²³ On the contrary, ^1H NMR spectra of copolymer (Table 1, run 8) reveal that only one signal assignable to methylene adjacent to the hydroxyl end group CH_2OH is found to have shifted from 3.63 to 4.38 ppm after TFA treatment, indicating that PO locates in the middle rather than the chain end (Figure S1). Only one crystalline peak with T_m of 55°C is observed in the thermal analysis of the copolymer contributing to a long PCL sequence (Figure S2). Moreover, the XRD pattern of the copolymer shows strong diffraction at 2θ of 21.5° and 23.8° ascribed to the PCL crystalline, but no peak appears at 19.8° and 24.4° of PTHF (Figure S3).^{27,29} The above results point out that the copolymer possesses long PCL sequences and random segments, i.e., $\text{PCL-}b\text{-P}(\text{THF-co-CL})$. Since THF can only be cationically polymerized,^{30–33} the random segments must be

Table 1. Copolymerization of Tetrahydrofuran (THF) with ϵ -Caprolactone (CL) Catalyzed by RE(OTf)₃/PO in Bulk at 25 °C

run	RE	RE(OTf) ₃ :PO:CL:THF (molar ratio)	time	conv ^a (%)		$M_{n,SEC}$ ^b (kDa)	PDI ^b	$M_{n,NMR}$ ^c (kDa)	$M_{n,theo}$ ^d (kDa)
				THF	CL				
1	Lu	1:1.5:200:200	17 h	4.3	2.9	3.4	1.23	1.6	1.5
2			21 h	5.2	3.80	4.1	1.22	1.9	1.7
3			91 h	5.2	58.5	27.6	1.08	14.6	14.2
4			16 days	13.7	100	81.6	1.81		24.8
5	Lu	1:1.5:200:200 +200 ^e	21 h +23 h	2.6 ^f	31.2	16.4	1.13	8.6	8.2
6			24 days	11.9 ^f	100	307.0	1.92		26.2
7	Lu	1:1.5:100:200	17 h	8.8	4.8	5.08	1.34	2.3	2.0
8			48 h	10.4	37.0	11.7	1.15	6.3	5.9
9			59 h	10.4	80.1	21.5	1.14	11.3	10.7
10			66 h	10.4	90.5	23.9	1.15	12.1	11.8
11			109 h	24.5	100	64.8	1.81		14.8
12			11 days	36.8	100	181.0	1.81		17.4
13	Lu	1:0:100:200	4 days	0	0				
14		1:1.5:100:0	24 h	0	0				
15	Y	1:1.5:200:200	20 h	1.9	1.6				
16			45 h	3.3	3.6	2.7	1.28	1.4	1.3
17			7 days	8.1	13.0	9.1	1.23	4.6	4.2
18			50 days	13.9	43.0	46.0	1.41	23.9	12.5
19	Sc	1:1.5:200:200	20 h	22.3	11.6	25.4	1.54	12.9	5.8
20			45 h	25.8	11.6	19.0	1.88	13.4	6.3
21			50 days	33.0	52.0	50.0	1.55		16.7

^aConversion determined by ¹H NMR spectroscopy. ^bNumber-average molecular weight and PDI were determined by size exclusion chromatography (SEC) calibrated with polystyrene standards. ^cCalculated from ¹H NMR spectra: $M_n = I_{3.38 \text{ ppm}}/I_{3.63 \text{ ppm}} \times 72 + I_{4.03 \text{ ppm}}/I_{3.63 \text{ ppm}} \times 2 \times 114 + I_{1.12-1.25 \text{ ppm}}/I_{3.63 \text{ ppm}} \times 2/3 \times 58$. ^dCalculated according to $M_{n,theo} = [CL]/[RE] \times \text{conv}(CL) \times 114 + [THF]/[RE] \times \text{conv}(THF) \times 72 + 58$. ^eThe copolymerization was carried out for 21 h first under the same condition of run 1; then another batch of THF (200 times of RE(OTf)₃) was added into the reaction and reacted for 23 h. ^fThe conversion of THF was related to the total amount of THF.

derived from CROP. The long PCL segments should come from the AROP site, as the CROP site deactivates during the chain-growth polymerization of CL (Table 1, runs 8–10).

Detailed kinetic study of the copolymerization of THF and CL gives us an insight into the Janus polymerization process (Figure 1). Three steps are included in the whole polymerization (Scheme 1). In step I, **1A** initiates a homopolymerization of CL slowly via AROP, while THF and CL copolymerize into the chain via CROP at **1B** site affording a P(THF-*co*-CL) random segment. The polymerization rate of THF $k_{app,THF}$ is

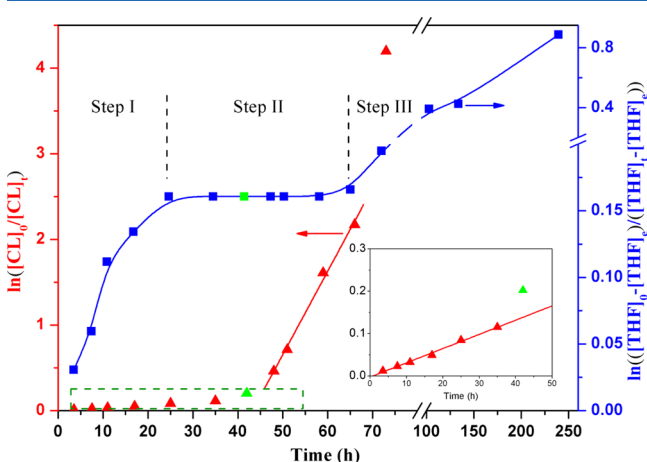


Figure 1. Kinetic plots for the Janus polymerization of THF with CL at 25 °C catalyzed by Lu(OTf)₃ in the presence of PO ([Lu(OTf)₃]₀: [PO]₀: [CL]₀: [THF]₀ = 1:1.5:100:200) in bulk: (▲) CL; (■) THF, [Lu(OTf)₃]₀ = 0.0365 mol L⁻¹, [THF]₀ = 2.50 mol L⁻¹.

$(5.00 \pm 0.97) \times 10^{-3} \text{ h}^{-1}$ compared with $k_{app,CL}$ of $(3.30 \pm 0.24) \times 10^{-3} \text{ h}^{-1}$.³⁴ In the second step, the polymerization of THF stops even after an additional batch of THF in step II (Table 1, runs 2–3, runs 5–6, and runs 8–10), indicating the dormancy of cationic living centers. Meanwhile, $k_{app,CL}$ approaches to $(97.3 \pm 4.8) \times 10^{-3} \text{ h}^{-1}$, about 30 times the value in step I. The decrease of the molar ratio of CL to THF leads to the consequent higher dormant THF conversion in step II (Table 1, runs 2 and 8), which suggests that it is CL that takes over the ROP process. Moreover, the first-order kinetic plot combined with the linearly increased number-average molecular weights (M_n s) against CL conversions in step II confirms a living polymerization with a constant concentration of active centers (Figure 2). The narrow and symmetrical SEC curves prove the well-defined PCL-*b*-P(THF-*co*-CL) diblock copolymers with PDIs lower than 1.20, which excludes any chain coupling or termination reaction (Figures 2 and 3). More importantly, $M_{n,NMR}$ s of the obtained polymers estimated from ¹H NMR measurement agree very well with $M_{n,theo}$ s calculated from the initial molar ratios of [THF]₀/[Lu(OTf)₃]₀ and [CL]₀/[Lu(OTf)₃]₀ and monomer conversions (Table 1, runs 1–3 and runs 7–10). A special rare earth triflate catalyst realizes the Janus polymerization combining AROP and CROP in a unimolecular chain without mutual interference or termination, though rare earth alkoxides complexes are generally considered as a base sensitive to cationic impurities.^{35–37}

When the conversion of CL reaches higher than 90%, the process comes into step III. The reconsuming of THF reveals that the dormant cationic living center is reactivated as THF polymerizes via CROP exclusively (Table 1, runs 4, 6, 11, and

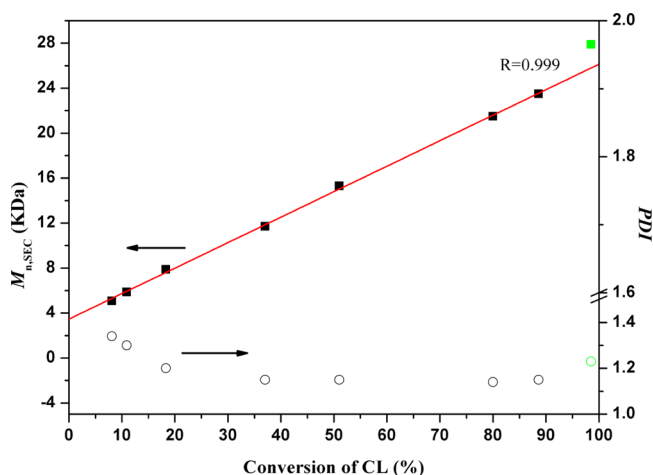


Figure 2. Dependence of molecular weight (M_n) and PDI on the CL conversion in the copolymerization of THF and CL of step II ($[\text{Lu}(\text{OTf})_3]_0/[\text{PO}]_0/[\text{CL}]_0/[\text{THF}]_0 = 1:1.5:100:200$ in bulk, $[\text{Lu}(\text{OTf})_3]_0 = 0.0365 \text{ mol L}^{-1}$, $[\text{THF}]_0 = 2.50 \text{ mol L}^{-1}$).

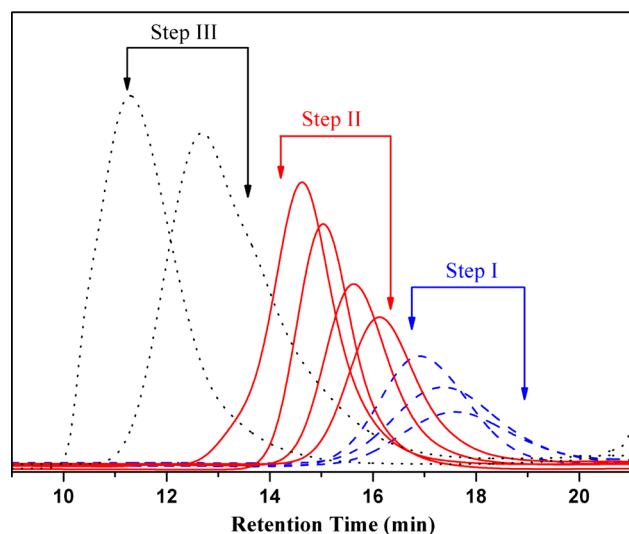


Figure 3. SEC traces of P(THF-co-CL) (step I, dashed blue line), PCL-*b*-P(THF-co-CL) (step II, solid red line), and multiblock [PCL-*b*-P(THF-co-CL)]_m (step III, dotted black line) copolymers.

12).^{33,38,39} In addition, the noninterfered active sites on the two chain ends in step I are no longer stable in step III after the gradual depletion of CL. The exponential increase of M_n from initial 23.9 kDa to 181 and 307 kDa demonstrates that self-condensation (step-growth) reaction happens via chain ends coupling of **1** (Scheme 1 and Figure 3). The PDIs of the obtained multiblock PCL-*b*-P(THF-co-CL) copolymers ([PCL-*b*-P(THF-co-CL)]_m) are between 1.81 and 1.92, which fall in the same range as those reported in condensation polymerizations.^{40,41}

PCL is a semicrystalline rigid polymer and PTHF is even more brittle;⁴² e.g., PCL with M_n of 74 kDa possesses high Young's modulus (E_a) of 300 MPa, and PTHF has a low strain at break of only 9% (Figure 4). Nevertheless, the obtained [PCL-*b*-P(THF-co-CL)]_m with similar M_n has lower E_a around 100 MPa but much higher strain at break of 1000% without sacrifice of tensile strength compared with PCL. Further condensation reaction results in higher M_n , lower E_a of 25 MPa, and ongoing increase of strain at break to 1300%. The improved

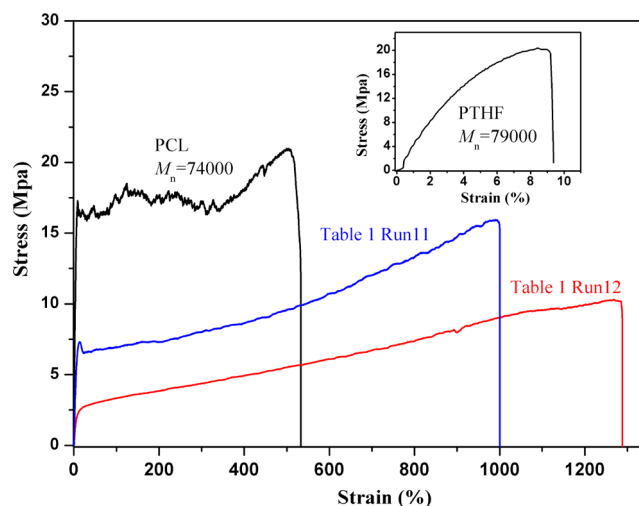


Figure 4. Stress-strain curves for PTHF, PCL, and multiblock [PCL-*b*-P(THF-co-CL)]_m copolymers.

mechanical property is attributed to the alternating soft (P(THF-co-CL)) and hard PCL segments that are similar to segmented polyurethane copolymers and styrene-base linear ABA triblock copolymers, such as poly(styrene-*b*-butadiene-*b*-styrene) (SBS).^{43,44} XRD analysis of the obtained [PCL-*b*-P(THF-co-CL)]_m demonstrates the absence of long PTHF sequence (Figure S3). The properties of this [PCL-*b*-P(THF-co-CL)]_m thermoplastic elastomers meet the requirements of biomedical and biodegradable materials applied in cardiovascular and other soft tissue engineering.^{45,46}

Mechanisms. On the basis of the kinetic study and structure analyses of the obtained copolymers, we demonstrate a Janus polymerization with detailed mechanism illustrated in Scheme 1. The whole process is monitored by NMR analysis in a flame-sealed tube using deuterated THF (THF-*d*₈) as solvent and monomer. In order to obtain high concentration of active species, the initial molar ratio of $[\text{Lu}(\text{OTf})_3]_0/[\text{PO}]_0/[\text{THF-}d_8]_0/[\text{CL}]_0 = 1/1.5/70/35$ is applied. In this case a model copolymerization using normal THF and CL shows similar kinetic plots in Figure 1. $\text{Lu}(\text{OTf})_3/\text{PO}$ does not initiate ROP of CL (Table 1, run 14),²³ and $\text{Lu}(\text{OTf})_3$ alone is not active for copolymerization of THF with CL (Table 1, run 13). In step I, an ether-type methylene (H^8) of CL adjacent to the THF-*d*₈ is found at 3.38 ppm, confirming the random copolymerization of THF and CL in the cationic side of **1B** via alkyl-oxygen bond cleavage (Figure 5, step I).^{47,48} Cationic living site **4B** is further confirmed by ¹H, ¹³C, ¹H-¹H COSY, and ¹H-¹³C HMQC NMR analyses (Figures S4-S7). A triplet peak at 4.78 ppm (H^b) ascribed to the macroester⁴⁹ indicates that the OTf⁻ ligand escapes from Lu and then reacts with the oxonium or the cyclic carbenium ion. The finally formed macroester **4B'** and **4C'** are dormant species as they are much less reactive, e.g. 500 times lower, than ionic species (**4B** and **4C**).³³ On the other hand, **2A** is an analogue to a classical rare earth alkoxides complex;^{24,25} thus, a similar AROP mechanism is involved in Scheme 1.

Tremendous experimental results proposed a multistep AROP mechanism including activation of CL by its carbonyl oxygen coordination onto the metal and subsequent CL insertion via acyl-oxygen bond cleavage.^{24,25,50} Despite the analogue of **4A** has been isolated and proved in experiments,^{25,51,52} no discrete intermediates from **1A** to **4A** have

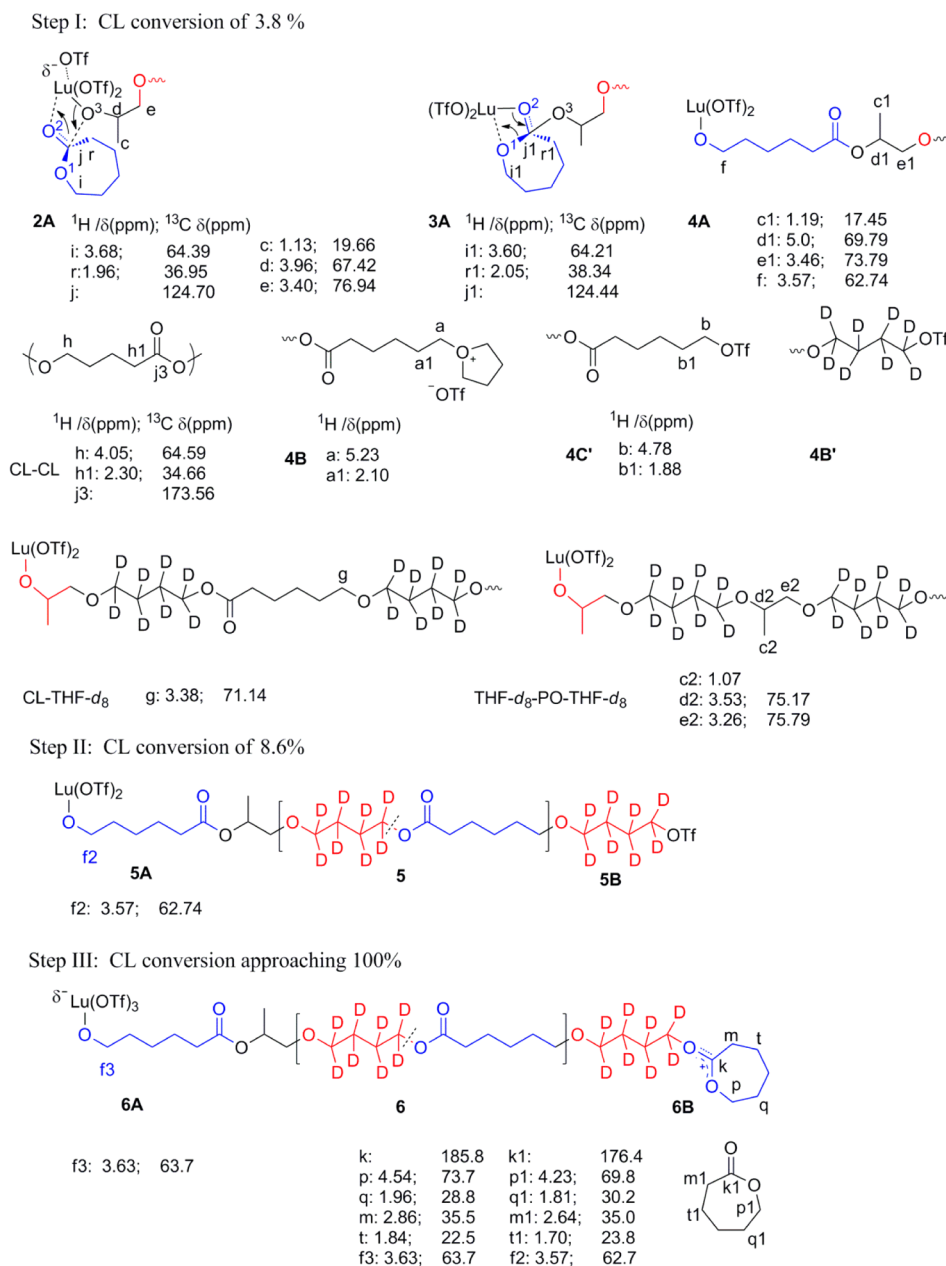


Figure 5. ^1H and ^{13}C NMR chemical shifts of the species throughout the Janus polymerization ($[\text{Lu}(\text{OTf})_3]_0/[\text{PO}]_0/[\text{THF-}d_8]_0/[\text{CL}]_0 = 1/1.5/70/35$).

been demonstrated except that some computational studies speculate their existence.^{53–55} Thanks to the slow copolymerization (CL conversion was only 3.8% after 3 h), we observe the two intermediates using real-time NMR technology during the coordinated anionic insertion polymerization. The transformation of **1A** to **2A** involves the addition of $\text{Lu}-\text{O}^3$ onto C^1-O^2 double bond, which lengthens the $\text{Lu}-\text{O}^3$ and shortens the $\text{Lu}-\text{O}^2$ bond. Thus, $\text{Lu}-\text{O}^3-\text{C}^1-\text{O}^2$ forms a four-membered ring having a sp^2-sp^3 hybridized C^1 which is located at higher field of 124.6 ppm compared with the initial carbonyl group of 176.4 ppm (Figure 5 and Figure S5).⁵⁶ The transformation of **2A** to **3A** involves rotation of the CL ring around C^1-O^2 bond, resulting in a decreased $\text{Lu}-\text{O}^1$ and increased $\text{Lu}-\text{O}^3$ distances. According to the quantum chemical computation,^{53,54} the C^1-O^1 bond distance in **2A** is a little shorter than that in **3A**; the chemical shift of methylene

adjacent to O^1 changes from 3.68 ppm (H^i) to 3.60 ppm (H^i) as illustrated in Figure 5 and Figure S4. The transformation from **3A** to **4A** is an actual ring-opening process of CL recovering a typical C^1-O^2 double bond with a sp^2 hybrid C^1 .

This unique Janus polymerization possesses both cationic (**1B** side) and coordinated anionic active centers (**1A** side) on a single chain. It differs from zwitterionic ROP of cyclic esters catalyzed by N-heterocyclic carbenes (NHCs),^{16,57,58} amidine,¹⁸ and $\text{Zn}(\text{C}_6\text{F}_5)_2$ -based Lewis pairs,²⁰ where only the negative oxygen ion initiates ROP alone while the inactive cationic partner simply serves as a counterion.

After the complete transformation of **4B** and **4C** to the corresponding dormant marcoesters (**4B'** and **4C'**), Janus polymerization comes into step II. In this step, only CL is polymerized into **5A** side of a living chain until the CL conversion reached over 90%. Further experiments are

performed to rule out the possibility of CL insertion into **SB** side via a “coordinated” cationic mechanism (Table S1) in step II.⁵⁹ P(Ph)_3 is a commonly used base to trap a cationic living center by forming a stable triphenylphosphonium complex.^{60,61} After an addition of 1 equiv of P(Ph)_3 to a cationic homopolymerization of THF initiated by $\text{Lu(OTf)}_3/\text{PO}$, the cationic living center is indeed terminated quantitatively, and no more THF polymerization occurs in the following 17.5 h (Table S1, runs 1–2). On the contrary, in the presence of P(Ph)_3 , CL keeps propagation to a conversion higher than 90% (Table S1, run 3), indicating that CL polymerizes via a coordinated anionic mechanism rather than a cationic one. Interestingly, the addition of CL alone inhibits THF polymerization as well before CL conversion of 52.5% in 77 h (Table S1, run 5). In these cases, well-defined PTHF-*b*-PCL diblock copolymers are confirmed by narrow and symmetrical SEC traces, the fact that experimental M_n values meet theoretical ones, which excludes reinitiation and chain coupling reactions, and T_m s of both PTHF and PCL segments in DSC (Figures S8 and S9). Therefore, a sequential ROP of THF and CL becomes a feasible way to synthesize pure PTHF-*b*-PCL block copolymers without any postpolymerization or transformation of the cationic growing center.⁶² The interaction of CL with Lu(OTf)_3 may play a pivotal role in the formation and stabilization of the dormant macroester in step II,⁶³ though it is not thoroughly understood yet. The macroester (**SB**) is not stable in CROP of THF and transforms to the active **4B** and **4C** through intramolecular and intermolecular interconversions between the macroesters and the macroion pairs.⁴⁹

Along with the further consumption of CL over 90% in step III, the dormant macroester (**SB**) is reactivated and allows THF propagation again. Newly emerging peaks appear at low field ascribed to the cationized CL in ^1H and ^{13}C NMR spectra (Figure 5). The C^k signal of cyclic carbenium is found at 185.8 ppm compared with that of CL monomer at 176.4 ppm. $\text{Lu}-\text{OCH}_2$ located in 3.57 ppm (H^2) and 62.7 ppm (C^2) in step I and II shifts downfield to 3.63 ppm (H^3) and 63.7 ppm (C^3), respectively, in step III (Figures S10–S13), indicating that the lutetium–oxygen complex is more electron withdrawing in step III than that in steps I and II, which reveals a migration of OTf^- from macroester (side **SB**) to lutetium metal center (side **5A**). Meanwhile, THF and CL attack the activated macroester (**SB**) forming the corresponding oxonium and carbonium, respectively. It is worth noting that the signals assignable to the intermediates (**2A** and **3A**) in the AROP of CL vanish in the NMR spectra due to the depletion of CL in step III (Figures S10 and S11). The regenerated **6A** and **6B** containing anionic oxygen and cyclic carbenium species, respectively, are subjected to a condensation polymerization, leading to a dramatic M_n increase (Figure 3).

CONCLUSIONS

A Janus polymerization is defined to include a cationic and an anionic polymerizations on both ends of a single living polymer chain. Herein we demonstrate an example to implement such a concept, where $\text{Lu(OTf)}_3/\text{PO}$ is used as the catalytic system for THF and CL polymerizations. It involves three separate steps. In step I, the *in situ* generated zwitterionic species **1** initiated simultaneous AROP of CL at **1A** side and CROP of THF with CL at **1B** side, producing PCL and P(THF-co-CL) segments, respectively, until a certain THF conversion. THF polymerization is suspended in step II due to the deactivation of cationic side, and a living chain-growth AROP of CL is achieved

toward high conversion of 90%. After the depletion of CL in step III, the activated cationic propagation sites perform continuous coupling reactions with coordinated anionic ones, which builds up a step-growth polymerization. A Janus polymerization shall essentially comprise a controlled chain-growth polymerization and the subsequently step-growth polymerization, which, as a consequence, is a feasible way to afford well-defined multiblock copolymers directly from two monomers in a one-step process without any tedious intermediate functionalization reactions or postpolymerizations.

The concept of Janus polymerization gives us an alternative insight into traditional understanding about incompatible cationic and anionic polymerization mechanisms coexisting in a single growing polymer chain. We believe more efforts could be made to reveal other Janus polymerizations through the elegant grasp of catalysis and thus unleash the power of polymer chemistry.

ASSOCIATED CONTENT

Supporting Information

Experimental information and characterization data. 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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