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Quasi-Living Copolymerization of Aryl Isocyanates and Epoxides

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ABSTRACT: Nontraditional polyurethane (PU) has been successfully synthesized by anionic copolymerization of some typical aryl isocyanates and epoxides with ammonium halide onium salt (Lewis base) as the initiator and triisobutylaluminum (Lewis acid) as the activator and the synergistic coordinator. In contrast to the traditional step-growth approach, this chain-growth copolymerization can maintain the anionic propagation site and exhibit some living features with a high

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activity, by which the copolymers synthesized have narrow molecular weight distributions and discrete end groups. The copolymer is primarily constituted by a urethane linkage, and the byproducts of isocyanurate trimer and oxazolidinone can be effectively suppressed as the polymerization proceeds. Density functional theory (DFT) calculations were also performed to support the proposed reaction mechanism.

P U is an important class of polymer applied widely in thermoplastics, foams, adhesives, and so on,¹⁻³ which is traditionally obtained by polyaddition of dihydric alcohol with diisocyanate, as shown in Scheme 1. About half a century ago, another strategy by ring-opening alternating copolymerization of monoisocyanates and epoxides was first reported.⁴⁻⁶ Unfortunately, a mixture of polyether and copolymer composed of primary acetalic units was obtained, the structure was poorly defined, and the mechanism was ambiguous at that time. Thereafter, controlled copolymerization of monoisocyanates and epoxides remains a great challenge and has aroused renewed interest very recently,⁷ in which a diamagnesium catalyst was utilized.

In contrast to the successful alternating copolymerization of epoxides with heteroallenes such as carbon dioxide $(CO_2)^{8-12}$ and carbonyl sulfide (COS),^{13,14} isocyanate, with two cumulated double bonds N=C and C=O, exhibits a very high reactivity, which could lead to severe side reactions and undesired products, for example, rapid formation of cyclic urethanes (oxazolidinones)^{15–18} and trimerization^{19,20} into isocyanurate. Meanwhile, propagation through the N=C or C=O bond can afford either an amide unit or an acetal unit. Remarkably, the work on the polyisocyanates has shown the preferential formation of the amide backbone via the anionic addition mechanism and provided a clue to prevent trimerization.²¹

In this work, we adopted the approach of Lewis pair polymerization, which has demonstrated great potential to fine-tune the polymerization process with regard to reaction conditions and livingness, as well as chemo- or regioselectivity.^{22–24} A weak Lewis base of onium salt (e.g., NOct₄Br) as a nucleophilic anion initiator was particularly introduced in order to afford anionic copolymerization, in which a large-sized cation is expected to shield the growing anionic species and thus minimize the chain backbiting and the formation of oxazolidinones. Lewis acid of *i*-Bu₃Al is combined to foster the ring-opening of epoxides on the one hand;^{25–28} on the other hand, its successive coordination with the propagating chain end and the incoming monomer could potentially mediate alternating copolymerization of isocyanates and epoxides, which is further supported by the DFT calculations.

The copolymerizations of 1,2-butylene oxide (BO) with 4methylphenyl isocyanate (MPI) were conducted at different ratios of comonomers, i-Bu₃Al and onium salts (NOct₄Br, NBu₄Br, or NBu₄Cl), as demonstrated in Table 1. In general, this strategy can afford efficient copolymerization to form a novel class of PUs possessing a primary alternating microstructure with a narrow molecular weight distribution, as demonstrated in Scheme 1 and testified by ¹³C NMR and gelpermeation chromatography (GPC) in Figure 1. In contrast to previous work,⁴⁻⁶ the resonances at 154.74-155.93 ppm and absence of signals at 163 ppm in the ¹³C NMR spectra (Figures 1a and S4) indicate the formation of a urethane unit instead of an acetalic structure, strongly suggesting the regioselective attack of C=N bond in MPI by the oxyanion. The resonances located at 152.44-153.35, 69.03-72.97, and 78.65-80.73 ppm indicate the existence of minor moieties constructed from consecutive MPI or BO units. This heterogeneous microstructure was also revealed by the ¹H NMR results in the Figure S5.

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Scheme 1. (a) Traditional Polyurethane Prepared by Condensation of Diisocyanates and Diols; (b) Novel Polyurethane Synthesized via Anionic Copolymerization of MPI and BO with Lewis Acid/Base (LA/LB); (c) Reaction Process of the Living Copolymerization; (d) Backbiting to Keep the Chain End Effectively Alive

(a) Traditional polyurethane:

 $HO-R_{1}-OH + OCN-R_{2}-NCO \xrightarrow{\text{Step growth}} (O-R_{1}-O-\overset{n}{C}-\overset{n}{H}-R_{2}-\overset{n}{H}-\overset{n}{C})_{n}$ (b) Novel polyurethane in this work: $Ar-NCO + \overset{n}{Po} \xrightarrow{\text{Chain growth}}_{\text{Lewis acid/base}} * (fo \overset{n}{C} \overset{n}{H} fo \overset{n}{G} \overset{n}{H} fo \overset{n}{G} f$

The representative MALDI-TOF MS spectrum (entry 6) in Figure 2 shows a narrow molecular weight distribution, consistent with the GPC results. The assignment of the peaks reveals the copolymerization of MPI and BO with



Figure 1. Representative ${}^{13}C$ NMR spectrum (entry 8) (a) and GPC traces (b) of the copolymers in Table 1.

discrete Br- and H- end groups (see Figure S10 for identification of terminal unit). The m/z interval value in major series matches the calculated mass of repeat unit of (BO-

Table 1. Conditions of the Copolymerization and the Chemical Characterizations of the Co
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entry ^a	LB	LB: <i>i</i> -Bu ₃ Al:MPI:BO	poly/oxa/tri ^b	$x/y/z^{c}$	$M_{\rm n,theo}^{d} ~({\rm kg/mol})$	M_n^e (kg/mol)	D^{e}
1		0:2:30:30					
2	NOct ₄ Br	1:1:30:30	29/71/0				
3	NOct ₄ Br	1:2:30:30	78/22/0	77/8/15	6.2	5.4	1.08
4	NOct ₄ Br	1:3:30:30	87/8/5	69/10/21	6.2	6.0	1.09
5	NOct ₄ Br	1:4:30:30	81/12/7	63/8/29	6.2	6.2	1.10
6	NOct ₄ Br	1:2:45:30	51/35/14	72/22/6	6.2	4.0	1.08
7	NOct ₄ Br	1:3:45:30	54/24/22	85/10/5	6.2	4.9	1.11
8	NOct ₄ Br	1:4:45:30	59/11/30	71/11/18	6.2	5.4	1.11
9	NOct ₄ Br	1:3:200:200	76/15/9	80/5/15	41.0	20.4	1.26
10	NOct ₄ Br	1:3:500:500	64/16/20	57/19/24	102.5	39.1	1.32
11	NOct ₄ Br	1:3:675:450	46/12/42	77/5/18	92.2	45.2	1.24
12	NOct ₄ Br	1:3:1500:1500	46/22/32	47/11/42	307.5	58.9	1.27
13	NOct ₄ Br	1:3:2250:1500	28/6/66	67/8/25	307.5	98.3	1.26
14	NBu ₄ Br	1:3:30:30	62/34/4	72/7/21	6.2	4.1	1.13
15	NBu ₄ Cl	1:3:30:30	76/19/5	58/18/24	6.2	4.4	1.14
16	NBu ₄ Cl	1:3:45:30	47/19/34	61/21/18	6.2	4.4	1.18
17 ^f	NOct ₄ Br	1:3:30:30	73/8/19	53/32/15	6.8	4.3	1.13
18 ^g	NOct ₄ Br	1:3:30:30	70/28/2	76/8/16	6.6	3.8	1.20

^{*a*}Entries 9–11 were performed at 0 °C in THF for 24 h, entries 12 and 13 for 72 h, and the rest for 4 h. ^{*b*}Molar ratios of the copolymer (poly), oxazolidinone (oxa), and trimer (tri) in the crude products determined by ¹H NMR spectra. ^{*c*}Composition of the pure copolymers (x/y/z = urethane/consecutive MPI/consecutive BO), determined by ¹H NMR spectra. ^{*d*}M_{n,theo} = 205 × 2DP_{BO} according to the feed ratios. ^{*c*}Determined by GPC measurements at 35 °C in THF using polystyrene as the standard. ^{*f*}Cyclohexene oxide (CHO) was used instead of BO. ^{*g*}4-Methoxyphenyl isocyanate (MOPI) was used instead of MPI.



Figure 2. (a) Representative MALDI-TOF MS spectrum of the copolymer (entry 6, Table 1). (b) Enlarged spectrum in (a).

MPI) (m/z = 72.1 + 133.1 = 205.2). The existence of unequal numbers of BO unit (A) and MPI unit (B) in the copolymers $(A_m B_n)$ suggests the possible consecutive oligomerization of A or B monomers, although they are minor in the backbone, as elucidated by the NMR results. The consecutive oligomerization of MPI has been investigated by using a PBO anionic macroinitiator to react with MPI monomers in the same condition as the copolymerization, as described in the SI. It was found that the reaction took place immediately and yielded a large amount of trimers. The MALDI-TOF MS spectrum of the resultant PBO (Figure S11) shows the major product of H-terminated PBO and trace amounts of one and two MPI units end-capped PBO; no more than two consecutive MPI units could be found. This indicates the fast reaction kinetics of the oxyanion with MPI and the trimerization, which essentially limits the further homopolymerization of MPI. Consequently, only the -B or -BB sequence of no more than three consecutive B could exist in the polymer backbone. From another aspect, this sort of self-maintaining process can effectively keep the anionic chain end alive.

The exploration of the copolymerization at different LB/*i*-Bu₃Al/MPI/BO ratios (Table 1) reveals that BO can be initiated by NOct₄Br in the presence of *i*-Bu₃Al, while no initiation of MPI/BO could take place without NOct₄Br as initiator (entry 1). When the [NOct₄Br]/[*i*-Bu₃Al] feed ratio is 1:1 (entry 2), the major product is oxazolidinone, probably due to no excess *i*-Bu₃Al available to activate epoxides. At higher ratios of [*i*-Bu₃Al]/[NOct₄Br] (entries 3–5), the yields of copolymers were generally over 78%. When the feed ratio of [MPI]/[BO] was increased to 1.5:1, the excess MPI monomers can contribute to the forming of trimers and a higher faction of -BB units in the copolymer (entries 6–8). The urethane content in the copolymer as high as 85% can be generated (entry 7). When increasing the feed ratio of monomer/initiator, relatively more trimers and oxazolidinones

were produced, while a copolymer of a high molecular weight $(M_n = 98.3 \text{ k}, D = 1.26)$ composed of 67% urethane unit was achieved (entry 13). NBu₄Br and NBu₄Cl were also able to initiate the polymerization (entries 14–16). However, a comparably large amount of oxazolidinones were observed, probably due to the relatively small-sized cation that could not shield the growing anionic species to efficiently prevent the backbiting process. Our synthetic approach can be successfully expanded to other epoxide (CHO, entry 17) and aryl isocyanate (MOPI, entry 18), while only oligomer in a low yield was produced in the same condition when aliphatic isocyanate (*n*-butyl isocyanate) was used, probably due to its relatively lower activity.^{1,2}

Kinetics study was performed to provide insights of the copolymerization process. As shown in the Figure 3a (and



Figure 3. (a) Representative conversions of MPI into copolymer, oxazolidinone and trimer during the copolymerization of MPI and BO in the condition of $[MPI]:[BO]:[i-Bu_3AI]: [NOct_4Br] = 80:80:3:1.$ (b) Plots of M_n and M_w/M_n (D) vs conversion of MPI into the copolymer.

Figures S13–16), oxazolidinones were found to be produced mainly at the early stage of copolymerization, which could be attributed to the tendency of backbiting of the carbamate anion to cleave the Br–C bond at the chain end until the polymer chain is of sufficient length to prevent displacement of the bromide initiator which is also a good leaving group.^{17,18} Linear fit was further applied to the kinetics, and the apparent rate constant (k_{app}) was calculated to be 0.42–0.63 h⁻¹, as demonstrated in the triplicate experiments (Figures 3a and S13). Meanwhile, the linear increase of M_n (D = 1.10-1.18) versus MPI conversion into the copolymer (Figure 3b) illustrates the living feature of the copolymerization in a relatively high activity (~14 kg mol⁻¹ h⁻¹) in this condition. We also found that the yield of trimer was generally low especially when the feedings of the comonomers were equal



Figure 4. Possible scenarios and energy profile of MPI/BO alternating copolymerization catalyzed by i-Bu₃Al.

(blew 10% when the [MPI]/[initiator] is not too high to afford a local high concentration of MPI, for example, 200:1, $k_{\rm app} \sim$ 0.16–0.21 h⁻¹, as shown in Figure S15). Although forming of trimers and oxazolidinones might interfere the overall polymerization kinetics especially at the early stage, it seems not to influence much the linearity of the later chain growth.

To further confirm the living anionic propagation site at the chain end, we have conducted a tandem synthesis, as described in Table S1 and Figure S17a. It was found that after the copolymerization of MPI and BO was complete, it can reinitiate copolymerization of MPI and PO. The GPC of the block copolymer P(MPI-*co*-BO)-*b*-P(MPI-*co*-PO) exhibits an increased molecular weight from 6.0 to 8.9 kg/mol with a narrow monomodal distribution of 1.14–1.18 (Figure S17b). The resonances of the methyl group from PO units at 0.9–1.2 ppm can be also clearly identified in the ¹H NMR spectrum of the block copolymer (Figure S17c).

Our results have shown that this type of PU is constituted primarily by the alternating units of MPI and BO irrespective of their feed ratios. It is worth mentioning that replacing aluminum alkyl with Lewis acids such as triethyl borane and triphenyl borane yielded no polymers (Table S2). We propose a synergistic coordination mechanism of *i*-Bu₃Al on the growing chain end and the incoming monomer, inspired by the work of Harada et al.,⁶ besides its activating effect on the epoxides (Figure S18).^{25,26} We utilized DFT calculation to explore the hypothesized anionic coordinated mechanism of the enchainment, as elucidated in Figure 4. Oxyanion is found to preferentially bond to MPI over BO monomer as the possible corresponding four-membered ring transition state involved with *i*-Bu₃Al has a much lower activation free energy barrier (ΔG^{\ddagger} = 18.2 vs 50.3 kcal/mol), thus, more energetically favorable to form the urethane structure than the ether structure. This may explain the fact that only minor consecutive BO units are present in the copolymer. For the amidate anion, it exhibits a higher energy barrier for addition of MPI than BO, ($\Delta G^{\ddagger} = 17.1$ vs 13.0 kcal/mol), and the thermodynamically more stable MPI/BO intermediate is resulted in comparison to the MPI/MPI intermediate (-71.6 vs -55.7 kcal/mol), which is consistent with the suppression of oligomerization of MPI observed in the experiments.

In summary, by utilizing Lewis pairs we have succeeded in the copolymerization of aryl isocyanates (e.g., MPI) and epoxides (e.g., BO) in a quasi-living fashion. The fast addition rate of MPI to oxyanion leads to the suppressed oligomerization of BO, while under the successive synergistic coordination of the aluminum catalyst, the amidate anion is more prone to react with BO, and suppress the consecutive oligomerization of MPI. With the fast backbiting/self-maintaining effect, the primary alternating polyurethanes with tertiary amine structure were afforded. It is expected that the simplicity of the catalyst, tunable polymer structures, and high accessibility of epoxides and isocyanates with a rich variety of pendent groups will forge this novel polyurethane into a new catalogue of useful polymeric materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00696.

Characterization of copolymerization, identification of the terminal unit of the copolymer, PBO macroinitiator experiment, copolymerization kinetics of MPI and BO, tandem synthesis of block copolymer, complexation of *i*-Bu₃Al, thermal behaviors of MPI/BO copolymers, and details of DFT computational calculation (PDF)

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Notes

The authors declare no competing financial interest.

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Alternating Chain Growth Copolymerization of Isothiocyanates and Epoxides

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ABSTRACT: A c	R ₃					

ABSTRACT: A class of heteroatom polymers through anionic chain growth copolymerization of epoxides and isothiocyanates has been successfully obtained under mild conditions *via* initiation by a simple salt of lithium alkoxide. The resulting polymers have characteristics of controlled molecular weights and low dispersity with a well-defined backbone of carbon-imidothioate repeat units (-OC(=N)S-) at 100% alternating degree, which have been confirmed in the ${}^{1}H^{-13}C$ heteronuclear multiple bond correlation NMR spectrum and mass spectrum. Side reactions have been greatly suppressed in the copolymerization, and no more than 5% cyclic small molecular byproducts have been produced. We have revealed the special role of lithium bonds in regulating the alternating copolymerization of these two types of monomers, which are involved in activating isothiocyanates as well as binding the incoming monomers to the growing chain ends due to the especial coordination capability of lithium ions to multiple nucleophilic sites.



The proposed mechanism of the alternating copolymerization process is supported by density functional theory calculations. Moreover, the copolymerization exhibits first-order kinetics with respect to the monomers and a quasi-living feature. Our strategy is expected to shed light on the incorporation of different types of cumulated double bonds as comonomers into polymer backbones, and the high availability of epoxides and isothiocyanates of various substitutions will forge the development of such kinds of heteropolymers.

1. INTRODUCTION

Heteroallenes possessing one or more heteroatoms are an important category in cumulated systems,¹⁻⁴ which include carbon dioxide (CO₂), carbonyl sulfide (COS), carbon disulfide (CS₂), isocyanate, isothiocyanate, carbodiimide, etc. They can exhibit distinct regioreactivities due to inclusion of different heteroatoms. Reactions of these heteroallenes with epoxides or episulfides have been utilized to prepare a variety of five-membered heterocycles and have been intensively studied in synthetic organic chemistry.¹⁻³ Recently, copolymerization of epoxides or episulfides with heteroallenes such as CO₂,⁵⁻¹⁰ COS,¹¹⁻¹³ CS₂,¹⁴⁻¹⁶ isocyanate,¹⁷⁻¹⁹ and isothiocyanate²⁰ has been developed as a potential methodology to produce heterochain polymers.

Introduction of heteroatoms into polymers can potentially endow them with diverse structures and intriguing properties. In nature, many biological reactivities of nucleic acids and proteins such as recognition and enzymatic reactions are ascribed to the presence of heteroatoms in their backbones.^{21,22} It is thus attractive to construct heterochain polymers to meet various specific requirements.^{23,24} On another aspect, synthetic polymers rich in heteroatoms are well-known for their enhanced preformance.^{25–28}

Among the aforementioned heteroallenes, copolymerization of isothiocyanates with epoxides remains to be explored up to this point, the study of which would help in better understanding the intricate reaction mechanism of heteroallenes of distinct electrophilicities and broaden their scopes as monomers to be incorporated into polymer backbones.^{2,4} Isothiocyanate possesses two different cumulated double bonds (-N=C=S) and has a relatively low electrophilic reactivity,² which makes copolymerization with epoxides a challenge. Moreover, undesired tendency of homopolymerization of epoxides under this condition and/or generation of cyclic byproducts such as oxathiolanes^{29,30} can also hinder the success of alternating copolymerization of epoxides with isothiocyanates.

Previously, anionic copolymerization of aryl isocyanates with epoxides has been accomplished by employing Lewis pairs, in which ammonium halide onium salt serves as an initiator and triisobutylaluminum as an activator and a synergistic coordinator.¹⁸ Unfortunately, we found that this approach could not be applied to synthesize copolymers of isothiocyanate and

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epoxide. Herein, we reported another strategy to achieve perfectly alternating copolymerization of isothiocyanates and epoxides with *t*-BuOLi, as shown in Scheme 1. Several essential

Scheme 1. Synthetic Strategy for Alternating Copolymerization of Isothiocyanates and Epoxides



aspects are particularly valued as follows. First, relatively strong nucleophilic initiators such as lithium alkoxides may be needed to attack isothiocyanates; second, it is also known that lithium alkoxides cannot initiate homopolymerization of epoxides due to the strong interaction of a lithium cation with an oxygen anion; $^{16,31-33}$ third, lithium bonds $^{34-36}$ among the lithium ion and isothiocyanates and epoxides may potentially promote the alternating insertion reaction of these two types of monomers.

A lithium cation is the smallest singly charged metal atom, which has binding to nucleophilic sites that is expected to be stronger than any other metal cations. The lithium bond is more of ionic in nature and has no saturation or directionality owing to the metallic nature of lithium. Compared to a H bond, the lithium bond is much stronger due to its larger dipole moment. In the lithium bond, a lithium atom tends to engage in multicenter interactions and is more shared among the coordinated atoms.^{37,38} It was also found that lithium ions could assist the copolymerization of CO_2 and cyclohexene oxide.³⁹ Our work herein reveals the unique role of lithium bonds in the alternating copolymerization of isothiocyanates and epoxides, which is supported by NMR experiments and DFT calculations. We also explored the use of organic bases such as 8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) for comparison; however, the polyether content in the resulting polymer backbones was observed and the polymer conversion was found to be comparably low.

2. MATERIALS AND METHODS

2.1. Materials. 1,2-Butylene oxide (BO), propylene oxide (PO), and cyclohexene oxide (CHO) were dried with calcium hydride (CaH₂) over 24 h and then distilled under high vacuum. Tetrahydrofuran (THF) was dried with sodium and distilled under high vacuum. Phenyl isothiocyanate (PIT) and isopropyl isothiocyanate (IPIT) were purchased from Macklin and distilled before use. Lithium tert-butoxide (t-BuOLi, 2.2 M in THF), potassium tertbutoxide (t-BuOK, 1 M in THF), and triisobutylaluminum (i-Bu₃Al, 1.1 M in toluene) were purchased from Innochem. Sodium tert-butoxide (t-BuONa, >99%), lithium bromide (LiBr, >99%), sodium bromide (NaBr, >99%), and tetraoctylammonium bromide (NOct₄Br, >98%) were purchased from TCI. LiBr, NaBr, and Noct₄Br were dried at 100 °C for 2 h in the vacuum line before use. t-BuOLi, t-BuONa, t-BuOK, and i-Bu₃Al were used without further purification. Hydrochloric acid (HCl, 12 mol/L), aniline (>99%), and ethyl acrylate (>99%) purchased from Sinopharm were used without further purification.

'ab	le	1. (Copo	lymerization	Cond	itions	and	C	hemical	I C	characterizations	of	the	Copol	ymers
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entry	LB	LB/i-Bu ₃ Al/PIT/BO	temp. (°C)	time (h)	Conv. ^b (%)	Poly/Oxa ^c	alternating degree ^{d} (%)	$M_n^e (M_{n,\text{theo}}^f) (\text{kg/mol})$	\overline{D}^{e}
1	t-BuOLi	1/0/10/10	25	12	>99	96/4	>99	2.8 (2.0)	1.13
2	t-BuOLi	1/0/30/30	25	12	>99	97/3	>99	6.0 (6.0)	1.14
3	t-BuOLi	1/0/100/100	25	48	>99	97/3	>99	17.9 (20.1)	1.10
4	t-BuOLi	1/0/200/200	50	48	>99	>99	>99		
5 ^a	t-BuOLi	1/0/400/400	50	12	87	98/2	>99		
6 ^{<i>a</i>}	t-BuOLi	1/0/600/600	50	12	86	98/2	>99		
7	t-BuOLi	1/0/30/0	25	12					
8	t-BuOLi	1/0/0/30	25	12					
9	t-BuOLi	1/0.3/30/30	25	12	>99	98/2	>99	7.1 (6.1)	1.10
10	t-BuOLi	1/1/30/30	25	12					
11 ^g	t-BuOLi	1/0/30/30	25	12	>99	95/5	>99	5.1 (4.5)	1.20
12 ^g	t-BuOLi	1/0.3/30/30	25	12	>99	95/5	>99	4.8 (4.5)	1.15
13 ^h	t-BuOLi	1/0.3/30/30	25	24	89	>99	>99	5.9	1.14
14 ⁱ	t-BuONa	1/0/30/30	25	12					
15 ⁱ	t-BuOK	1/0/30/30	25	12					
16	LiBr	1/0/30/30	50	48	41	45/55	>99	7.9	1.13
17 ^j	NaBr	1/0/30/30	50	48					
18	DBU	1/0/30/30	50	48					
19	DBU	1/1/30/30	50	48	49	95/5	50	4.5	1.10
20	TBD	1/1/30/30	50	48	55	93/7	72	3.4	1.16
21 ^k	NOct ₄ Br	1/2/30/30	25	24				1.1 ^k	1.50 ^j

^{*a*}Entries 5 and 6 were performed in bulk, and other entries were performed in THF. ^{*b*}Conversion of PIT was determined by the ¹H NMR spectra of crude products. ^{*c*}Molar ratios of the copolymer (poly) and cyclic byproduct (oxathiolane) or copolymer selectivities were determined by the ¹H NMR spectra of crude products. ^{*d*}The molar percentages of the -OC(=N)S- unit in the polymer backbone were determined by the ¹H NMR spectra of pure products. ^{*c*}Determined by GPC measurements using polystyrenes as standards at 35 °C in THF. The GPC peaks of entries 4–6 are bimodal, thus not shown. ^{*f*}Theoretical molecular weights at full conversions. ^{*g*}IPIT was used instead of PIT. ^{*h*}CHO was used instead of BO. ^{*i*}No copolymer. ^{*j*}Salt not fully dissolved; no copolymer yielded. ^{*k*}Only PBO was afforded. Representative NMR spectra and GPC curves are included in the Supporting Information (Figures S1–S10).

2.2. General Procedures for Copolymerization. All the polymerizations were performed at 25-50 °C under nitrogen. We took the copolymerization of BO and PIT as a typical example. Briefly, a 25 mL reactor with a magnetic stirrer was placed under a vacuum line and flame-dried three times. PIT (0.8 g, 5.92 mmol), BO (0.52 mL, 5.92 mmol), and THF (2 mL) were distilled into the reactor through the vacuum line. *t*-BuOLi (2.2 M in THF, 89.7 μ L, 0.197 mmol) was added to the reactor under a nitrogen atmosphere. The reaction was kept at 25 °C and finally quenched by excess methanol. The final product was redissolved in dichloromethane, re-precipitated in methanol several times, and dried in vacuum. For the kinetics experiments, aliquots were taken from the reactants at different periods of time and quenched with methanol. The crude or the purified products were used to determine the conversion of PIT, the compositions of the copolymers and the byproducts, and the molecular weights of the polymers.

2.3. Characterization Methods. ¹H NMR and ¹³C NMR were performed on a Bruker spectrometer (400 MHz) using d-CDCl₂ or d-DMSO as a solvent. ¹H-¹³C heteronuclear multiple bond correlation (HMBC) spectrum was recorded by employing the standard pulse sequence in the Bruker software package. Briefly, a 9 μ s ¹H 90° pulse width and a 9 μ s ¹³C 90° pulse width were used. The HMBC spectra resulted from 4096 \times 512 data matrices, corresponding to data acquisition times of 459 ms (t_1) and 9.3 ms (t_2) . Four scans were acquired per t_1 , and the delay time between scans was 1.4 s, yielding a total measuring time of 1 h. The molecular weights of resulting polymers and their distributions (D) were characterized by gel permeation chromatography (GPC, Wyatt Dawn EOS) with polystyrenes as standards. Matrix-assisted laser desorption ionizationtime of flight mass spectra (MALDI-TOF MS) were recorded on a Bruker Ultraflex III TOF/TOF (Bruker Dalonics, Inc., Billarica, MA) using trans-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix in dichloromethane. LC-MS/ MS spectra were performed on a Thermo Scientific Q Exactive Plus mass spectrometer (ESI, electrospray ionization) equipped with a Thermo EASY nano LC system (ReproSil-Pur 120 C18-AQ column) $(0.075 \times 250 \text{ mm}, 1.9 \,\mu\text{m})$. The thermal behaviors were investigated on a PerkinElmer differential scanning calorimeter (DSC-8000) under a nitrogen atmosphere. Temperature scans were performed at a rate of 10 °C/min.

3. RESULTS AND DISCUSSION

3.1. Anionic Copolymerization of Isothiocyanates with Epoxides. A series of copolymers were obtained via initiation by t-BuOLi at various BO/PIT/t-BuOLi feed ratios (10/10/1-600/600/1) (entries 1-6), as demonstrated in Table 1. They exhibit comparably narrow distributions (1.10 < D < 1.20). The content of the cyclic small molecular byproduct of oxathiolane is generally below 5%. The molecular weights of the copolymers are shown to depend on the monomer-to-initiator ratios. A turnover frequency (TOF) of 43 h^{-1} (entry 6) has been achieved for the copolymerization in bulk. Remarkably, it shows perfectly alternating copolymerization of PIT and BO as illustrated below, and no homopolymerization of PIT or BO monomers could occur under such a condition (entries 7 and 8). We also explored the scope of the copolymerization of BO and PIT by choosing different alkoxides (t-BuOLi, t-BuONa, and t-BuOK), LiBr, NaBr, organic bases such as DBU and TBD, and ammonium halide onium salt $(NOct_4Br)$ for comparison, as demonstrated in Table 1.

The alternating microstructure of the copolymer was first confirmed using ${}^{1}\text{H}{}^{-13}\text{C}$ HMBC spectrum, as shown in Figure 1. The proton resonances at 5.23–5.41 ppm (d_H) in the ${}^{1}\text{H}$ NMR spectrum are ascribed to the formation of the alternating linkage of BO and PIT. The absence of the proton resonances at 3.26–3.67 ppm in the ${}^{1}\text{H}$ NMR as well as the carbon resonances at 65.00–77.00 ppm in the ${}^{13}\text{C}$ NMR spectrum indicates no polyether content in the copolymer. Only one resonance (i_C)



Figure 1. Representative ¹H-¹³C HMBC spectrum of the copolymer (entry 3). No signal at the cross of the dashed lines indicates no correlation between resonances of hydrogen (c_H) and carbon (e_C).

from the carbonimide unit at 156.20 ppm that appears in the ¹³C NMR spectrum suggests no consecutive PIT units present in the polymer backbone. Notably, the alternating linkage of BO and PIT units results in the correlation of the proton resonances of c_H and the carbon resonances of i_{C_1} as demonstrated in the ¹H-¹³C HMBC spectrum in Figure 1. Meanwhile, the fact that no correlation between the proton resonance of c_H and the carbon resonance of e_C could be detected in the ¹H-¹³C HMBC spectrum strongly suggests the formation of the -OC(=N-Ph)Sunit rather than the -OC(=S)N(Ph)- unit in the copolymerization. Otherwise, the nucleophilic attack of the C=N bond in isothiocyanate by an oxyanion would generate a three-bond cross peak due to the close proximity of c_H to e_C in the benzene ring in the -OC(=S)N(Ph)- unit. Similarly, the ¹H and ¹³C NMR spectra of the copolymer initiated by t-BuOLi in the presence of *i*-Bu₃Al (entry 9) also reveal a well-defined alternating microstructure composed of -OC(=N-Ph)S-, and solely one resonance at 156.20 ppm from the carbonimide unit is present in the ¹³C NMR spectrum, as demonstrated in Figure S2. The formation of this alternating microstructure suggests that the C=S bond in the isothiocyanates should be more vulnerable to the nucleophilic attack than the C=N bond, as observed similarly in the anionic alternating copolymerization of isothiocyanates with episulfides.²⁰

In order to identify the existence of the terminal group of -OC(=N-Ph)SH after the alternating copolymerization is terminated by protonation, we have specifically investigated the copolymer in a low molecular weight (entry 1, $M_{\rm p} \approx 2.8$ kg/ mol) by ¹H-¹³C HMBC NMR and MALDI-TOF MS, as illustrated in Figures S11 and S12. The carbon resonance at 152.62 ppm is attributed to the terminal group of -OC(=N-Ph)SH, which also exhibits correlation with the proton resonance at 4.85–4.90 ppm belonging to the terminal group. The absence of the characteristic resonance of its possible rearranged form of -OC(=S)N(-Ph)H expectedly at 180.00-200.00 ppm indicates the relative stability of the -OC(=N-Ph)SH chain end.⁴⁰ The thiol group in the terminal group of -OC(=N-Ph)SH is expected to react with ethyl acrylate via Michael addition, which has been thus utilized to further verify the end group of the polymer. The detailed experiments and characterizations by ¹H NMR (Figure S13), MALDI-TOF MS

(Figure S14), and Raman scattering spectroscopy (Figure S15) are illustrated in the Supporting Information. Those results further confirmed the terminal group of -OC(=N-Ph)SH in the polymer.

The alternating sequence was also confirmed by the representative MALDI-TOF MS (entry 9), as shown in Figure 2. The two distributions of equal interval were observed, and the



Figure 2. Representative MALDI-TOF MS of the copolymer (entry 9). The inset is the enlarged spectrum representing two types of polymer species of $[C_4H_9O + PIT + (BO+PIT)_6 + H + H^+] (m/z = 1452.527)$ and $[C_4H_9O + PIT + (BO+PIT)_6 + H + Li^+] (m/z = 1458.535).$

interval value (m/z = 207.1) matches the mass of repeat units composed of alternating PIT and BO units (m/z = 135.0 + 72.1= 207.1). These two distributions are ascribed to the polymer species of [C₄H₉O + PIT + (BO+PIT)_n + H] associated with two different cations of H⁺ or Li⁺. The presence of polymer species containing Li⁺ is understandable considering the strong affinity of Li⁺. The MALDI-TOF MS results also indicate the absence of side reactions and/or chain transfer during polymerization. In order to identify all the possible end groups in this copolymerization, the polymer obtained at a low conversion (16%) during copolymerization was investigated by MAIDI-TOF MS, as illustrated in Figure S16. Two major distributions bearing thiol and hydroxy end groups were observed in the MS, consistent with the alternating nature of copolymerization.

The molecular weights and the distributions of the synthesized copolymers were characterized by GPC. It is found that when the molecular weight of the copolymer is relatively small (entry1, BO/PIT/t-BuOLi feed ratio = 10:10:1), the GPC trace is symmetric, as shown in Figure 3a. When the molecular weight of the copolymer is higher (e.g., entry2, BO/ PIT/t-BuOLi feed ratio = 30:30:1), the GPC trace of the copolymer turns bimodal. It is known that the tendency of association of charged polymer chain ends with lithium counterions of particularly high coordination capability often leads to complex polymerization kinetics and/or molecular weight distribution, especially in solvents of low or medium polarity.^{31,41,42} In order to alleviate possible association of the growing chains in the polar solvent of THF in our work, bulky triisobutylaluminum $(i-Bu_3Al)$ was added into the system, which was anticipated to interact with chain ends to separate the dynamic ionic clusters around the chain ends, and change the local environment of polarity.³⁹ Remarkably, it was found that addition of a small amount of *i*-Bu₃Al relative to *t*-BuOLi could



Figure 3. Representative GPC traces of PIT/BO copolymers of entries 1, 2, and 9 in Table 1 (a). GPC traces of the PIT/BO copolymers at different polymerization times under the condition of [PIT]:[BO]:[*t*-BuOLi]:[*i*-Bu₃Al] = 45:45:1:0.3 (b).

indeed lead to a monomodal distribution (entry 9, i-Bu₃Al/t-BuOLi = 0.3:1), as shown in Figure 3a. This strategy has been successfully applied to copolymerizations of other types of isothiocyanates (e.g., IPIT, entries 11 and 12) and epoxides (e.g., CHO, entry 13). Monomodal distributions in GPC traces with good molecular weight control were observed, as demonstrated in Figures S4 and S6.

As the counterparts of *t*-BuOLi, alkoxides of *t*-BuONa and *t*-BuOK have been also used in the copolymerization of BO and PIT. Alkali metal ions Na⁺ and K⁺ are expected to be more separated from the oxygen anions in contrast to Li⁺. Sodium and potassium alkoxides are expected to possess stronger nucleophilicity. However, different from the case by use of Li⁺-based initiators, no copolymers were obtained by use of sodium and potassium alkoxides (entries 14 and 15). In order to further confirm the unique role of Li⁺ in the copolymerization of BO and PIT, we chose LiBr as the initiator (entry 16, BO/PIT/LiBr = 30/30/1), despite the fact that halide anions may possess weak nucleophilicity and thus low initiation efficiency. It was found that polymerization did not take place at room temperature. When the temperature increased to 50 $^{\circ}$ C, the conversion of PIT is found to be about 41% for 48 h, and a low copolymer selectivity (copolymer/oxathiolane = 45/55) was observed. This can be ascribed to the fact that the halide initiator can also serve as a good leaving group, thus backbiting is favored immediately after initiation. This phenomenon was reported in our previous work on copolymerization of epoxide and aryl isocyanates catalyzed by NOct₄Br/*i*-Bu₃Al.¹⁸ Nonetheless, the resulting copolymer afforded by LiBr does exhibit alternating linkage of PIT and BO units as revealed by ¹H and ¹³C NMR spectra (Figure S7), which confirms the special regulating effect from lithium ions. The system with NaBr as an initiator was investigated for comparison despite the poor solubility of NaBr in THF (entry 17, BO/PIT/NaBr = 30/30/1). In contrast, no copolymer was obtained.

To obtain further insights into the copolymerization of BO and PIT, typical organic bases such as DBU and TBD were also chosen for comparison. We found no occurrence of copolymerization of BO and PIT even at 50 °C for 48 h with DBU (entry 18), which has been ascribed to the low nucleophilicity of DBU and/or the low activity of monomers without activation. After introducing *i*-Bu₃Al additionally, the copolymerization of BO and PIT did occur (entry 19, [PIT]:[BO]:[DBU]:[*i*-Bu₃Al] = 30:30:1:1), yielding the copolymers of alternating degree of only 50% and a PIT conversion of 49%. This indicates that *i*-Bu₃Al could indeed interact with monomers and promote ring-opening of BO monomers and their consecutive polymerization as well as copolymerization with PIT. Similarly, we found that



Figure 4. Representative kinetic plots of conversion and $\ln([M]_t/[M]_0)$ *versus* time for copolymerization of BO (open and solid squares) and PIT (open and solid circles) in the conditions of [PIT]:[BO]:[*t*-BuOLi]:[*i*-Bu₃Al] = 45:45:1:0 (a) and [PIT]:[BO]:[*t*-BuOLi]:[*i*-Bu₃Al] = 45:45:1:0.3 (c). [M]₀ represents the normalized initial molar concentration of PIT; [M]_t represents the molar concentration of the monomers at time *t*. Plots of M_n and *D versus* conversion of PIT into the copolymer under the conditions of [PIT]:[BO]:[*t*-BuOLi]:[*i*-Bu₃Al] = 45:45:1:0 (b) and [PIT]:[BO]:[*t*-BuOLi]:[*i*-Bu₃Al] = 45:45:1:0 (c). [M]₀ represents the molar concentration of PIT into the copolymer under the conditions of [PIT]:[BO]:[*t*-BuOLi]:[*i*-Bu₃Al] = 45:45:1:0 (c). [M]₀ represents the molar concentration of PIT into the copolymer under the conditions of [PIT]:[BO]:[*t*-BuOLi]:[*i*-Bu₃Al] = 45:45:1:0 (c). [M]₀ represents the molar concentration of PIT]:[BO]:[*t*-BuOLi]:[*i*-Bu₃Al] = 45:45:1:0 (c). [M]₀ represents the molar concentration of PIT]:[BO]:[*t*-BuOLi]:[*i*-Bu₃Al] = 45:45:1:0 (c). [M]₀ represents the molar concentration of PIT]:[BO]:[*t*-BuOLi]:[*i*-Bu₃Al] = 45:45:1:0 (c). [M]₀ represents the molar concentration of PIT]:[BO]:[*t*-BuOLi]:[*i*-Bu₃Al] = 45:45:1:0 (c). [M]₀ represents the molar concentration of PIT]:[BO]:[*t*-BuOLi]:[*i*-Bu₃Al] = 45:45:1:0 (c). [M]₀ represents the molar concentration of PIT]:[BO]:[*t*-BuOLi]:[*i*-Bu₃Al] = 45:45:1:0 (c). [M]₀ represents the molar concentration of PIT]:[BO]:[*t*-Bu₃Al] = 45:45:1:0 (c). [M]₀ represents the molar concentration concentra

the utilization of the TBD/*i*-Bu₃Al pair could also produce copolymers containing 28% polyether content at 55% PIT conversion (entry 20). In our previous work, the NOct₄Br/*i*-Bu₃Al pair has been utilized in the copolymerization of aryl isocyanates with epoxides successfully;¹⁸ however, for PIT of a lower activity, copolymerization of BO with PIT failed at ratios of *i*-Bu₃Al:NOct₄Br = 0:1 and 1:1, while only the PBO homopolymer was generated at a ratio of *i*-Bu₃Al:NOct₄Br = 2:1 when *i*-Bu₃Al was excessive (entry 21).

3.2. Kinetics of Copolymerization. We have investigated the kinetics of the copolymerization of BO and PIT with adding t-BuOLi solely or together with i-Bu₃Al, as shown in Figure 4. Polymer samples have been taken from the copolymerization at different periods of time and characterized by ¹H NMR and GPC (Figure 3b and Figures S19 and S20). The linear dependence of $\ln([M]_t/[M]_0)$ on time (Figure 4a,c) suggests the first-order kinetics of copolymerization with respect to PIT or BO monomers, which yield the observed rate constants (k_{obs}) of PIT and BO monomers equal to 0.27 and 0.28 h^{-1} for the *t*-BuOLi system and 0.17 and 0.17 h⁻¹ for the *t*-BuOLi/*i*-Bu₃Al system. The almost identical rate constants of PIT and BO monomers also reflect the alternative character of the copolymerization process. The plot of the samples' molecular weights as a function of percent conversion of PIT into the copolymer in Figure 4b,d can be fitted with straight lines, and the polydispersities (D) of these polymers typically fall within a range of 1.10-1.26. It is worth mentioning that compared to the GPC traces of the copolymers initiated solely by t-BuOLi (Figure S20), all the GPC traces of the copolymers initiated by *t*-BuOLi/*i*-Bu₃Al exhibit symmetric mono-modal distributions, as shown in Figure 3b and discussed previously. The linear dependence indicates the feasibility of essential control of the polymer molecular weight. In fact, generation of a trace amount of oxathiolanes (below 2%) during the copolymerization of BO and PIT has no discernible effects on the kinetics, and actually identical chain ends persist throughout the course of polymerization. The quasi-living character of polymerization was further confirmed by generation of block copolymers by chain extending the PIT-alt-BO block with the IPIT-alt-PO block, as shown in Figure S21. The observed rate constants also imply slower kinetics of copolymerization in the t-BuOLi/i-Bu₃Al system than the t-BuOLi system. This could be ascribed to the decreased activation effect of lithium ions on PIT as the formation of ate complexes is anticipated to partially weaken the affinity of available Li on PIT in THF.^{39,42} It is worth noting that the interaction between *i*-Bu₂Al and the lithium initiator would decrease the effective amount of the initiator as well, thus leading to a comparably higher molecular weight of the polymers when the [Al]/[Li] ratio was less than 1, as illustrated in Figure 3. When [Al]/[Li] is equal to 1, no polymer can be obtained. This deactivation effect may be also inferred from the fact that the ate complex in toluene was found inert and could not initiate the homopolymerization of BO either, unless much excess of trialkylaluminum with respect to the lithium initiator (e.g., [Al]/ [Li] = 4) was introduced to activate the monomer and thus trigger polymerization.⁴² In our system of *t*-BuOLi/*i*-Bu₃Al, a fraction of the bulky ate complex incorporated around the growing chain ends is postulated to alleviate the formation of complex aggregates, thus leading to a monomodel distribution of molecular weight. Meanwhile, forming of ate complexes would result in a comparably smaller kinetics of copolymerization. Future study of the reaction mechanism of this intermediate aluminum complex in the polymerization process will be enlightening.

3.3. Mechanism of Alternating Copolymerization. The experimental results of the copolymerization of BO and PIT suggest that lithium ions could regulate the alternating insertion reaction. As introduced previously, a lithium cation is expected to interact preferentially with electron-rich donors such as oxygen, nitrogen, and sulfur atoms to form a unique lithium bond.^{34–36} In order to obtain insights into the possible formation of lithium bonds during copolymerization, DFT

calculations were utilized to first investigate binding of Li⁺ to the PIT monomer in comparison with Na⁺ (Figure S25). As demonstrated in the structures of the complexes, the bond angle of N=C=S changes from 163.9 to 121.7° and the electron density of carbon in the cumulated double bond decreases from 0.911 to 0.872 upon binding with a lithium ion. Compared to the PIT/LiBr complex, a sodium ion exhibits a weaker impact on PIT, as a smaller variation of electron density from 0.911 to 0.895 and bond angle of N=C=S $(36.2^{\circ} vs 42.2^{\circ})$ is observed. It is also found that the bond lengths of Li–N (1.91 Å) and Li–S (2.42 Å) in the PIT/LiBr complex are much shorter than those of Na-N and Na-S in the PIT/NaBr complex (2.40 and 2.69 Å, respectively). The above results indicate that a lithium ion can indeed bind strongly with isothiocyanate to increase the electrophilicity of the carbon atom in the cumulated double bond, eventually leading to forming activated isothiocyanates and lithium bonds around the chain ends.

Accordingly, a possible scenario for the copolymerization of BO and PIT comonomers is demonstrated schematically in Figure 5. Because of a strong interaction between an oxygen



Figure 5. Proposed mechanistic pathway for alternating copolymerization of isothiocyanates and epoxides initiated by *t*-BuOLi and possible backbiting processes.

anion and a small-sized lithium cation,^{24,31-34} lithium ions bind tightly with the chain ends; therefore, the activity of an oxygen anion at the chain end turns low and unable to initiate epoxides. On another aspect, the activation of isothiocyanates by a lithium ion could promote the attack of t-BuOLi on isothiocyanates in the initiation step to form the -OC(=N)S- unit. Compared to an oxyanion, a sulfur anion has a reduced electronegativity, and thus the interaction of lithium ions with the sulfur anion at the chain ends is weakened and the reactivity of the chain ends with epoxides is reinforced. Meanwhile, no homopolymerization of isothiocyanates can occur, as confirmed by the control experiment (entry 7). Consequently, ring-opening of BO by nucleophilic attack of a sulfur anion proceeds exclusively and the chain end of an oxygen anion is retrieved. Alternating insertion of these two types of monomers gives rise to carbonimidothioate units (-OC(=N)S) till terminated by methanol. Whenever any oxathiolane was generated from polymer chain ends via a

backbiting reaction, an oxygen or sulfur anion recovers at the chain end and propagation proceeds constantly. In fact, only a trace amount of oxathiolane (generally less than 5%) was generated during copolymerization, which can influence the polymerization negligibly, as demonstrated in the experiments (Table 1).

The above hypothesized pathway is supported by DFT calculations, as elucidated in Figure 6. For the oxyanion with a Li⁺ counterion, ring-opening of BO by nucleophilic attack of INT1 is not energetically favorable due to a comparably high activation free energy barrier of 41.3 kcal/mol (INT1 \rightarrow TS1). In contrast, the reaction of an oxyanion with PIT is found to be favored with a lower energy barrier of 19.6 kcal/mol (INT1 \rightarrow TS2), and a more thermodynamically stable BO/PIT intermediate (INT3) possessing a lower energy of -37.1 kcal/ mol can be produced. In the transition state of TS2, a lithium ion forms a four-centered transition structure. The above calculations are consistent with the experimental fact that an oxyanion with a Li⁺ counterion can solely react with PIT, while consecutive ring-opening of BO could not proceed. When the generated carbonimidothioate anion (INT3) reacts with incoming comonomers of PIT and BO, continuing insertion of PIT would be kinetically ruled out since a much higher energy barrier has to be overcome (INT3 \rightarrow TS3, $\Delta G^{\ddagger} = 47.9$ kcal/ mol) in comparison to its reaction with BO (INT3 \rightarrow TS4, ΔG^{\ddagger} = 15.6 kcal/mol). It is also found that the resulting PIT/BO intermediate is much more stable than the PIT/PIT intermediate (-83.5 kcal/mol vs -53.5 kcal/mol). The above results suggest that the reaction of INT3 with BO should be both kinetically and thermodynamically more favored over the dimerization of PIT. The DFT calculations elucidate that the concerted addition of epoxides and isothiocyanates mediated by a Li ion should be a favorable pathway to produce perfectly alternating copolymers, consistent with the experiment results. It is noted that the energy barrier for BO ring-opening (INT1 \rightarrow TS2) is 15.6 kcal/mol while that for PIT enchainment (INT3 \rightarrow TS4) is 19.6 kcal/mol. As a matter of fact, these two elementary steps of alternating copolymerization have their own pros and cons for the enchainment, as discussed previously. The calculated energy difference between these two steps might not be dramatic enough to determine which one would be ratelimiting. As elucidated in Figure S27, the hypothesized pathways of backbiting are also explored by DFT calculations, where these two possible pathways show comparably high activation energies, in line with the small probability of the backbiting event in the copolymerization process.

4. CONCLUSIONS

By employing *t*-BuOLi as an initiator, anionic copolymerization of epoxides and isothiocyanates in a controlled manner was developed. The resulting polymers were composed exclusively of -OC(=N)S- repeat units from alternating addition of epoxides and isothiocyanates, as revealed by ¹H-¹³C HMBC NMR spectroscopy and the MALDI-TOF MS. The polymer with a comparably narrow D in a range of 1.10-1.20 can be obtained, and a TOF as high as 43 h⁻¹ has been achieved. The anionic chain ends are effectively living, which can be utilized to make well-defined block copolymers. The role of lithium bonds in regulating the alternating copolymerization has been explored by the control experiments and further supported by the NMR experiments and the DFT calculations. The DFT results show that, in comparison with consecutive addition processes, the concerted addition of epoxides and isothiocyanates mediated by



Figure 6. Hypothetic scenarios and energy profile of PIT/BO alternating copolymerization initiated by *t*-BuOLi. The optimized conformations of INT1, TS2, INT3, and TS4 are illustrated according to DFT calculations, and the bond length and bond angle are marked accordingly.

lithium bonds is the favorable pathway in kinetics and thermodynamics. Given the simplicity of the catalyst and welldefined polymer microstructures, the heteroatom-enriched polymers could hopefully find potential applications in optical and biological fields.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.1c01561.

Characterization and kinetics of copolymerization of isothiocyanates and epoxides, identification of the polymer terminal group, block copolymers, thermal behaviors, and hydrolysis of polymers, and DFT calculations (PDF)

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Notes

The authors declare no competing financial interest.

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