

Urea-welded Anionic Vinyl-addition and Ring-opening Polymerizations for One-pot Hybrid Block Copolymer Synthesis

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Electronic Supplementary Information

Abstract Structural and functional diversity of block copolymers can be vastly expanded by combining carbon-chain and heterochain segments. However, options for one-pot controlled synthesis of such hybrid block copolymers remain scarce. Herein, we report a tandem anionic polymerization strategy that addresses this challenge. Classic anionic vinyl-addition polymerization of isoprene or styrene is performed first, followed by end-capping with ethylene oxide to generate a macromolecular lithium alkoxide. A *N,N'*-disubstituted (thio)urea is then introduced to interact with the alkoxide, creating an ionic initiating/catalytic system through exchange of proton and lithium cation. The *in situ* generated bifunctional catalytic species allows the ring-opening polymerization (ROP) of the subsequently added ϵ -caprolactone (CL) to occur with markedly enhanced selectivity. Well-defined hybrid block co- and ter-polymers are obtained even at full CL conversion. Urea with medium acidity (pK_a) and structural symmetry is shown optimal mediator to achieve both high efficiency and good control of the ROP step.

Keywords Anionic polymerization; Ring-opening polymerization; Vinyl-addition polymerization; Block copolymer; Polyester

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INTRODUCTION

Block copolymers constitute a pivotal class of functional polymeric materials as they integrate chemically distinct segments within a single macromolecular framework, thereby giving rise to properties inaccessible to the corresponding homopolymers.^[1–4] In particular, block copolymers that combine non-polar carbon chain (polyolefin) segments, such as polybutadiene, polyisoprene (PI), and polystyrene (PS), with polar heterochain segments, including aliphatic polyesters, *e.g.* poly(ϵ -caprolactone) (PCL) and polylactides, have attracted sustained research interest owing to their unique physicochemical properties, especially versatile self-assembly behaviors.^[5,6] The pronounced polarity contrast between the constituent blocks drives spontaneous microphase separation into ordered nanostructures,^[7,8] while the polyester segment imparts crystallinity, degradability, and broad compatibility with polar substrates.^[9–12] The interplay of these features underpins a diverse set of mechanical, interfacial, rheological, and solution properties, supporting their utility in advanced nanostructured and functional material systems.^[13,14]

However, the synthesis of such hybrid block copolymers in

a controlled and operationally simple manner remains a non-trivial task. Although living and controlled polymerization techniques have enabled the routine preparation of block copolymers *via* sequential monomer addition, this strategy is intrinsically limited when constituent monomers polymerize through fundamentally distinct mechanisms.^[15–19] Specifically, chain ends derived from vinyl-addition polymerization (*i.e.* carbanions) are generally incompatible with the subsequent ROP of cyclic esters. In most cases, such species are either insufficiently (Lewis) acidic towards monomer activation or excessively basic and nucleophilic, leading to undesirable side reactions, including monomer deprotonation and transesterification of polyesters. Consequently, achieving efficient chain extension while preserving the structural fidelity remains a long-standing challenge.^[20] Alternative approaches, including end-group transformations and bifunctional initiators, have been explored, yet they often entail additional synthetic steps or suffer from limited generality.^[21–23] PI/PS-*b*-PCL copolymers provide a representative example that highlights these limitations.^[24,25] In a typical protocol, anionic polymerization of diene or styrene monomers is followed by addition of ϵ -caprolactone (CL). Capping the carbanionic chain end with electrophiles such as ethylene oxide (EO) is commonly employed to attenuate its nucleophilicity and basicity, thereby suppressing undesired initiation pathways.^[26–29] Nevertheless, this modification alone is insufficient to fully control

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the subsequent ROP process; transesterification reactions remain prevalent, resulting in a broadened molar mass distribution and diminished block definition.^[28] These observations underscore that precise modulation of chain-end activity during ROP is essential for achieving well-defined block architectures under one-pot conditions.^[30]

Recent advances in organocatalysis have opened new opportunities to address this challenge.^[31–35] Bifunctional catalytic systems based on (thio)urea motifs have demonstrated remarkable capability to mediate the ROP of cyclic esters with high efficiency and selectivity.^[36–42] These systems typically operate through cooperative hydrogen bonding and ion-pairing interactions, enabling simultaneous activation of the monomer and modulation of the propagating chain end.^[43–45] This behavior is particularly noteworthy, given that these two factors are often mutually antagonistic in conventional ROP processes. Based on these insights, we envisaged that introducing (thio)urea into a macromolecular lithium alkoxide system would generate a dynamic proton-lithium-exchange equilibrium, thereby producing a bifunctional ionic catalytic species capable of modulating chain-end activity. Within this framework, lithium alkoxide serves as an active center, while (thio)urea attenuates and optimizes its activity through hydrogen bonding and (partial) proton transfer. Such *in situ* cooperative modulation is expected to suppress side reactions, particularly transesterification, while maintaining sufficient activity for efficient ROP of CL. Importantly, the position of this equilibrium, and consequently, the overall catalytic performance, should be tunable through the structural features and acidity (pK_a) of (thio)urea, thereby providing a rational approach for refining block copolymerization.^[46]

Herein, we report a tandem anionic polymerization strategy that enables one-pot synthesis of well-defined carbon-chain/heterochain hybrid block copolymers. First, anionic

vinyl-addition polymerization of isoprene and/or styrene was conducted, followed by end-capping with ethylene oxide to generate a lithium alkoxide macroinitiator. Subsequent introduction of (thio)urea into this macroinitiator system generates a bifunctional ionic catalytic species that mediates the ROP of CL with enhanced selectivity. This strategy allows for the one-pot synthesis of well-defined block copolymers and terpolymers, even at full monomer conversion. Furthermore, the effects of the (thio)urea acidity, loading, and structural symmetry on the efficiency and selectivity of the ROP process were systematically investigated, and the generality of this approach was demonstrated through the synthesis of PS-*b*-PI-*b*-PCL triblock terpolymers.

EXPERIMENTAL

The experimental section and complementary data are presented in the electronic supplementary information (ESI).

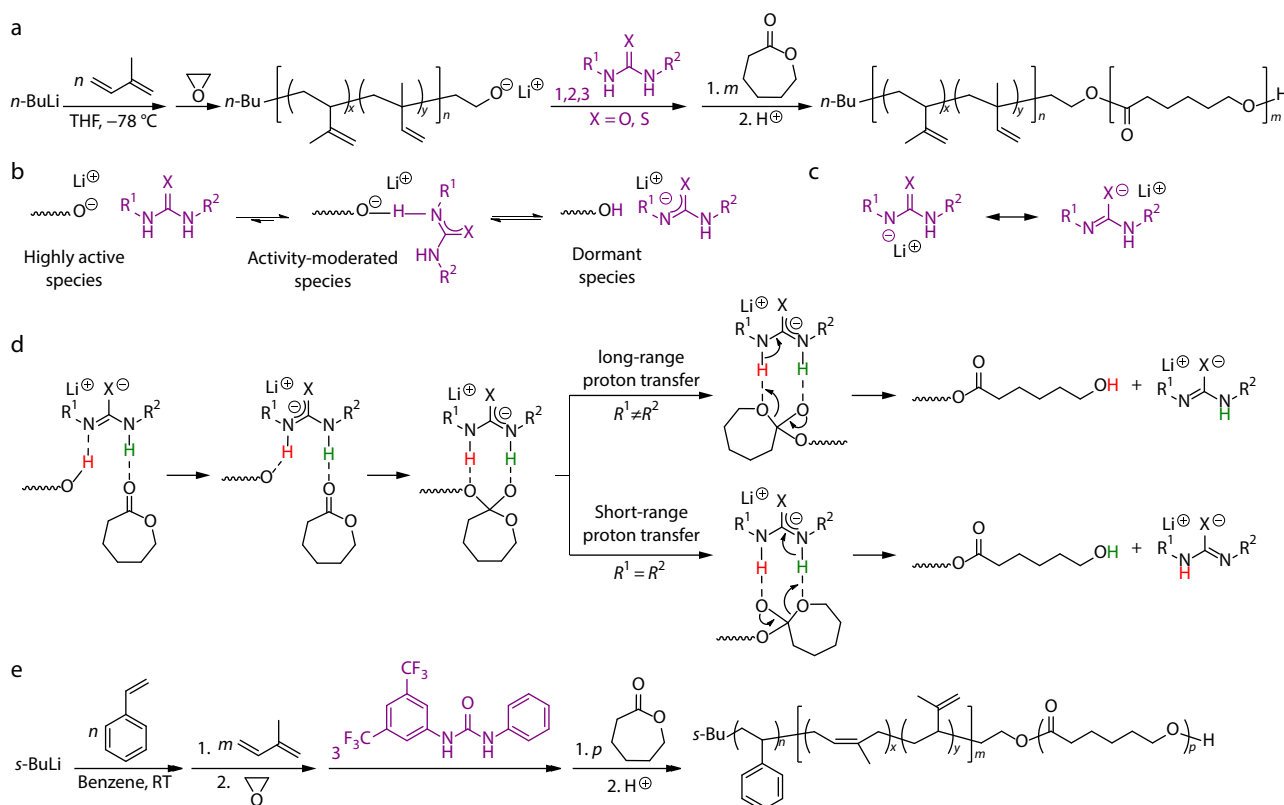
RESULTS AND DISCUSSION

To evaluate the intrinsic suitability of the polyolefin-alkoxide macroinitiator for the synthesis of PCL, CL was directly added at room temperature (RT) to the EO-end-capped living PI-alkoxide (I1 in Table 1). The product exhibited a broad molar mass distribution ($\bar{M}_w=2.37$, I1CL1 in Table 1). This confirms that the nucleophilicity of the pristine lithium alkoxide chain end is too high to allow adequate chemoselectivity (transesterification suppression) and controlled ROP of the CL to form a well-defined PI-*b*-PCL hybrid block copolymer. It is hypothesized that introducing (thio)urea would establish a proton-lithium-exchange equilibrium and generate bifunctional ionic catalytic species (Schemes 1a–1d). Partial protonation of the alkoxide attenuates its nucleophilicity, so that transesterification is suppressed, while sufficient activity is preserved for ROP. In other words, the alkoxide is

Table 1 Conditions and results of sequential polymerization of vinyl monomers and CL mediated by (thio)ureas. ^a

Entry	(T)U	[M] ₀ /[init] ₀ / [(T)U] ^b	Temp. (°C)	Time (h)	Conv. (%)	$M_{n,theor}$ ^c (kg·mol ⁻¹)	$M_{n,NMR}$ ^d (kg·mol ⁻¹)	$M_{n,SEC}$ ^e (kg·mol ⁻¹)	$\bar{M}_w$ ^e
I1	–	147/1/0	–78	48	>99	10.0	8.0	11.7	1.09
I1CL1	–	100/1/0	RT	5 min	>99	18.1	17.9	13.9	2.37
I1CL2	TU1	100/1/3	RT	23	4	8.5	8.1	10.7	1.14
I1CL3	TU2	100/1/3	RT	0.5	72	16.2	14.5	11.8	1.31
I1CL4	U1	100/1/3	RT	1	63	15.2	15.1	18.8	1.14
I1CL5	U2	100/1/3	RT	21	93	18.6	19.6	25.8	1.19
I1CL6	U2	100/1/2	RT	19	93	18.6	18.5	25.1	1.19
I1CL7	U2	100/1/1	RT	5	89	18.1	17.3	23.6	1.27
I1CL8	U3	100/1/2	RT	20	93	18.6	19.5	25.9	1.18
I1CL9	U4	100/1/2	RT	93	93	18.6	18.4	24.8	1.17
I1CL10	U5	100/1/2	RT	2.5	95	18.8	19.8	25.2	1.16
I2	–	588/1	–78	72	>99	40.0	38.0	42.3	1.09
I2CL1	U2	400/1/2	RT	144	59	64.9	66.0	63.5	1.20
I2CL2	U5	400/1/2	RT	48	59	64.9	67.0	66.7	1.15
S1	–	96/1/0	RT	24	>99	10.0	9.4	11.8	1.04
S1CL	U2	100/1/2	RT	13	99	20.7	21.0	24.9	1.14
S11	–	(96+147)/1/0	RT	48	>99	20.0	23.3 ^f	23.6	1.07
S11CL	U2	150/1/3	RT	6	80	37.0	37.2	34.2	1.20

^a Data given for each entry are related to the synthesis of polyolefin precursors (I1, I2, S1, S11) or PCL segments; ^b Feed ratio of monomer, (macro)initiator (butyllithium for polyolefin segment and polyolefin-alkoxide for PCL segment), and (thio)urea; ^c Theoretical number-average molar mass calculated from the monomer-to-macro-(macro)initiator feed ratio and monomer conversion; ^d Number-average molar mass calculated from ¹H-NMR spectrum of the isolated product using integrals of the characteristic signals of the PCL end group (–CH₂OH) and the copolymer main body; ^e Number-average molar mass and molar mass distribution determined by SEC (THF, 35 °C, PS standards); ^f $M_{n,NMR}(PS) = 13.2 \text{ kg}\cdot\text{mol}^{-1}$, $M_{n,NMR}(PI) = 10.1 \text{ kg}\cdot\text{mol}^{-1}$.



Scheme 1 (a) Schematic illustration of sequential polymerization of isoprene and CL mediated by (thio)urea; (b) Plausible proton-lithium-exchange equilibrium between alkoxide and (thio)urea species during the ROP of CL in the process depicted in (a); (c) Two possible deprotonated forms of (thio)urea; (d) Proposed long/short-range proton transfer pathways; (e) Sequential polymerization of styrene, isoprene, and CL mediated by U2.

converted from a highly active but poorly selective species into an activity-moderated but selectively improved species (Scheme 1b). Concurrently, bifunctional catalysts also activate CL through hydrogen bonding, effectively increasing its electrophilicity and local accessibility.^[47] Therefore, the polymerization outcome is governed by a balance between nucleophilicity moderation and monomer activation, which can be optimized by the acidity, structure, and loading of (thio)urea.

To probe the role of acidity, a series of (thio)ureas with different pK_a values was examined to determine the optimal window for activity and selectivity (Fig. 1). With the highest acidity, TU1 (added to 3 equiv. of PI-alkoxide) leads to largely dormant system (I1CL2 in Table 1), indicating excessive protonation of the alkoxide, which minimizes the chain-end nucleophilicity and inhibits ROP. With lower acidity, TU2 allows the ROP to proceed much faster but fails to maintain good control at high CL conversion (I1CL3 in Table 1). U1 is structurally analogous to TU2, but with a higher pK_a . Interestingly, U1 results in slower ROP of CL and affords low $\bar{D}_M$ (<1.15) at similar CL conversion (I1CL4 in Table 1). This apparent “anti- pK_a ” order between TU2 and U1 may be rationalized by lithium coordination preference. According to HSAB theory, the lithium cation should preferentially coordinate with the oxyanion of deprotonated U1 over the sulfide anion of deprotonated TU2.^[48,49] Therefore, protonation of the lithium alkoxide by U1 is favored despite its lower acidity than TU2 (Scheme 1b), thus causing a lower polymerization rate. However, the pK_a of

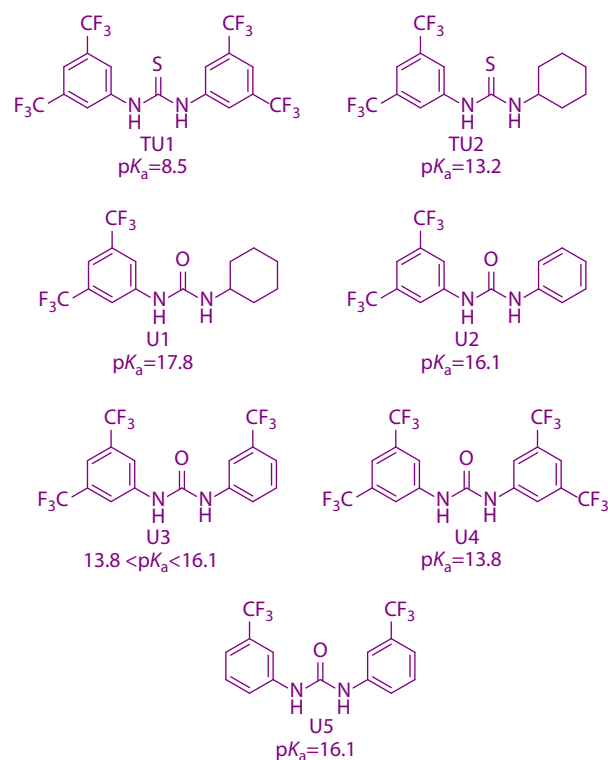


Fig. 1 Formula of the (thio)ureas used in this study and their pK_a values in DMSO.^[50]

U1 was still too high to adequately attenuate the nucleophilicity of the propagating alkoxide, as indicated by the broadening of the molar mass distribution observed at higher CL conversions.

With a lower pK_a than U1, U2 resulted in a much slower ROP but significantly improved selectivity (I1CL5 in Table 1). SEC revealed a unimodal and narrow molar mass distribution that was maintained until full CL conversion (Figs. 2A and 3a). ^1H -NMR spectrum confirmed the expected block copolymer structure with well-matched integrals from both segments and the PCL end group ($-\text{CH}_2\text{OH}$), verifying the formation of a well-defined PI-*b*-PCL copolymer with complete monomer consumption (Fig. 2B). ^1H DOSY-NMR presented a single diffusion coefficient for all resonances (Fig. 2C), in clear contrast to the distinct diffusion behaviors observed for a mixture of the corresponding homopolymers (Fig. S1 in ESI). Collectively, these results demonstrate that the optimal acidity of urea enables simultaneous control over both the activity and selectivity of the ROP of CL from the PI-alkoxide macroinitiator, effectively suppressing transesterification.

Reducing the amount of U2 from 3 to 2 and adding 1 equiv. of the PI-alkoxide results in a progressively higher polymerization rate (I1CL5-7 in Table 1), consistent with a shift in the proton-lithium-exchange equilibrium towards more active (less moderated) alkoxide species. At 2 equiv. of U2, good control was retained, whereas at 1 equiv. of U2, the markedly enhanced activity was accompanied by diminished selectivity, especially at full CL conversion (Figs. 3b and 3c). These observations provide strong support for the proposed equilibrium model in which urea loading affects the fraction of moderated versus fully active chain ends. This trend was further corroborated by experiments employing more acidic ureas (U3 and U4, used in 2 equiv.). Although narrow molar mass distributions are maintained at (near) full CL conversion, appreciably longer reaction times are required, especially for U4, which has the lowest pK_a of all the ureas used (I1CL8-9 in Table 1, Figs. 3d and 3e), consistent with stronger protonation and considerably reduced chain-end nucleophilicity.

Longer PCL segments were also targeted, with U2, U3, and U4 as mediators, yielding PI-*b*-PCL block copolymers with

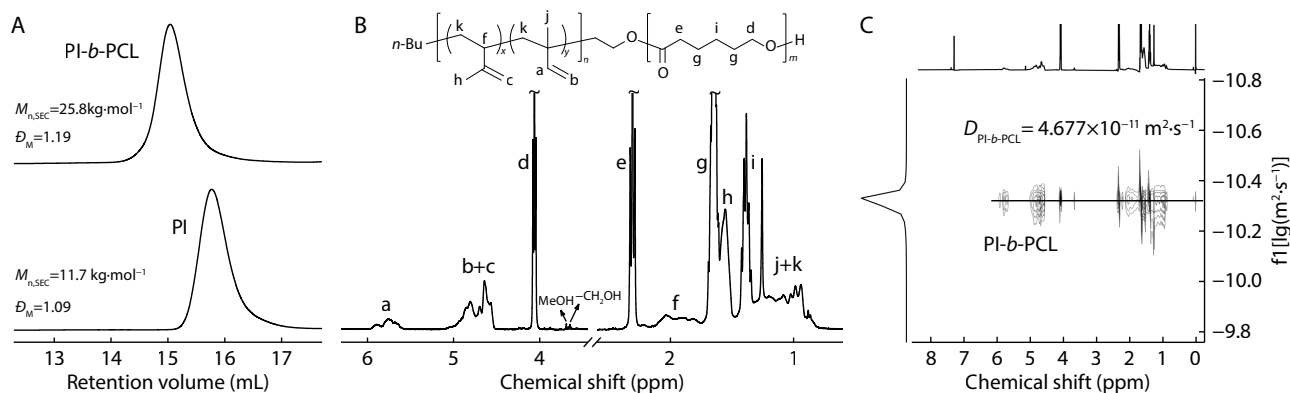
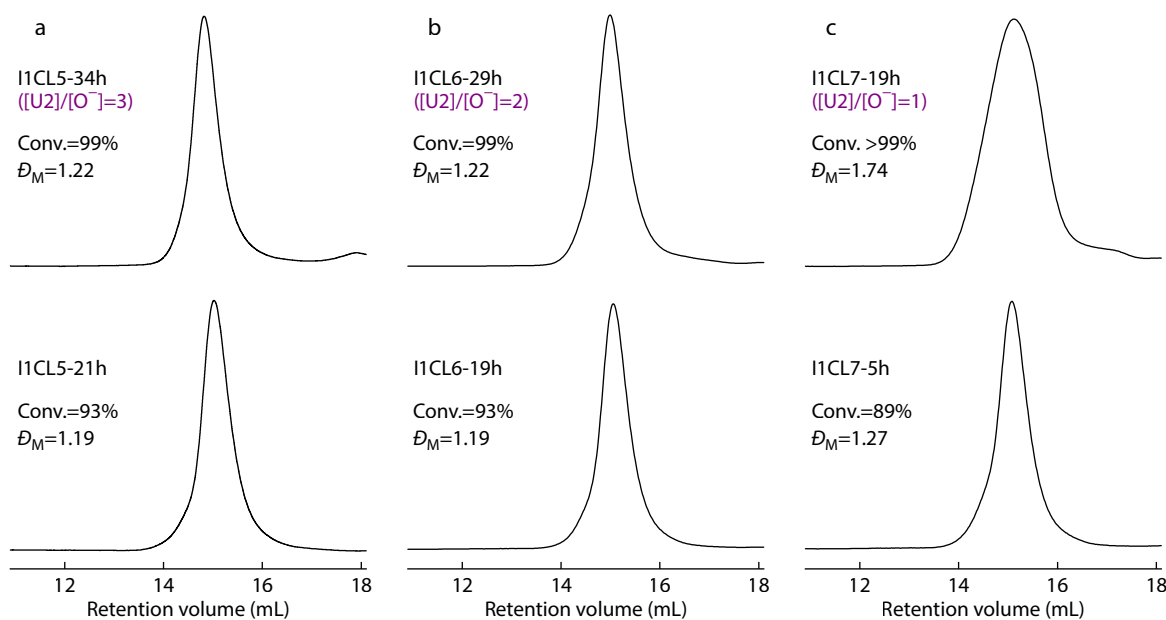


Fig. 2 (A) SEC traces (RI signal in THF at 35 °C), (B) ^1H -NMR spectrum, and (C) ^1H DOSY-NMR spectrum of a representative PI-*b*-PCL diblock copolymer synthesized by sequential polymerization of isoprene and CL mediated by U2 (I1CL5 in Table 1).



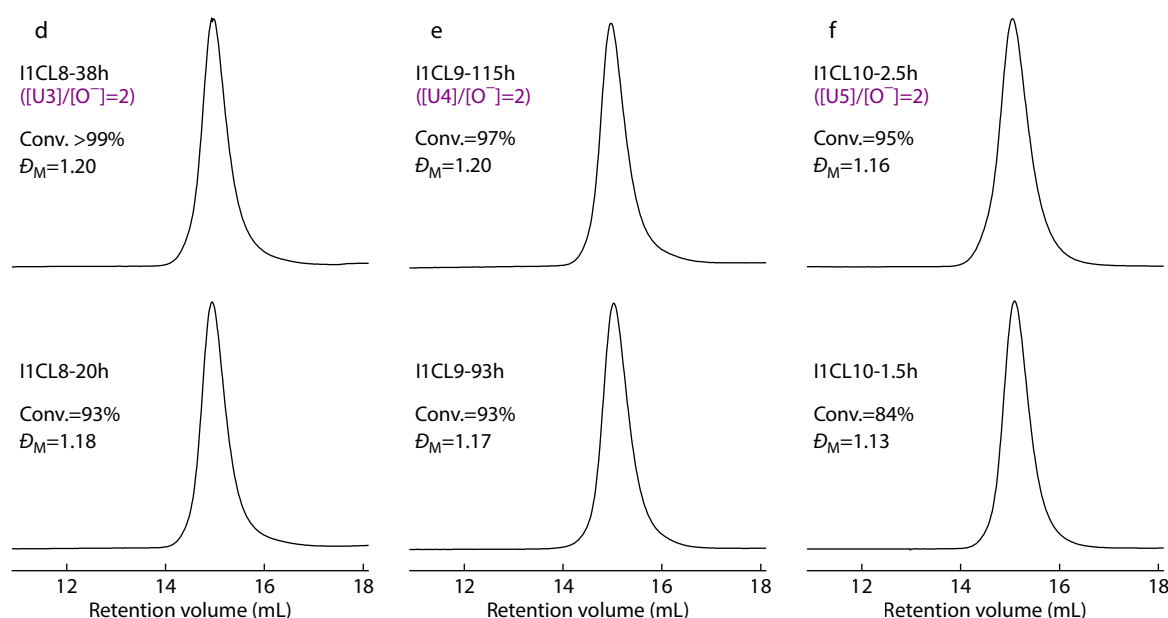


Fig. 3 SEC traces (a–f, RI signal in THF at 35 °C) of PI-*b*-PCL diblock copolymers synthesized by sequential anionic polymerization of isoprene followed by urea-mediated ROP of CL under different urea identities and urea-to-initiator ratios (I1CL5–10 in Table 1). The traces in each panel correspond to samples obtained at high CL conversions after different reaction times. The reaction time, CL conversion, $\bar{D}_M$, urea identity, urea-to-initiator ratio, and sample designation are indicated in the corresponding panels.

controlled molar masses and narrow distributions at high CL conversions (Table S1 in ESI). A similar dependence of the polymerization rate on urea acidity was observed. A linear plot of $\ln([M]_0/[M])$ versus time was obtained by a kinetic study, demonstrating the living polymerization character (Fig. S2 in ESI). Taken together, these results indicate that the pK_a value and loaded amount of urea are the two principal parameters governing the position of the equilibrium depicted in Scheme 1(b), through which the degree of chain-end modulation can be rationally controlled. It is also important to note that urea can be readily removed by precipitation of the block copolymer in methanol, as confirmed by the disappearance of aromatic signals in the $^1\text{H-NMR}$ spectrum of the purified product (Fig. S3 in ESI).

To decouple the structural effects of acidity, U5 (Fig. 1), which has a pK_a close to that of U2 but a symmetric structure, was employed (I1CL10 in Table 1, Fig. 3f). Remarkably, the ROP was much faster, reaching 95% CL conversion within only 2.5 h while maintaining a narrow molar mass distribution ($\bar{D}_M=1.16$), representing a substantial rate enhancement without compromising selectivity/control. This indicates that the structural symmetry of urea introduces an additional dimension of modulation beyond acidity. As depicted in Scheme 1(d), urea first interacts with the chain-end alkoxide and subsequently engages the incoming monomer through cooperative hydrogen bonding interactions. For symmetric U5, the two equivalent N–H moieties allow more efficient proton transfer to the newly formed chain end (alkoxide from the cleaved CL ester group), presumably *via* a short-range and energetically more favorable pathway. However, asymmetric ureas require less efficient (long-range) proton transfer pathways that lead to slower kinetics. In addition, the remaining N–H group in U5 after partial proton transfer may serve as a stronger hydrogen-bond donor than that in U2, which further facilitates ROP by strengthening monomer activa-

tion.^[51,52] These findings highlight the previously underestimated role of structural symmetry of urea in modulating catalytic activity.

To further evaluate the robustness and generality of this method, its applicability to macroinitiators with higher molar masses was examined. Using I2, which has an approximately four-fold higher molar mass than I1, well-defined PI-*b*-PCL diblock copolymers were obtained by U2, albeit at a reduced polymerization rate due to the lower concentration of active chain ends (I2 and I2CL1 in Table 1, Fig. S4 in ESI). Replacing U2 with symmetric U5 significantly accelerates the ROP without compromising control, further underscoring the advantage of symmetric ureas under kinetically demanding conditions (I2CL2 in Table 1, Fig. S5 in ESI). The generality of this approach has been extended to different polyolefin macroinitiators. Sequential polymerization of styrene and CL in benzene using U2 afforded a well-defined PS-*b*-PCL diblock copolymer. SEC showed a unimodal and narrow molar mass distribution, even at 99% CL conversion, and $^1\text{H-NMR}$ spectroscopy confirmed the expected block structure (S1 and S1CL in Table 1, Fig. S6 in ESI). The acceleration of ROP in benzene is attributable to solvent–catalyst interactions. THF, as a Lewis basic solvent, may compete with CL for hydrogen bonding with the N–H moiety of the catalyst, thus attenuating the catalytic activity, whereas benzene does not have such an effect. In addition, the low polarity of benzene may promote hydrogen-bonding interactions owing to poor solvation.^[53] PS-*b*-PI-*b*-PCL triblock terpolymers were achieved *via* the sequential polymerization of styrene, isoprene, and CL (SI1CL in Table 1, Scheme 1e). Compared to the corresponding diblock system, a higher CL polymerization rate was observed, which can be ascribed to the higher monomer concentration as well as the solvent effect.^[53] SEC and $^1\text{H-NMR}$ analyses confirmed the successful generation of the targeted triblock structure (Fig. 4).

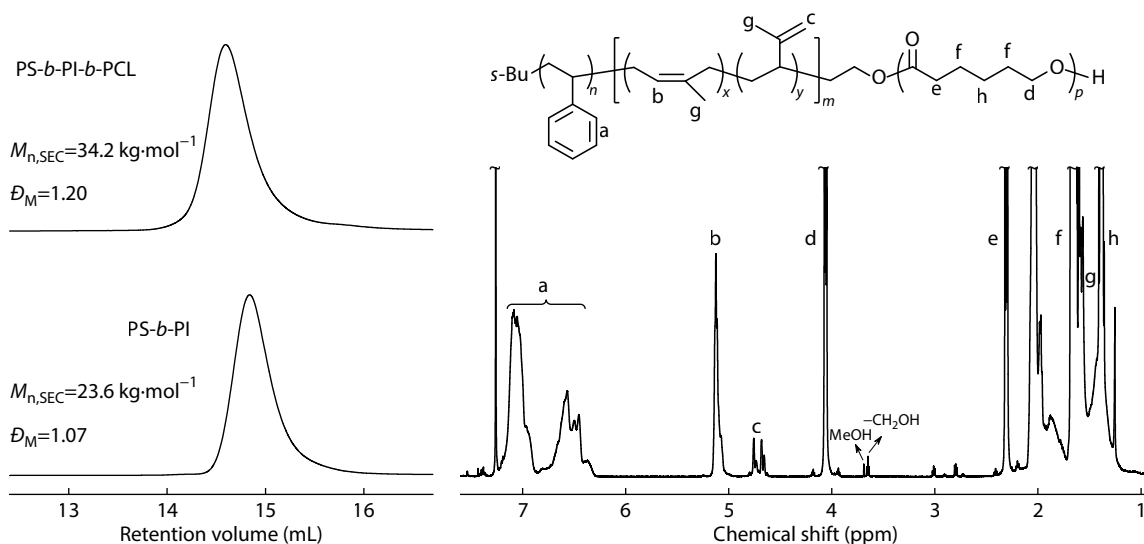


Fig. 4 SEC traces (left, RI signal in THF at 35 °C) and ^1H -NMR spectrum (right) of a representative PS-*b*-PI-*b*-PCL triblock terpolymer synthesized by sequential polymerization of styrene, isoprene, and CL mediated by U2 (S11CL in Table 1).

CONCLUSIONS

In summary, we have developed a tandem anionic polymerization strategy that enables one-pot controlled synthesis of a carbon-chain/heterochain hybrid block copolymer (polyolefin-*b*-PCL). By introducing (thio)urea into a macromolecular lithium alkoxide system, a bifunctional ionic catalytic system was established through a proton-lithium-exchange equilibrium, which effectively modulated the activity of the propagating alkoxide species. This modulation suppresses transesterification while maintaining sufficient activity for the ROP of CL, thereby allowing the formation of PI-*b*-PCL, PS-*b*-PCL, and PS-*b*-PI-*b*-PCL block co/terpolymers with high structural fidelity, even at full monomer conversion. The experimental results revealed that ureas outperform thioureas, probably because of the stronger interaction between urea anions and lithium cations. The optimal $\text{p}K_{\text{a}}$ value and loading of urea are crucial for achieving an activity-selectivity balance, while the structural symmetry of urea further influences the efficiency of the ROP step. This strategy features operational simplicity, good controllability, and potential generality towards various nonpolar vinyl and polar cyclic monomers. The discrepancy between symmetric and asymmetric ureas provides new mechanistic insights into (thio)urea-based catalysis and offers useful guidelines for the rational design of acid-base catalytic systems.

BIOGRAPHY

2026 Rising Scholar: Jun-Peng Zhao received his B.S. (2005) and Ph.D. (2010) from University of Science and Technology of China under the supervision of Prof. Guangzhao Zhang. From 2007 to 2009, he undertook a CSC-supported joint Ph.D. appointment in National Hellenic Research Foundation, Greece, under the supervision of Prof. Stergios Pispas. He was then a postdoctoral researcher at Max-Planck Institute of Colloids and Interfaces, Germany, with Prof. Helmut Schlaad and Prof. Markus Antonietti (2011–2012), and at King Abdullah University of Science and Technology, Saudi Arabia, with Prof. Nikos Hadjichristidis (2012–2014). In the beginning of 2015, he joined South China University of Technology (School of Materials Science and

Engineering) and began his professorship. His research mainly focuses on synthesis and functionalization of polymers by ionic and organocatalytic/metal-free methods, and also includes synthesis of polymers from (bio)renewable resources, structure-property relationship of polymers especially in terms of interactions with bio-entities. He is the coauthor of 110 peer-reviewed papers on JACS, Angew, Macromolecules, ACS Macro Letters, Chinese Journal of Polymer Science, etc., 17 issued Chinese patents and 1 US patent. He is now an editorial board member of ACS Macro Letters (ACS) and Polymer Chemistry (RSC).

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-026-3823-2>.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request. The authors' contact information: msjzpzhao@scut.edu.cn (J.P.Z.).

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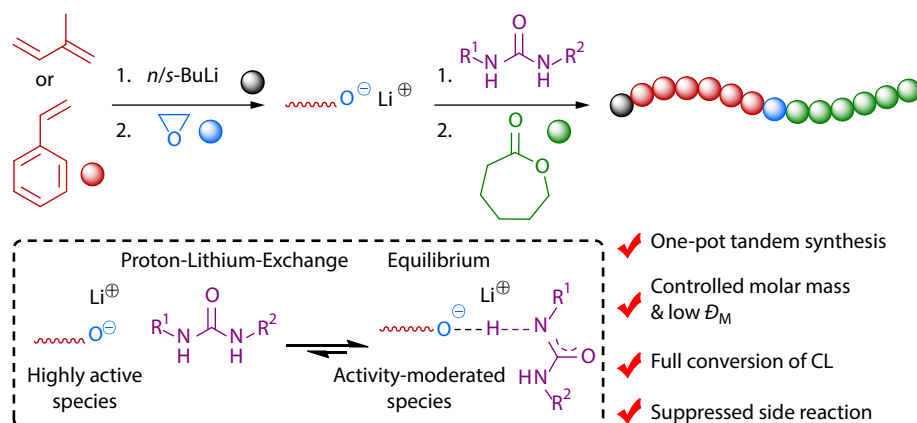
Graphical Abstract

Urea-welded Anionic Vinyl-addition and Ring-opening Polymerizations for One-pot Hybrid Block Copolymer Synthesis

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Urea with proper N-substituents facilitates anionic vinyl-addition polymerization of nonpolar olefins and ring-opening polymerization of ϵ -caprolactone to enable one-pot controlled synthesis of carbon-chain/heterochain hybrid block copolymers by modulating the activity and selectivity of chain-end alkoxide species.



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