Urea Anions: Simple, Fast, and Selective Catalysts for Ring-Opening Polymerizations

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S *Supporting Information*

ABSTRACT: Aliphatic polyesters and polycarbonates are a class of biorenewable, biocompatible, and biodegradable materials. One of the most powerful methods for accessing these materials is the ring-opening polymerization (ROP) of cyclic monomers. Here we report that the deprotonation of ureas generates a class of versatile catalysts that are simultaneously fast and selective for the living ring-opening polymerization of several common monomers, including lactide, δ-valerolactone, ε-caprolactone, a cyclic carbonate, and a cyclic phosphoester. Spanning several orders of magnitude, the reactivities of several diaryl urea anions correlated to the electron-withdrawing substituents on the aryl rings. With the appropriate urea anions, the polymerizations reached high conversions (~90%) at room temperature within seconds (1−12 s), yielding polymers with narrow molecular weight distributions ($Đ$ = 1.06 to 1.14). These versatile catalysts are simple to prepare, easy to use, and exhibit a range of activities that can be tuned for the optimal performance of a broad range of monomers.
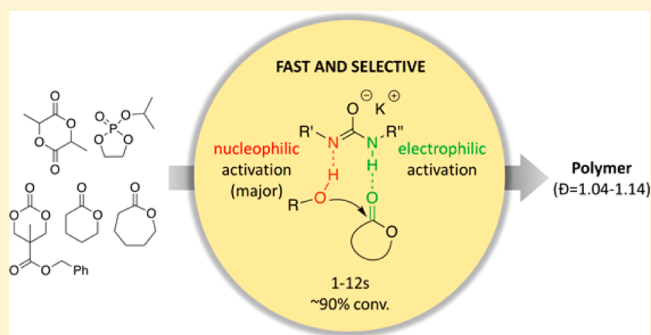
INTRODUCTION

The progress in new catalytic methods and polymerization processes continues to drive innovation in polymer chemistry.[1−8] The development of simple, user-friendly, and controlled polymerization processes has spawned a renaissance in polymer chemistry.[9,10] The versatility of these methods, coupled with the ability to generate well-defined, functional materials has enabled scientists with a wide array of backgrounds to exploit the unique properties of well-defined macromolecules to address an extensive range of scientific and technological problems not only in chemistry, but also in medicine, biology, physics, and materials science.[9,11,12]

A variety of enzymatic,[13,14] metal-based,[12,15] and organic catalysts[5,16−19] are known for ring-opening polymerization reactions. Considerable efforts in recent years have provided catalysts systems that are highly active[20−29] or highly selective,[17,24,25,30−40] but rarely both. As the ring-opening polymerization of lactones is a transesterification reaction, competitive transesterification of the resulting polymer can lead to broadening of the molecular weight distribution, depending on the relative rates of propagation (ring-opening) and chain transfer (transesterification, backbiting).[41] Organic catalysts based on H-bonding motifs,[17,42,43] such as thiourea (TU, 1-[3,5-bis(trifluoromethyl)phenyl]-3-cyclohexylthiourea)/DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) (Scheme 1a),[24,31,32] are unusual as polymerization catalysts in that they exhibit high selectivities for the ring-opening of the lactones relative to transesterification of the polymer, leading to narrow molecular weight distributions.[16,24,31,44] However, these cata-

lysts typically exhibit modest activities. Recently, we reported a new concept for generating bifunctional catalysts by reacting alkoxides with thioureas (Scheme 1b);[44] these catalysts retained the high selectivity of the thiourea/amine catalyst systems for enchainment over other competing reactions (epimerization, transesterification and backbiting), but are more active. In this contribution, we report a hyperactive class of selective catalysts derived from urea anions, which are highly tunable and effective for the selective polymerization of several common cyclic monomers (Scheme 1c).

RESULTS AND DISCUSSION

Neutral ureas are readily prepared from commercially available isocyanates and amines with minimal workup (Scheme 2a); a series of several representative ureas (Scheme 2b) were studied in detail for the ring-opening polymerization of several common monomers (Scheme 2c) in THF.

To evaluate the polymerization behavior of urea anions as catalysts for ring-opening polymerization, urea **1** and KOMe were combined in THF and added to a THF solution of L-lactide (LA) at room temperature. Under these conditions, 94% of the monomer was converted in just 6 s to generate isotactic poly(L-lactide) ($M_{n,GPC}$ = 20.6 kDa, molecular weight distribution $Đ$ = M_w/M_n = 1.06; Table 1, entry 3). The high tacticity of poly(L-lactide) samples prepared with this approach was confirmed by ^{1}H homonuclear decoupled NMR spectros-

Scheme 1[a]
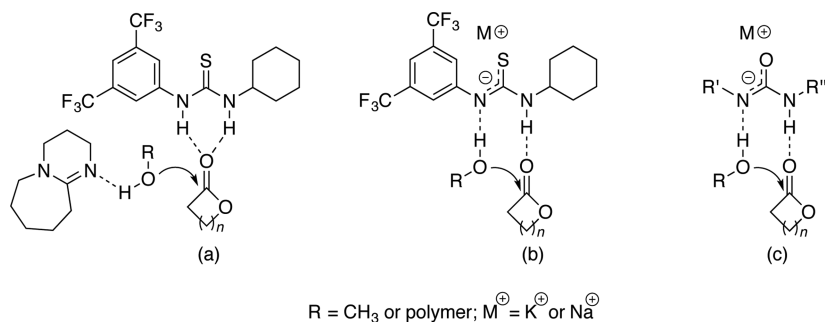
R = CH$_3$ or polymer; M$^{\oplus}$ = K$^{\oplus}$ or Na$^{\oplus}$

[a](a) Catalysis with thiourea (TU)/DBU. (b) Catalysis with thiourea anions. (c) Catalysis with urea anions.
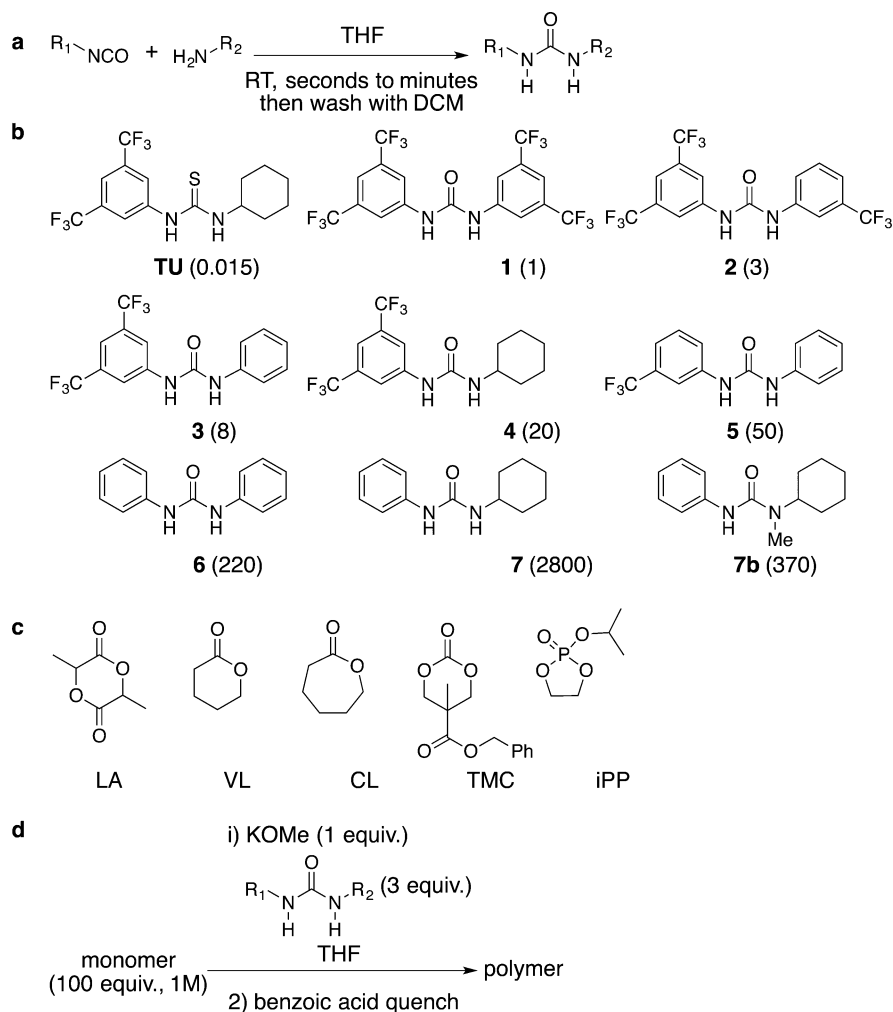
Scheme 2[a]

[a](a) Synthesis of ureas (excluding **7b**). (b) Thiourea (TU) and ureas used for ROP (in parentheses are the relative k_{obs} for the polymerization of CL with KOMe normalized with respect to urea **1**). (c) Monomers polymerized. (d) Typical reaction conditions for ROP.

copy and differential scanning calorimetry (T_m = 171 °C; Figures S1 and S2 in the Supporting Information). Analysis of a lower molecular weight sample prepared under analogous conditions by MALDI-TOF mass spectrometry shows a single series of ions separated by m/z 144, revealing minimal transesterification of the polymer backbone (Figure 1). In contrast, the anionic polymerization of L-lactide with KOMe alone, under comparable conditions, was almost 200 times slower than in the presence of KOMe/urea **1**, and yielded poly(LA) with a broad molecular weight distribution (Đ = 2.22; Table 1, entry 1). Moreover, the polymerization with KOMe alone[45,46] results in epimerization of lactide and a corresponding decrease in tacticity and melting points for the resulting polymer.[44] The combination of urea and KOMe in THF generates a catalyst/initiator solution that is homogeneous, leading to simultaneous initiation of polymer chains and fast kinetics, and is less basic, minimizing lactide epimerization. This hypothesis is supported by ^{1}H NMR studies, which reveal that

Table 1. Ring-Opening Polymerization with KOMe in the Presence and Absence of Ureas/TU[a]

entry	monomer	base/initiator	urea/TU	time (s)	conv (%)[b]	k_{obs} (min^{-1})	$M_{n,GPC}$ (kDa)[c]	Đ
1	L-LA	KOMe		1200	86	0.14 ± 0.05	23.0	2.22
2		KOMe	TU	90	89	1.05 ± 0.05	24.5	1.07
3		KOMe	1	6	94	26.8 ± 1.5	20.6	1.06
4[d]		KH (0.1%)/PyOH	2	5	89	25.0 ± 1.6	20.0	1.10
5	δ-VL	KOMe		360	88	0.265 ± 0.109	39.5	2.23
6		KOMe	1	630	58	$0.0825 \pm 1 \times 10^{-4}$		
7		KOMe	6	9	90	23.7 ± 0.1	15.3	1.06
8[e]		KOMe	7	1	85	>110	15.1	1.09
9	ε-CL	KOMe		90	91	1.16 ± 0.60	39.8	3.52
10		KOMe	1	720	5	$0.00385 \pm 7 \times 10^{-5}$		
11		KOMe	4	1840	90	0.074 ± 0.002	19.0	1.09
12		KOMe	5	360	67	0.183 ± 0.003		
13		KH/PyOH	5	315	58	0.146 ± 0.001		
14		KOMe	7	12	89	10.8 ± 0.1	17.9	1.14
15[f]	TMC-Bn	KOMe	4	5	86	24.1 ± 1.3	17.7	1.14
16	iPP	KOMe	6	10	90	24.9 ± 0.1	7.8	1.05

[a]Unless otherwise specified, [KOMe]:[urea] or **TU**]$_0$:[monomer]$_0$ = 1:3:100 and [monomer]$_0$ = 1 M in THF at room temperature (reactions quenched with benzoic acid). [b]Conversion determined by NMR. [c]Polystyrene standard calibrated $M_{n,GPC}$. [d][KH]$_0$:[PyOH]$_0$:[**2**]$_0$:[monomer]$_0$ = 1:10:3:1000, catalyst (urea anion) loading = 0.1 mol %. [e][KOMe]$_0$:[**7**]$_0$:[monomer]$_0$ = 1:5:100. [f][TMC-Bn]$_0$ = 0.5 M.

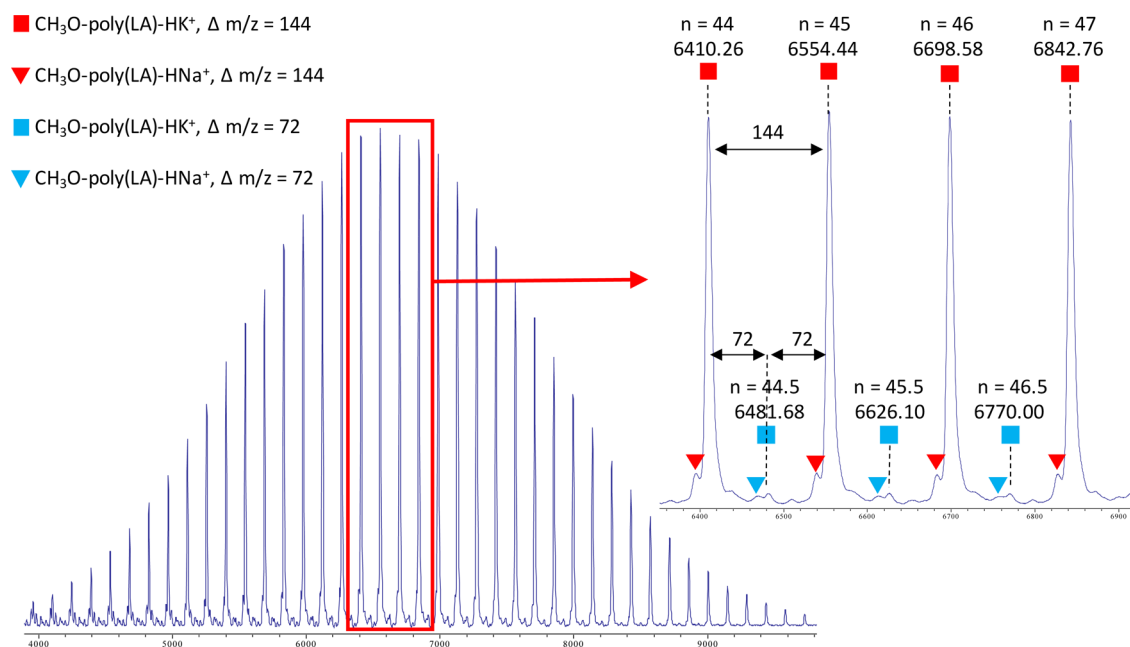**Figure 1.** MALDI-TOF of a poly(L-lactide) sample (88% conv., M_n = 12.6 kDa, Đ = 1.06) prepared with [KOMe]:[**1**]:[LA] = 1:3:50.

the treatment of urea **5** with KOMe generates a urea anion H-bonded to MeOH (Figure S3 in Supporting Information).

The KOMe/urea **1** catalyst system, despite being the slowest in the urea anion series (see relative rates in Scheme 2b), is 25 times more active than the recently reported[44] thiourea anions (KOMe/TU, Table 1, entry 2) for the polymerization of LA in THF, while still maintaining the high degree of control. Faster rates were also observed for the neutral ureas[47] with the DBU cocatalyst: both urea **4** and urea **1**, when combined with DBU, exhibited faster rates for the polymerization of δ-valerolactone in THF than TU (Table S1 in the Supporting Information).

The ring-opening polymerizations with urea anions can be carried out either by combining KOMe with urea and then introducing monomer, or alternatively, by first reacting urea with KH, and subsequently initiating the polymerization from a primary alcohol (Figure S4 in the Supporting Information). For

example, polymerization of LA with a combination of KH (low catalyst loading: 0.1 mol % vs LA), PyOH (1-pyrenebutanol), and urea **2** reached 89% conversion in 5 s (Table 1, entry 4).

The high catalytic activity and selectivity extends to the polymerization of other cyclic monomers, such as δ-valerolactone (VL), ε-caprolactone (CL), a cyclic carbonate (benzyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate, TMC-Bn) and a cyclic phosphoester (2-isopropoxy-2-oxo-1,3,2-dioxaphospholane, iPP) (Scheme 2c and Table 1). The activity of urea anions can be tuned to these monomers' different reactivities. For example, the polymerization of VL with KOMe/**7** reaches 85% conversion in 1 s to yield poly(VL) (Đ = 1.09; Table 1, entry 8), and the polymerization of CL reaches 89% conversion in only 12 s to generate poly(CL) (Đ = 1.14, Table 1, entry 14). The relative activities of the different urea anions for the polymerization of CL reveal that the most
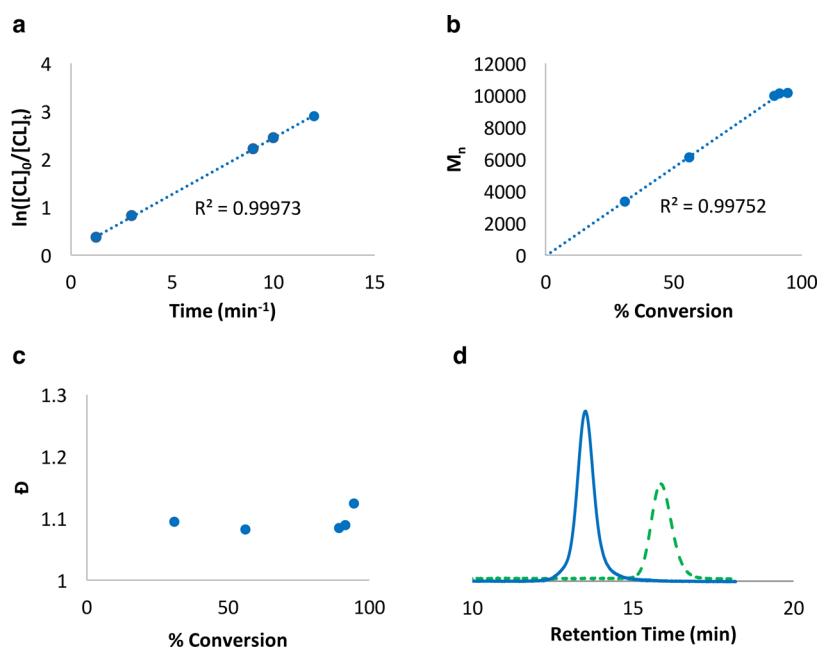
Figure 2. For (a)−(c), $[KH]_0 = 0.01$ M, $[ROH]_0 = 0.02$ M, $[5]_0 = 0.03$ M and $[CL]_0 = 1$ M (DP50). (a) Kinetic Plot of $\ln([CL]_0/[CL]_t)$ vs time. (b) Evolution of M_n vs conversion. (M_n determined GPC vs polystyrene in THF.) (c) Evolution of molecular weight distribution $Đ$ vs conversion of ε-caprolactone. (d) Block copolymer synthesis (chain extension): GPC traces of poly(VL$_{43}$) (dashed line, 9.8k Da, $Đ = 1.06$) and its subsequent poly(VL$_{43}$)-b-poly(LA$_{200}$) block copolymer (solid line, 57k Da, $Đ = 1.10$).
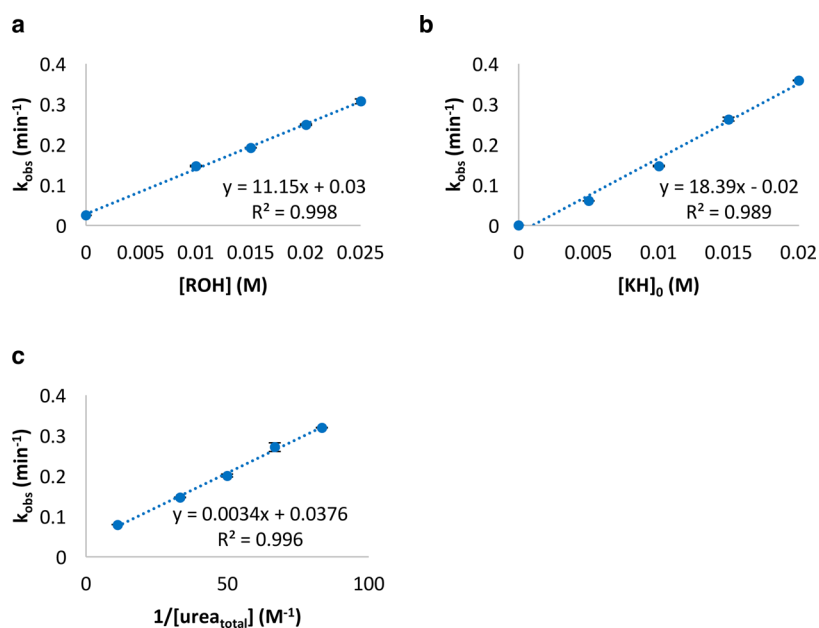

Figure 3. Rate Law: plots of k_{obs} against (a) [ROH], (b) $[KH]_0$, and (c) $1/[urea_{total}]$. Reaction conditions were [ROH] = 0.01 M, $[KH]_0 = 0.01$ M, $[5]_0 = 0.03$ M, $[CL]_0 = 1$ M, unless the reaction component was the variable.

active urea anion, derived from urea 7, is approximately 2,800 times more active than the one derived from urea 1 (Scheme 2b and Table 1, entry 10 and 14). These catalysts are more active than other organic catalysts[16,19,44,47,48] and are faster than or competitive with even the most active metal catalysts,[48−58] while maintaining the high levels of selectivity observed for the thiourea/amine type catalysts.

To probe the polymerization behavior, we investigated the ring-opening polymerization of CL with a mixture of KH/5/1-pyrenebutanol in THF. This combination yields polymerization rates that can be conveniently monitored, in contrast to the

polymerizations of LA, which are too fast to monitor easily even with the slowest urea in the series. As shown in Figure 2, the polymerization of CL with PyOH/KH/5 exhibits the characteristic of a living polymerization, exhibiting first-order kinetics in CL (Figure 2a) and a linear increase in molecular weight (M_n) with conversion (Figure 2b), while the molecular weight distribution remains low up to high conversion (Figure 2c).

Similar behavior is observed for the polymerizations carried out with the entire family of ureas (Figure S5 in the Supporting Information), indicating that the rate of polymerization is

Scheme 3. Proposed Mechanism for Urea Anion Catalyzed Ring-Opening Polymerization of ε-Caprolactone
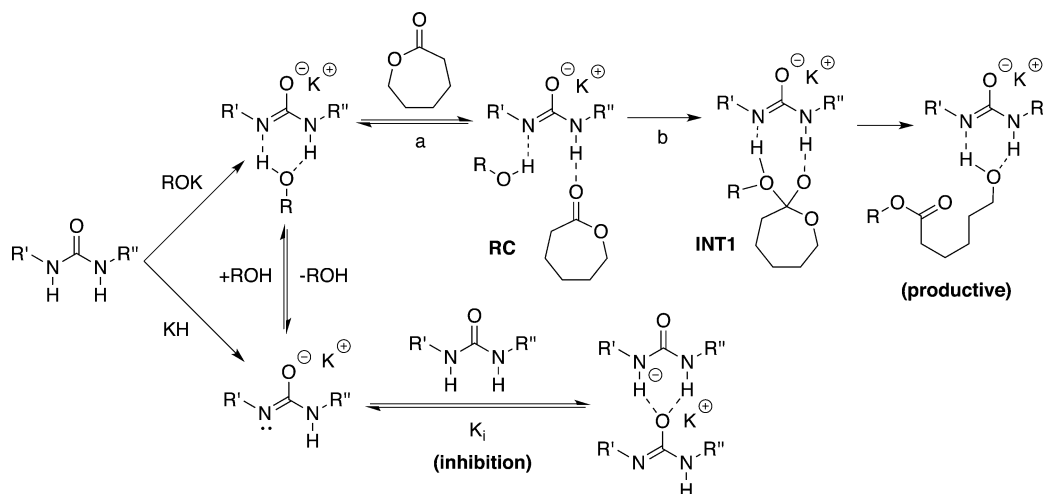
considerably faster than other competitive reactions, such as the catalytic transesterification of the polymer backbone.[41] Further evidence for its living behavior is demonstrated by the close correspondence of the observed number-average molecular weights (M_n) with the initial monomer/initiator ratio ([M]$_0$/[I]$_0$) and conversion (Table S2 and Figure S7 in the Supporting Information), as well as the synthesis of a well-defined poly(VL)-*b*-poly(LA) block copolymer by sequential introduction of VL and LA to the initiator/catalyst generated from KOMe/urea **1** (Figure 2d and Figure S8 in the Supporting Information).

The kinetics for the polymerization of CL with a PyOH initiator, KH and urea **5** reveal that the rate is first order in monomer concentration [CL] (Figure 2a), first order in alcohol concentration [ROH] (Figure 3a), first order in base concentration [KH]$_0$ (Figure 3b), and inverse first order in the total concentration of ureas species [urea$_{total}$] ([KH]$_0$ ≤ [urea$_{total}$] Figure 3c), consistent with the rate law:

$$\frac{-d[CL]}{dt} = k_{obs}[CL] = k_p \frac{[KH]_0[ROH]}{[urea_{total}]}[CL]$$

$$([KH]_0 \leq [urea_{total}]) \qquad (1)$$

As shown in Figure 3a, the rate remains first order in [ROH] even when [ROH] > [KH]$_0$, suggesting that the alcohol can be reversibly activated by the urea anion, and that the urea anion function as a catalyst for ring-opening, even at concentrations lower than those of the propagating alcohol chain-ends [ROH] (also see Table 1, entry 4). Similarly, the rate remains first order in [KH]$_0$ when [KH]$_0$ > [ROH] (Figure 3b), consistent with the reversible activation of the propagating alcohol by the urea anion. As shown in Figure 3c, an increase of total urea loading leads to a decrease in k_{obs}, suggesting that neutral urea inhibits the catalytic activity of the urea anion. We note, however, that for some of the more reactive urea anions, the additions of excess neutral ureas improves the solubilities of the initiator/urea anion mixtures. Therefore, a ratio of [urea$_{total}$]:[urea anion] = 3:1 was adopted to ensure good solubilities for the entire family of ureas studied.

On the basis of the kinetic data, the mechanism in Scheme 3 for the ring-opening polymerization of CL is proposed. Reaction of a neutral urea with potassium alkoxide or KH generates a urea anion that can reversibly activate the alcohol

initiator or polymer chain-end by H-bonding. The decrease in rate observed with excess urea can be attributed to the reversible formation of dimers (or oligomers)[59,60] of the urea anion with neutral urea, which are proposed to be inactive for polymerization. The productive ring-opening step is proposed to be facilitated by the bifunctional activation of the alcohol through H-bonding to the anionic portion of the urea anion and of the lactone through H-bonding to the N−H of the urea anion in intermediate RC. Nucleophilic attack by the H-bond activated alcohol leads to ring-opening and regeneration of an alcohol/urea anion adduct.

The facile synthesis of a broad array of ureas enabled us to carry out investigations on the rates of polymerization as a function of urea substituents. Displayed in Figure 4 is the linear
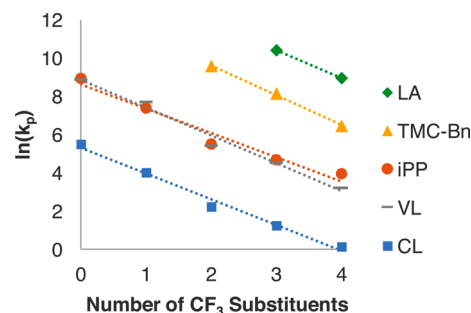

Figure 4. Plot of ln(k_p) vs the number of CF$_3$ groups on diaryl ureas. Left to right: ureas containing zero (urea **6**), one (urea **4**), two (urea **3**), three (urea **2**), or four (urea **1**) CF$_3$ substituents. All k_p shown are the average from two reaction runs (see Table S3 in Supporting Information for k_{obs}). The relative reactivities (K_p) of the monomers (LA:TMC-Bn:iPP:VL:CL) are 6200:390:38:24:1 (calculated using k_p in reactions with urea **1** and urea **2**).

free energy relationship between the observed rate constants (k_p, eq 1) for polymerization and the number of CF$_3$ substituents on the diaryl ureas, specifically those containing zero (urea **6**), one (urea **4**), two (urea **3**), three (urea **2**), or four (urea **1**) CF$_3$ substituents. As shown in Figure 4, there is a clear negative linear correlation observed between ln(k_p) and the number of CF$_3$ substituents on the diaryl ureas, and this trend is consistent for all the monomers studied. Schreiner has observed a linear decrease in pK_a with the number of CF$_3$ substituents attached to the aromatic rings of diaryl ureas and

thioureas in DMSO.[61,62] If this trend were to hold true for the ureas in THF, this would indicate a correlation between the rate of polymerization and the pK_a of the neutral ureas; that is, less acidic ureas (more basic urea anions) correlate to faster rates.

This reactivity trend suggests that the nucleophilic activation of the alcohol through H-bonding to the anionic urea plays a key role in influencing the rate. More basic urea anions (derived from less acidic ureas) are more effective at activating the H-bonded alcohol toward nucleophilic attack, leading to faster rates for the formation of the tetrahedral intermediate (INT1, Scheme 3). Nevertheless, the role of the remaining N–H in the urea anion appears important, as evidenced by the poor selectivity exhibited by the methylated urea **7b** in the polymerization of CL with KOMe, resulting in a bimodal molecular weight distribution for the polymer (Figure S9 in the Supporting Information). **7b** also exhibited reaction rate 7.6 times slower than its nonmethylated counterpart **7**.

The high polymerization rates and selectivities for ring-opening relative to transesterification are characteristic features of these urea anion catalysts. To address the origin of the high selectivity for monomer ring-opening relative to that for polymer transesterification, the relative rates of transesterification of δ-valerolactone and ethyl acetate (a model for the open chain esters of the polymer chain) with 1-pyrenebutanol using the anion of urea **1** were measured. Analysis of the initial rates revealed that the ring-opening of VL (k_{obs} = 9.8 min^{-1}) was significantly faster than transesterification of ethyl acetate (k_{obs} = 1.5 × 10^{-3} min^{-1}). These relative rates provide clear kinetic evidence that the urea anions exhibit high selectivities for ring-opening of lactones relative to transesterification of open chain esters. Nevertheless, at high conversion when the concentration of the lactone monomer is very low,[41] transesterification of the polymer chains will occur, as evidenced by the broadening of the molecular weight distributions at high conversions (Figures S4–S6 in the Supporting Information).

The origin of this high selectivity is not fully understood. We previously proposed[24,44] that the selectivity for ring-opening of thiourea/amine and thiourea anion catalysts could be partially rationalized by the preferential binding of the *s-cis* lactones to the thioureas or thiourea anions. However, due to solubility limitations and high reactivities of the urea anions, we were unable to measure the binding constants of lactones and ethyl acetate to the urea anions. Further computational studies are in progress, as we hypothesize that both the reversible binding of carbonyls (Scheme 3, step a) as well as the formation of the key tetrahedral intermediates (Scheme 3, step b, INT1) may have lower barriers for lactones than open chain esters.

The bifunctional mechanism proposed in Scheme 3 represents a new motif[44] for catalysis by ureas and thioureas, which are typically considered as H-bond donors.[17,31,42,43,47,61] While ureas and thioureas are widely utilized as H-bond activators for a variety of organic substrates,[42,43,63] they have also been investigated extensively as anion receptors[43,64–66] and in some cases deprotonations of the urea/thiourea have been observed,[66,67] depending on their pK_a. Our results suggest that this latter behavior can be exploited to generate efficient ring-opening polymerization catalysts in which the urea anions act as bifunctional catalysts to activate both the propagating alcohol and the monomer. This mechanism is reminiscent of that proposed[24,25,30,34,68] for the ring-opening polymerization by the guanidine TBD (1,3,5-triazabicyclo[4.4.0]dec-5-ene, Scheme 4), another versatile organic catalyst for ring-opening polymer-

Scheme 4. Proposed Bifunctional Mechanisms for the Guanidine TBD and Urea Anions
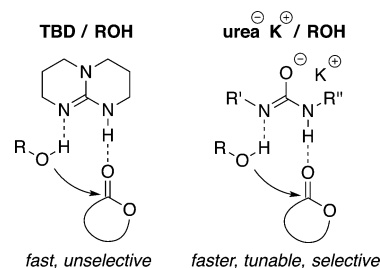
ization. An additional advantage of the approach reported here is that the activities of the urea anions (or thiourea anions[44]) can be tuned by the introduction of different substituents on the ureas, whereas the reactivity of TBD is considerably more difficult to modulate.

CONCLUSION

In summary, urea anions constitute a versatile class of readily accessible bifunctional catalysts for ring-opening polymerizations. Depending on the substituents on the urea anions, the activities of these catalysts span 3 orders of magnitude and can be readily matched to the reactivity of different classes of monomers. With the urea anions, polymerization of several common monomers reach high conversion in just seconds with excellent control. Kinetics studies reveal that the urea anions function as catalysts, and can mediate polymerization at catalyst concentrations lower than that of propagating chain ends. The operational simplicity of the urea anions, coupled with their high activities and selectivities, illustrate the potential of this class of catalysts both for ring-opening polymerization and other reactions that require the simultaneous activation of nucleophiles and electrophiles.

METHODS

For general experimental procedures and characterizations, please see the Supporting Information.

Polymerization of L-LA (Table 1, Entry 3). In a N$_2$-filled glovebox, 72 mg of L-LA (0.5 mmol) was dissolved in 0.25 mL of THF in a 4 mL vial containing a micro stir bar. A stock solution containing 1.0 mg of KOMe (0.015 mmol) and 21.8 mg of **1** (0.045 mmol) in 0.6 mL of THF was prepared in a separate vial. Then 0.2 mL of the stock solution containing the initiator and the catalyst was added to the L-LA solution. At 6 s, the reaction was quenched by the addition of 0.3 mL of THF containing about 10 mg of benzoic acid. The reaction mixture was taken out of the glovebox, and the solvent was removed. Analysis: 94% conversion by NMR, M_n (vs PS) = 20.6 kDa, Đ = 1.06. Poly(L-LA): ^{1}H NMR (CDCl$_3$): δ 5.15 (1H, q), 1.57 (3H, d).

Polymerization of VL (Table 1, Entry 7). In a N$_2$-filled glovebox, 50 mg of VL (0.5 mmol) was dissolved in 0.25 mL of THF in a 4 mL vial containing a micro stir bar. A stock solution containing 3.5 mg of KOMe (0.05 mmol) and 31.8 mg of **6** (0.015 mmol) in 2 mL of THF was prepared in a separate vial. Then 0.2 mL of the stock solution containing the initiator and the catalyst was added to the VL solution. An aliquot of the reaction was removed and at 9 s was added to approximately 10 mg of benzoic acid to be quenched. The aliquot was taken out of the glovebox, and the solvent was removed. Analysis: 90% conversion by NMR, M_n (vs PS) = 15.3 kDa, Đ = 1.06. Poly(VL): ^{1}H NMR (CDCl$_3$): δ 4.08 (2H, t), 2.34 (2H, t), 1.67 (4H, m).

Polymerization of CL (Table 1, Entry 14). In a N$_2$-filled glovebox, 57 mg of CL (0.5 mmol) was dissolved in 0.25 mL of THF in a 4 mL vial containing a micro stir bar. A stock solution containing 1.8 mg of KOMe (0.025 mmol) and 16.4 mg of 7 (0.075 mmol) in 1

mL of THF was prepared in a separate vial. Then 0.2 mL of the stock solution containing the initiator and the catalyst was added to the CL solution. An aliquot of the reaction was removed and at 12 s was added to approximately 10 mg of benzoic acid to be quenched. The aliquot was taken out of the glovebox, and the solvent was removed. Analysis: 89% conversion by NMR, M_n (vs PS) = 17.9 kDa, Đ = 1.14. Poly(CL): ^{1}H NMR (CDCl$_3$): δ 4.05 (2H, t), 2.30 (2H, t), 1.64 (4H, m), 1.37 (2H, m).

Polymerization of TMC-Bn (Table 1, Entry 15). In a N$_2$-filled glovebox, 125 mg of TMC-Bn (0.5 mmol) was dissolved in 0.7 mL of THF in a 4 mL vial containing a micro stir bar. A stock solution containing 1.8 mg of KOMe (0.025 mmol) and 26.1 mg of **4** (0.075 mmol) in 1 mL of THF was prepared in a separate vial. Then 0.2 mL of the stock solution containing the initiator and the catalyst was added to the TMC-Bn solution. An aliquot of the reaction was removed and at 5 s was added to about 10 mg of benzoic acid to be quenched. The aliquot was taken out of the glovebox, and the solvent was removed. Analysis: 86% conversion by NMR, M_n (vs PS) = 17.7 kDa, Đ = 1.14. Poly(TMC): ^{1}H NMR (CDCl$_3$): δ 1.19 (3H, s), 4.24 (4H, m), 5.09 (2H, s), 7.26 (5H, m).

Polymerization of iPP (Table 1, Entry 16). In a N$_2$-filled glovebox, 83 mg of iPP (0.5 mmol) was dissolved in 0.25 mL of THF in a 4 mL vial containing a micro stir bar. A stock solution containing 1.8 mg of KOMe (0.025 mmol) and 15.9 mg of **6** (0.075 mmol) in 1 mL of THF was prepared in a separate vial. Then 0.2 mL of the stock solution containing the initiator and the catalyst was added to the iPP solution. An aliquot of the reaction was removed and at 10 s was added to approximately 10 mg of benzoic acid to be quenched. The aliquot was taken out of the glovebox, and the solvent was removed. Analysis: 90% conversion by NMR, M_n (vs PS) = 7.8 kDa, Đ = 1.05. Poly(iPP): ^{1}H NMR (CDCl$_3$): δ 1.33 (6H, d), 4.23 (4H, m), 4.69 (1H, m).

Poly(VL)-*b*-poly(LA) Block Copolymer Synthesis (Figure 2d). In a N$_2$-filled glovebox, 50 mg of VL (0.5 mmol) was dissolved in 0.15 mL of THF in a 4 mL vial containing a micro stir bar. A stock solution containing 3.5 mg of KOMe (0.05 mmol) and 48.4 mg of urea **1** (0.1 mmol) in 1.5 mL of THF was prepared in a separate vial. Then 0.3 mL of the stock solution containing the initiator and the catalyst was added to the VL solution. An aliquot of the reaction was removed and at 7 min 55 s was added to approximately 10 mg of benzoic acid to be quenched, while simultaneously 0.25 mL of the reaction was transferred to a LA solution containing 144 mg of LA in 0.65 mL of THF. An aliquot from the new reaction mixture was subsequently removed after 26 s and added to approximately 10 mg of benzoic acid to be quenched. The aliquots were taken out of the glovebox, and the solvent was removed. Analysis: poly(VL) aliquot at 7 min 55 s: 86% conversion by NMR, M_n (vs PS) = 9.8 kDa, Đ = 1.06. Poly(VL)-*b*-poly(LA) aliquot at (7 min 55 s + 26 s): 86% conversion for VL and 94% conversion for LA by NMR, M_n (vs PS) = 57 kDa, Đ = 1.10. Poly(VL)-*b*-poly(LA): ^{1}H NMR (CDCl$_3$): δ 5.15 (9.3H, q), 4.08 (2H, t), 2.34 (2H, t), 1.67 (4H, m), 1.57 (28.5H, d).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11864.

Supplemental figures and information regarding materials used, instrumentation, synthetic procedures, characterization data, and kinetic data (PDF)

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Notes

The authors declare no competing financial interest.

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