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Ultrafast and Controlled Ring-Opening Polymerization with Sterically Hindered Strong Bases

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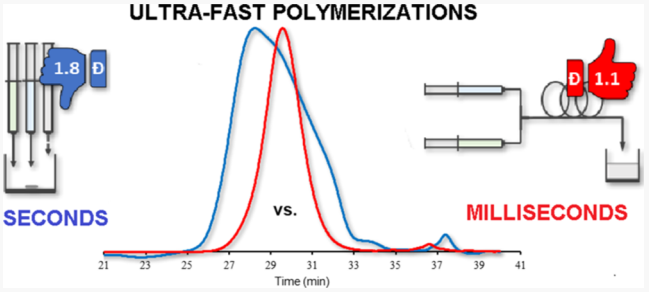
ABSTRACT: The controlled anionic ring-opening polymerization of lactones and siloxanes is carried out in continuous-flow reactors. Anionic ring-opening polymerization of cyclic esters with strong, soluble bases such as potassium *tert*-butoxide (KO*t*Bu) is typically performed as batch reactions, leading to broad dispersity and poor control over the molecular weight (M_n) mainly because of transesterification reactions. Although reactions with strong bases give rise to "uncontrolled" polymerizations, a variety of transition metal-based and organocatalysts have been developed with the goal of reliably controlling the dispersity and M_n. Herein, we show that the rapid mixing and short residence times accessible with a continuous-flow apparatus can enable the controlled polymerization of low-reactivity monomers such as δ-valerolactone and ε-caprolactone on millisecond time scales using a base [such as KO*t*Bu or potassium bis(trimethylsilyl)amide (KHMDS)] in conjunction with a primary alcohol. These reactions exhibit characteristics capable of producing narrow dispersity with predictable molecular weights and can rapidly generate well-defined block copolymers with residence times below 0.1 s.



INTRODUCTION

Alkali metal alkoxide and amide bases have been routinely applied as initiators in the ring-opening polymerization (ROP) of epoxides,[1−4] thiolactones,[5,6] cyclic esters,[7−17] and cyclic carbonates.[18−20] These conditions typically involved either long reaction times[10,12] or lead to uncontrolled reactions.[9] For example, Sipos, et al.[12] demonstrated that polymerization of L-lactide (L-LA) using potassium *tert*-butoxide (KO*t*Bu) is characterized by poor initiator efficiency, leading to broad dispersity ($Đ$ > 1.4) and long reaction times to reach high conversion (83% at 22 h). Kricheldorf and Boettcher[15] demonstrated the use of a *n*-butyllithium/primary alcohol initiator system for L-LA ROP but observed intermolecular and intramolecular transesterification reactions (backbiting) and epimerization, leading to the formation of cyclic oligomers and loss of tacticity, similar to that observed with KO*t*Bu-initiated ROP.[7,8,14] Sterically hindered amide bases have also been studied as initiators for ROP. Lithium diisopropyl amide was used for the ROP of L-LA and D-lactide monomers, but these reactions also exhibited poor control over the dispersity ($Đ$ > 1.5 above 70% conversion).[21] When added along with a sulfonamide nucleophile, potassium bis(trimethylsilyl)amide (KHMDS) has been demonstrated for the living ROP of *N*-sulfonylaziridines, leading to low dispersity polymers.[22] However, the rate of initiation compared to the rate of propagation for aziridines is greater than that of lactones and carbonates, making them better substrates for ROP with strong bases. Together, these studies demonstrate that under batch reaction conditions, the high activity of alkoxide and amide initiators cannot be utilized without sacrificing control over selectivity and dispersity. Consequently, the development of ROP catalysts for cyclic esters has largely focused on more selective catalytic systems based on metal coordination complexes[23,24] or organocatalysts.[25−27]

Given the poor initiator efficiency of sterically hindered alkoxide and amide bases and our recent work with urea and thiourea anion ROP catalysts,[28−30] we hypothesized that controlled polymerization with a highly active base such as KO*t*Bu and KHMDS and a primary alcohol as the initiator could be achieved using continuous-flow processes. Continuous-flow processes provide a means to consistently control reaction times,[29,31] even on the millisecond time scale, so reactions can be quenched before transesterification side reactions broaden the dispersity after reaching the target conversion. We anticipated that this level of control may be particularly important for the more active alkoxide bases relative to the (thio)urea anion catalysts, where hydrogen

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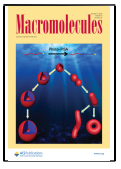

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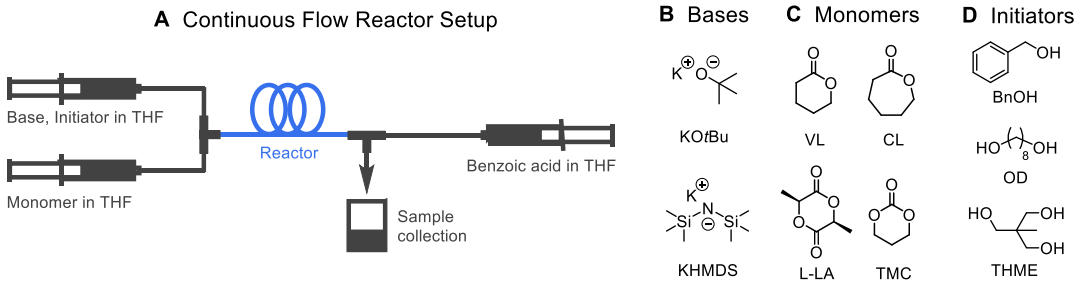

Figure 1. Continuous-flow homopolymerization reactions.

Table 1. Example Polymerizations with KO*t*Bu and KHMDS in Continuous Flow[a]

entry	monomer	base	DP_{Target}	τ (ms)	conversion (%)	DP_{NMR}	$M_{n,GPC}$ (kDa)	$Đ$
1	VL	KO*t*Bu	50	8.7	87	45	5.5	1.13
2		KHMDS		4.1	83	42	4.6	1.13
3[b]	CL	KO*t*Bu	25	55	90	23	3.9	1.12
4[c]		KHMDS		12	83	21	3.3	1.14
5		KO*t*Bu	50	24	91	46	7.6	1.18
6		KHMDS		12	84	44	6.5	1.14
7[d]		KO*t*Bu	80	14	91	77	12	1.24
8[e]			100	10	86	91	14	1.25
9	L-LA	KO*t*Bu	50	38	86	47	8.5	1.13
10		KHMDS			86	47	8.3	1.13
11[c]	TMC	KHMDS	25	55	92	25	2.9	1.11

[a]Conversion and the resulting polymer DP were determined by NMR (see the Supporting Information). $Đ = M_w/M_n$. $M_{n,GPC}$ was determined by GPC in THF, calibrated with PS standards. Unless otherwise specified, reaction conditions are as follows: $[base]_0 = 0.005$ M, $[BnOH]_0 = 0.02$ M, and $[monomer]_0 = 1$ M in THF at RT. [b]$[BnOH]_0 = 0.04$ M. [c]$[monomer]_0 = 0.5$ M. [d]$[BnOH]_0 = 0.0125$ M. [e]$[BnOH]_0 = 0.01$ M.

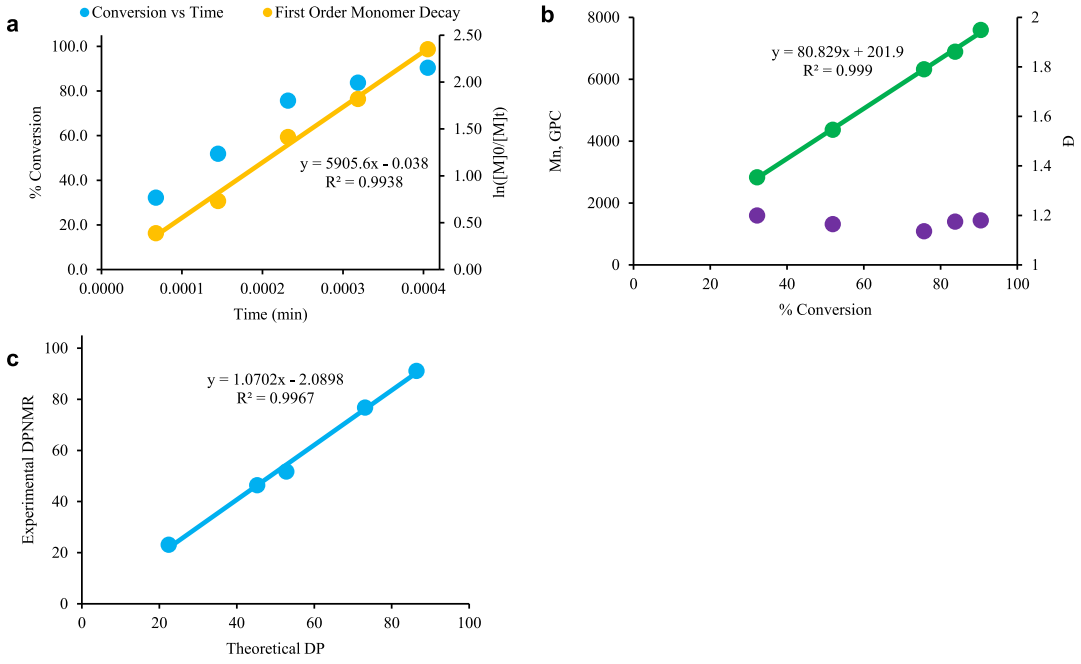

Figure 2. Living behavior of KO*t*Bu-catalyzed polymerization of CL in continuous flow $[KOtBu]_0 = 0.005$ M, $[CL]_0 = 1$ M, $[BnOH]_0 = 0.02$ M: (a) time conversion and 1st order monomer decay plot, (b) $M_{n,GPC}$ and molecular weight distribution ($Đ$) vs conversion plot, and (c) experimental vs theoretical DP varying $[BnOH]_0$.

bonding effects play a role in selectivity for chain elongation over transesterification.[26,28,30] Manipulation of flow rates allows for faster and more efficient mixing than can be achieved in batch reactors,[32,33] which is important to ensure that the relative rate of initiation, propagation, and chain transfer is controlled to achieve narrow dispersities. In the presence of primary alcohols, the stronger basicity of KO*t*Bu and KHMDS would ensure the formation of primary alkoxides as the initiating species as *t*BuOH has a higher pK_a than primary alcohols ($pK_{a\ DMSO,tBuOH}$[34,35] > $pK_{a\ DMSO,EtOH}$[34,35] > $pK_{a\ DMSO,BnOH}$). Furthermore, the steric bulk of KO*t*Bu and KHMDS renders the rate of initiation slow relative to the rate

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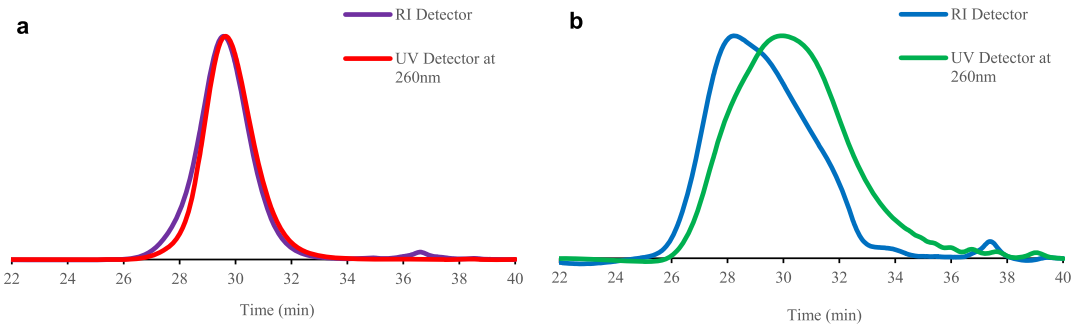

Figure 3. UV/RI GPC trace overlays for P(VL), target DP 50, synthesized under (a) continuous-flow conditions (Table S1, entry 1, $Đ$ = 1.19, 0.0087 s) and (b) batch conditions (Table S1, entry 2, $Đ$ = 1.59, 2 s).

of propagation of the primary alkoxide of the growing polymer chain, affording much larger M_n than what would be expected from the feed ratios. Hence, a controlled ROP with high end group fidelity should be attainable using sterically hindered amide and alkoxide bases with primary alcohols in continuous flow.

RESULTS AND DISCUSSION

The use of KO*t*Bu and KHMDS as bases for the primary alcohol-initiated ROP of lactones was investigated with several model monomers. To avoid any potential initiation from KO*t*Bu or KHMDS, we employed a 3-fold excess of a primary alcohol relative to the base to ensure full conversion to the corresponding primary alkoxide. Using a continuous-flow reactor (Figure 1), the polymerization of δ-valerolactone (VL) (1 M) initiated by benzyl alcohol (BnOH, 20 mM) and KO*t*Bu (5 mM) reached 87% conversion and the expected degree of polymerization (DP) in 8.7 ms with a narrow dispersity of the resulting polymer (Table 1, entry 1; $Đ$ = 1.13). The same reaction employing KHMDS/BnOH reached 83% conversion in just 4.1 ms (Table 1, entry 2; $Đ$ = 1.13). The polymerization of ε-caprolactone (CL) also reached high conversions with short residence times and good control (Table 1, entries 3−8). Although KO*t*Bu/BnOH- and KHMDS/BnOH-initiated polymerizations are not as well-controlled as those employing urea anions, particularly for higher DP polymerizations in which smaller initiator/base ratios are used, their activities for the polymerization of CL are 2 orders of magnitude higher than reactions employing urea anions. Interestingly, the polymerizations of L-LA and TMC (monomers that are much more active when polymerized using urea anions; Table 1, entries 9−11) exhibited slower kinetics than the polymerizations of CL and VL. The origin of these differences is not clear but likely a consequence of the different turnover-limiting steps; calculations[26] and kinetic studies[28] suggest that the rate-determining step for ROP by (thio)urea anions is the nucleophilic attack by the activated alcohol;[26,28] for alkoxides, it is likely that ring opening of the tetrahedral intermediate is rate limiting, analogous to that calculated for ROP by nucleophilic N-heterocyclic carbenes.[36,37] In addition to monofunctional primary alcohols, polyols such as 1,8-octanediol (OD) and 1,1,1-tris(hydroxymethyl)ethane (THME) can be used as initiators for polymerization with no loss of rate of conversion or control over molecular weight (entry 1, Table S1 and entries 1−3 Table S2, Supporting Information).

The living behavior of KO*t*Bu/ROH-initiated ROP of CL was further investigated. Under continuous-flow conditions, CL ROP exhibited (1) first-order rate dependence on monomer concentration (Figure 2a), (2) a linear increase in molecular weight with conversion, (3) and narrow dispersity up to high conversions (Figure 2b). Furthermore, the measured DP as determined by ^{1}H NMR end group analysis matched closely with theoretical DP as calculated by the initiator-to-monomer ratio (Figure 2c). Upon substitution of the alkoxide counterion to Li^+, the polymerization still exhibits typical living behaviors, albeit at slower rates (Figure S1). In parallel, polymerizations by MHMDS bases (M = K^+, Na^+, and Li^+) with a primary alcohol also exhibited living polymerization behaviors, with the rate of reaction dependent on the counterion identity (Figures S2−S4). Counterion effects in anionic ROP are well-known;[38] the decrease in rates (K^+ > Na^+ > Li^+, Figures S2−S4) correlates with the alkoxide-M^+ association constants.[39]

Although the results in Table 1 and Figure 2 demonstrate highly controlled and rapid polymerizations using KO*t*Bu and KHMDS in continuous flow, it is important to ensure that no loss of the initiator end groups occurred. To test this, we utilized 1-pyrenemethanol as a UV-active initiator for the ROP of VL with KO*t*Bu in continuous flow (see the Supporting Information). End group analysis via ^{1}H NMR spectroscopy of the resulting material demonstrated that the experimental DP values match well with theoretical DP values calculated by the monomer-to-primary alcohol ratio (47 vs 50, Figure S5). Additionally, the near-exact overlay of gel permeation chromatography (GPC) traces from UV and RI detectors suggests minimal loss of the 1-pyrenemethanol end groups under continuous-flow polymerization conditions (Figure 3a). Consistent with these data, thermal analysis of the homopolymers shows T_m thermal transitions close to the literature values[40] (Figure S6).

In contrast, polymerization in batch using the same conditions afforded broadly dispersed materials following short reaction times (Table S4). Samples from batch polymerizations show a poor match in overlays of UV and RI GPC traces, consistent with transesterification side reactions causing the loss or scrambling of initiator end groups (Figure 3b). Additionally, end group analysis by ^{1}H NMR shows a larger experimental DP of 67 compared to the theoretical DP of 50, suggesting loss of control over M_n (Figure S13). To further investigate the extent of potential competitive initiation from *t*BuOH or KO*t*Bu as compared to the primary alkoxide, we performed matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) on a representative P(VL) sample prepared in continuous flow using KO*t*Bu and 4-methylbenzyl

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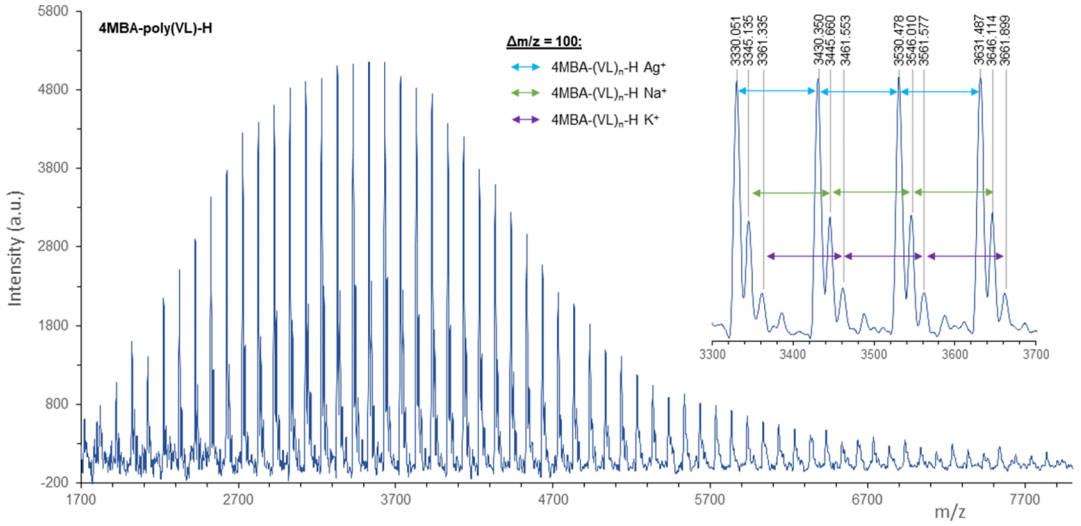

Figure 4. MALDI-TOF-MS of a P(VL) sample initiated from 4MBA and KO*t*Bu using a ratio of 4MBA/KO*t*Bu/VL = 4:1:50 (85% conversion, M_n = 5.1 kDa, $Đ$ = 1.17).

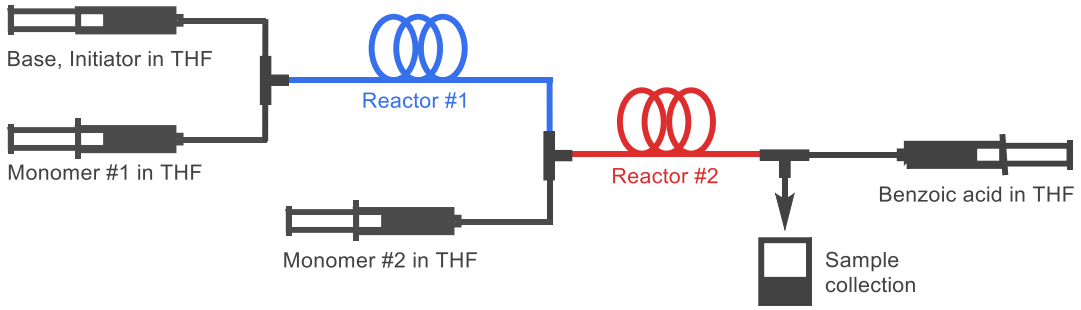

Figure 5. Continuous-flow block copolymerization reactions.

Table 2. Block Copolymerizations with KO*t*Bu and KHMDS in Continuous Flow[a]

			block 1				block 2					
entry	initiator	base	monomer	DP_{Target}	τ (ms)	conversion (%)	monomer	DP_{Target}	τ (ms)	conversion (%)	$M_{n,GPC}$ (kDa)	$Đ$
1	BnOH	KO*t*Bu	VL	50	8.7	85	L-LA	25	88	83	9	1.11
2	BnOH	KO*t*Bu	VL	50	8.7	86	L-LA	50	88	94	13	1.13
3	BnOH	KHMDS	CL	50	12	91	L-LA	50	88	87	15	1.13
4	BnOH	KHMDS	CL	25	12	87	TMC	25	51	97	5.5	1.13
5	OD	KO*t*Bu	VL	25	10	90	L-LA	20	10	86	12	1.13
6	THME	KO*t*Bu	VL	25	20	88	L-LA	20	20	93	17	1.12

[a]See the Supporting Information for further reaction details.

alcohol (4MBA). The mass spectrum (Figure 4) shows three subsets of signals for Ag^+, Na^+, and K^+ adducts of P(VL) chains bearing 4-methylbenzyloxy and hydrogen as end groups. Signals corresponding to *tert*-butyl end groups were absent, suggesting a sole initiation by the alkoxide derived from 4MBA. Additionally, no indication for the presence of macrocycles lacking end groups could be determined from the spectrum. This latter result is consistent with the absence of intramolecular transesterification (backbiting). Taken together, these experiments suggest that reactions employing primary alcohols and hindered bases have all the properties of a living polymerization (control over M_n and dispersity, facile block copolymer synthesis, etc.) and can reliably be achieved using continuous-flow processes with reproducibly short reaction times.

To probe additional utility of polymerization initiation by the combination of the hindered base and primary alcohols for lactones and cyclic carbonates, we prepared block copolymers via sequential addition of monomers (Figure 5, Table 2). The GPC traces of $P(VL)_{50}$-*b*-$P(L\text{-}LA)_{25}$ and $P(VL)_{50}$-*b*-$P(L\text{-}LA)_{50}$ prepared using the combination of KO*t*Bu and BnOH are cleanly shifted compared to the homopolymer $P(VL)_{50}$ (Figure 6a). Similarly, well-defined block copolymers $P(CL)_{50}$-*b*-$P(L\text{-}LA)_{50}$ (Figure 6b) and $P(CL)_{25}$-*b*-$P(TMC)_{25}$ (Figure 6c) were synthesized using KHMDS/BnOH as the initiating system. Starting from multifunctional initiators, $P(LA)_{25}$-*b*-$P(VL)_{25}$-OD-$P(VL)_{25}$-*b*-$(LA)_{25}$ and $[P(LA)_{25}$-*bl*-$P(VL)_{25}]_3$-THME were synthesized using a similar reactor design (see the Supporting Information). These polymers demonstrate the versatility of the method for various architectures while maintaining excellent control over dispersity ($Đ$ < 1.15)

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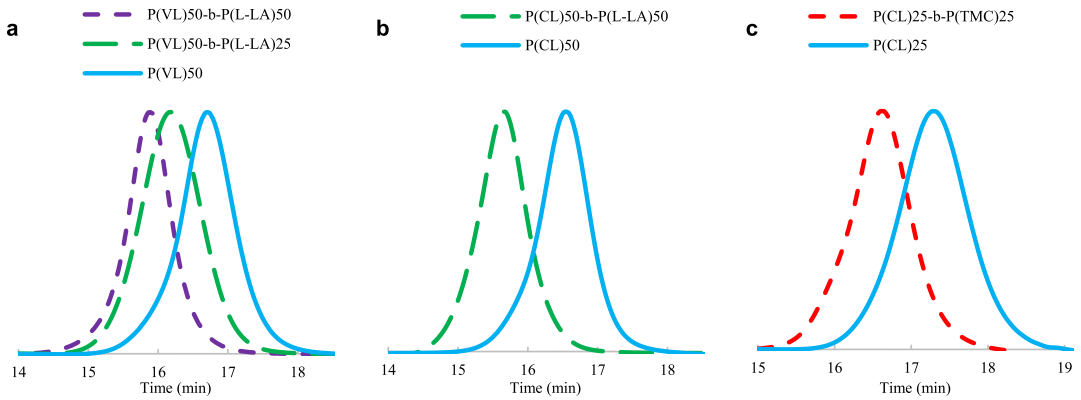

Figure 6. Selected GPC chromatograph overlays for homo- and block copolymers initiated by KO*t*Bu or KHMDS in the presence of a primary alkoxide. (a) P(VL)$_n$-*b*-P(L-LA)$_m$ block copolymers, (b) P(CL)$_n$-*b*-P(L-LA)$_m$ block copolymers, and (c) P(CL)$_n$-P(TMC)$_m$ block copolymers. See the Supporting Information for experimental procedures and additional GPC overlays.

(Tables S1 and S2, Figures S7 and S8). Finally, differential scanning calorimetry (DSC) thermograms of the block copolymers show sharp T_m transitions for each of the blocks (Figure S9).

Given the similar reactivities of the monomer employed, changing the nature of the initiator or its counterion[29] was not needed under the employed conditions (Tables 2, S3, Figures S10–S12). The flow syntheses of these block copolymers were rapid, with residence times less than or equal to 0.1 s.

We next investigated the application of these polymerization conditions to less-reactive cyclic monomers. In this context, we selected the carbosiloxane 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentance (TMOSC). ROPs were successfully performed in flow with reaction times from 100 ms to 1.0 s, with conversions and molecular weights (M_n) gradually increasing from 4.3 to 32.2% and 2200 to 7000 g/mol, respectively (Table 3, Figure 7a). Just as with the cyclic ester monomers,

Table 3. Conversion and GPC Results for ROPs of TMOSC in Flow and in Batch at Various Residence Times[a]

entry	residence time (s)	conversion[b] (%)	M_n[c] (g/mol)	M_w[c] (g/mol)	$Đ$[c]
1	0.1	4.3	2200	2400	1.12
2	0.2	7.8	2750	3150	1.16
3	0.3	11.3	3250	3900	1.18
4	0.5	17.9	4900	5300	1.09
5	1.0	32.2	7000	7750	1.10
6[d]	3.0	98.9	12,000	13,200	1.10
7[d]	15.0	99.6	12,100	13,400	1.11

[a]Conditions: DP_{Target} = 50, [TMOSC] = 0.49 M, KO*t*Bu/4MBA/TMOSC = 1:4:200, THF, rt. [b]By ^{1}H NMR from the crude sample: monomer methylene signal (0.66 ppm) vs polymer methylene signal (0.30 ppm). [c]By GPC in THF relative to calibration with PS standards. [d]Batch polymerization.

the ROP of TMOSC by KO*t*Bu with 4MBA exhibited characteristics of a living polymerization: (1) first-order rate dependence on the concentration of TMOSC (Figure 7b), (2) a linear increase in M_n with conversion (Figure 7c), (3) and a dispersity of below 1.20 (decreasing below 1.10 with increasing conversion). Continuous-flow polymerization at higher monomer concentrations led to similar results (Table S5, Figure S14). To investigate longer reaction times (3–15 s), batch polymerizations were performed, leading to complete monomer conversion and PTMOSCs with narrow dispersity ($Đ \leq 1.11$) (Table S6, Figures S15 and S16). These promising results suggest that these conditions should also be applicable to other less-reactive cyclic monomers such as hexamethylcyclotrisiloxane and related monomers while offering good control of the dispersity and significantly reduced reaction times compared to those in the existing literature.[41−44]

CONCLUSIONS

In summary, we report the use of sterically hindered bases in combination with a primary alcohol for the controlled ROP of lactones, carbonates, and carbosiloxanes in a continuous-flow reactor. Remarkably, traditionally low-activity monomers such as CL and VL were controllably polymerized in milliseconds. These reactions exhibited living polymerization behaviors with a strong dependence on the reaction rate based on the identity of the counterion. With reaction rates that are orders of magnitude higher than the fastest rates reported with the use of urea anions, these reaction conditions greatly expand the breadth of materials accessible.

EXPERIMENTAL SECTION

Materials. L-LA (Purac, 99%) was used as received. VL and CL were dried by storing the monomers with activated molecular sieves. Trimethylene carbonate (TMC) was purified by dissolving in dichloromethane and filtration and then recrystallized by dissolution in a minimal amount of dichloromethane, adding Et_2O until the cloud point, and then cooling the mixture to −20 °C in a freezer. TMC crystals were collected via filtration and washing with additional cold Et_2O. Benzoic acid (BA) (≥99.5%), benzyl alcohol (BnOH) (anhydrous, 99.8%), 1-pyrenemethanol (99%), potassium *tert*-butoxide (KO*t*Bu) (min. 98%, Strem Chemicals), sodium *tert*-butoxide (NaO*t*Bu) (99.9%) and lithium *tert*-butoxide (LiO*t*Bu) (97%), potassium bis(trimethylsilyl)amide (KHMDS) (95%), sodium bis(trimethylsilyl)amide (NaHMDS) (95%), and lithium bis(trimethylsilyl)amide (97%) were purchased from Sigma-Aldrich and used as received. TMOSC was purchased from Gelest, Inc. and distilled under an inert atmosphere. 4MBA was purchased from Sigma-Aldrich and sublimed under vacuum at 60–80 °C. Tetrahydrofuran (THF, 99.9%, Fisher Scientific) was degassed with nitrogen and passed through two columns of alumina under nitrogen in a solvent purification system. The urea catalysts were prepared according to the literature methods.[28] Materials for the flow reactor, including the perfluoroalkoxy alkane (PFA) tubing (1507L—PFA Tubing Natural 1/16″ OD × 0.040″ ID; 1512L—PFA Tubing Natural 1/16″ OD × 0.020″ ID), connectors (P-249—Super Flangeless One-Piece Fitting, 1/4-28 Flat-Bottom, for 1/16″ OD;

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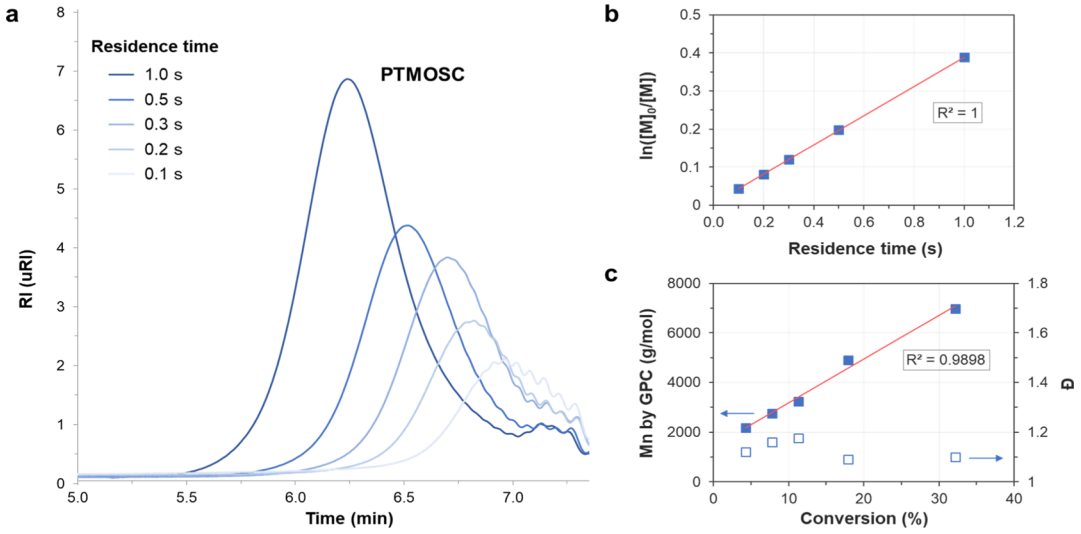

Figure 7. Results for ROP of TMOSC in continuous flow: (a) GPC results for ROP of TMOSC, (b) kinetic plot of $\ln([TMOSC]_0/[TMOSC]_t)$ vs residence time, and (c) evolution of M_n and $Đ$ vs conversion.

or P-235X—Flangeless Nut PEEK, Short, 1/4-28 Flat-Bottom, for 1/16″ OD paired with P-200X—Flangeless Ferrule Tefzel (ETFE), 1/4-28 Flat-Bottom, for 1/16″ OD), adapters (P658—Luer Adapter 1/4-28 Female to Female Luer, PEEK), and T-mixers (P-712—PEEK Low Pressure Tee Assembly 1/16″ PEEK 0.020″ through hole; P-714—PEEK Low Pressure Tee Assembly 1/16″ PEEK 0.040″ through hole) were purchased from IDEX Health & Science. NORM-JECT syringes (Luer lock) and PhD Ultra syringe pumps (70-3007, Harvard Apparatus) were used.

Instrumentation. All NMR spectra were collected at 20 °C on 300/400 MHz Varian Instruments, with chemical shifts referenced to residual solvent peaks and reported in ppm relative to tetramethylsilane. Polystyrene (PS)-calibrated molecular weights were determined using a two PLgel 10 μm mixed-B LS columns (Agilent Technologies) in series, with a DAWN 8+ multiangle laser light scattering (Wyatt Technology) detector and an Optilab T-rEX differential refractometer (Wyatt Technology).

MALDI-TOF-MS was performed using a Bruker microflex LT in the linear mode equipped with the systems' standard N_2 laser (337 nm, 150 μJ pulse energy, 3 ns pulse width). The polymer sample solution (in THF, 10 mg/mL), the matrix solution (dithranol in THF, 10 mg/mL), and the cationization agent solution (silver(I) trifluoroacetate in THF, 10 mg/mL) were combined in a ratio of 10:10:1 and deposited on the target. To calibrate the system, protein calibration standard 1 by Bruker Daltonics was previously deposited on the target on three different locations in accordance with Bruker Daltonics' preparation guidelines.

GPC measurements were performed on a Waters advanced polymer chromatography equipped with a Waters 410 differential refractometer. The set of columns consisted of three Waters ACQUITY APCTM AQ (pore sizes: 450/200/125, dp: 2.5 μm). THF was used as the eluent at a flow rate of 0.75 mL/min and at 25 °C. The advanced polymer chromatograph system was calibrated with PS standards and elution time shifts checked with a 13 kDa PS standard injected with each sample set.

DSC measurements were performed on a TA Instruments Q2000, using a heating rate of 10 °C/min.

Typical Flow Polymerization Setup. In general, the reaction solutions were prepared in an N_2-filled glovebox and transferred to syringes. The syringes are then connected to the reactor outside of the glovebox. Flow rates per inlet should be high to ensure optimal mixing (we recommend a flow rate of at least 20 mL/min per inlet for tubing with inner diameters of 0.5 or 1 mm). The T-mixers for combining the initiator and monomer solutions had an inner diameter of 0.5 mm, and the T-mixers for introducing the BA solution had an inner diameter of 0.5 or 1 mm. The crude samples can be purified by precipitation into methanol followed by centrifugation, but the time in methanol should be minimized to avoid significant transesterification.

Representative Polymerization Procedures. *Synthesis of P(VL)$_{50}$ in Flow with KOtBu.* In an N_2-filled glovebox, a 2 M solution of VL was prepared by dissolving 1400 mg of VL (14 mmol) in 5.6 mL of THF. An initiator stock solution was prepared by dissolving 11.2 mg of KO*t*Bu (0.1 mmol) and 92.9 mg of 1-pyrenemethanol (0.4 mmol) in 9.9 mL of THF. A total of 6 mL of each solution was transferred to two 10 mL syringes. A third syringe containing 6 mL of BA in THF was prepared.

Outside of the glovebox, the syringes containing the monomer solution and initiator solutions were connected to the flow reactor. The syringe pump was set to a flow rate of 35 mL/min for each inlet. The initiator and monomer solutions were combined via a T-mixer (0.5 mm inner diameter). The tubing (PFA, 0.5 mm inner diameter) for polymerization was 5 cm long, corresponding to a residence time of 0.0087 s. A second T-mixer (1 mm inner diameter) combined the BA solution with the reaction mixture to quench the reaction.

Conversion was determined by integrating the peaks at 4.35 ppm (monomer) and 4.08 ppm (polymer) (NMR in $CDCl_3$). DP_{NMR} was determined by the integrating the peak at 5.85 ppm (benzyl end group) and the peak at 4.08 ppm (polymer).

Conversion = 88%. DP_{NMR} = 47. $M_{n,GPC}$ = 8.0 kDa. $Đ$ = 1.19.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (m, 10H), 5.85 (s, 2H), 4.08 (t, J = 5.4 Hz, 95H), 2.34 (t, J = 6.8 Hz, 98H), 1.65 (m, 195H).

Synthesis of P(VL)$_{50}$ in Batch with KOtBu. In an N_2-filled glovebox, a 2 M solution of VL was prepared by dissolving 1400 mg of VL (14 mmol) in 5.6 mL of THF. An initiator stock solution was prepared by dissolving 11.2 mg of KO*t*Bu (0.1 mmol) and 92.9 mg of 1-pyrenemethanol (0.4 mmol) in 9.9 mL of THF. A total of 700 μL of monomer solution was dispensed into a 4 mL glass vial with a stir bar. With rapid stirring, 700 μL of initiator solution was added to the vial. After 2 s, 300 μL of BA solution (25 mg/mL in THF) was added to quench the reaction.

Conversion was determined by integrating the peaks at 4.35 ppm (monomer) and 4.08 ppm (polymer) (NMR in $CDCl_3$). DP_{NMR} was determined by the integrating the peak at 5.85 ppm (benzyl end group) and the peak at 4.08 ppm (polymer).

Conversion = 90%. DP_{NMR} = 67. $M_{n,GPC}$ = 8.5 kDa. $Đ$ = 1.59.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (m, 10H), 5.85 (s, 2H), 4.09 (m, 133H), 2.36 (m, 137H), 1.69 (m, 269H).

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c01571.

Experimental details, NMR spectra, DSC thermograms, GPC chromatograms, and kinetic data (PDF)

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Notes

The authors declare no competing financial interest.

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