N-Heterocyclic Carbenes for the Organocatalytic Ring-Opening Polymerization of ε-Caprolactone

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ABSTRACT: We report the synthesis of poly(ε-caprolactone) utilizing N-heterocyclic carbene (NHC) organocatalysts. Sterically unencumbered NHCs were found to be highly effective for the living ring-opening polymerization of ε-caprolactone under mild conditions. The NHCs were able to produce poly(ε-caprolactone)s with controlled molecular weights, low polydispersities, and well-defined end groups derived from the alcohol initiator. Star-shaped poly(ε-caprolactone)s with three and four arms were prepared using NHC organocatalysts and characterized by ^{1}H NMR and GPC.

Introduction

Poly(ε-caprolactone) (PCL) is a versatile biocompatible aliphatic polyester. Because of its biocompatibility, biodegradability, high permeability, and compatibility with biopolymers, it is utilized in a variety of biomedical and pharmaceutical applications such as medical sutures and drug-delivery vehicles.[1−5] Poly(ε-caprolactone) is a tough, crystalline thermoplastic material with a melting point (T_m) of ca. 61 °C and glass transition temperature (T_g) of ca. −60 °C.[1,4] Hydrolytic or enzymatic degradation of PCL generates 6-hydroxyhexanoic acid, a metabolite in the citric acid cycle.

A common synthetic route to PCL and other aliphatic polyesters is the ring-opening polymerization (ROP) of cyclic esters using metal−alkoxide initiators and catalysts derived from alkali, transition, and rare-earth/lanthanides metals.[5−19] These metal catalysts allow for the preparation of polyesters with controlled molecular weight, molecular weight distribution, and microstructure. While impressive advances have been made with the development of a wide variety of metal complexes,[5−18] all are proposed to involve the insertion of the monomer into a metal−alkoxide bond as a key step. Enzymatic[20−22] and organic catalysts[3,23−36] provide an alternate approach for ring-opening polymerization reactions as these catalysts exhibit different mechanisms of enchainment with complementary selectivities that enable the construction of novel architectures.[35,37]

As part of our efforts to develop new classes of organocatalysts for ring-opening polymerization reactions,[29,33,34,38−40] we have shown that N-heterocyclic carbenes (NHCs)[41−44] are versatile ring-opening polymerization catalysts for the controlled synthesis of block and graft copolymers, polysiloxanes,[45,46] and polycarbonates[47] as well as novel macromolecular architectures, such as cyclic[35] and H-shaped polylactides.[37] Previous studies have shown that the rates and selectivities for ring-opening depend sensitively on both the nature of the carbene and the monomer. For example, while the carbene IMes **1** is very active for the ring-opening polymerization of lactide, it is much less active for the ROP of ε-caprolactone (ε-CL).[30−32,39,48,49] In this article, we report more detailed studies on the polymerization of ε-caprolactone with carbene catalysts and demonstrate that the carbenes **3** and **4** are efficient catalysts for the generation of poly(ε-caprolactone) of defined molecular weight and polydispersity (PDI).

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Experimental Section

General Considerations and Materials. All polymerizations were performed in a glovebox under nitrogen. Tetrahydrofuran (THF) was distilled from sodium/benzophenone and degassed by three freeze−pump−thaw cycles. Benzyl alcohol and anhydrous ethylene glycol were purchased from Aldrich and distilled twice from calcium hydride prior to use. 1-Pyrenebutanol was purchased from Aldrich and recrystallized twice from dry toluene prior to use. Pentaerythritol was purchased from Aldrich and sublimed prior to use. Carbon disulfide was purchased from Acros and distilled from calcium hydride. ε-Caprolactone was purchased from Acros and distilled twice from calcium hydride. Deuterated chloroform ($CDCl_3$) was purchased from Aldrich and Cambridge Isotope Laboratories, Inc., and used as received. Deuterated tetrahydrofuran (d_8-THF) was purchased from Cambridge Isotopes, dried over sodium/benzophenone, and degassed by three freeze−pump−thaw cycles. 1,2,4,5-Tetramethylbenzene (durene) was purchased from Aldrich, recrystallized from THF, and sublimed. 1,3-Bis(2,4,6-(trimethylphenyl)imidazol-2-ylidene (**1**),[42] 1,3-bis(2,6-diisolpropylphenyl)imidazol-2-ylidene (**2**),[50] 1,3,4,5-tetramethylimidazol-2-ylidene (**3**),[51] and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**4**)[51] were prepared according to literature procedures.

Characterization. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded at room temperature on 400 and 500 MHz (and 600 MHz where indicated) Varian spectrometers with shifts reported in parts per million downfield from tetramethylsilane and referenced to the residual solvent peak. The percent conversion is determined by ^{1}H NMR spectroscopy comparing the integration of the monomer and poly(ε-caprolactone) C(═O)OCH_2 signals from an aliquot of the crude polymer mixture. Gel permeation chromatography (GPC) was performed in THF on a Waters chromatograph using four 5 μm Waters columns (300 mm × 7.7 mm) connected in series with increasing pore size (10, 100, 1000, 10^5, 10^6 Å). A Waters 410 differential refractometer and 996 photodiode array detector were employed for data in Table 1 and Figure 3. For all other data, a Viscotek S3580 refractive index detector and Viscotek GPCmax autosampler were employed. The GPC system was calibrated using monodisperse polystyrene standards.

Polymerization of ε-Caprolactone with Benzyl Alcohol. A solution of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**4**) (0.0024 g, 0.013 mmol) in THF (1.3 mL) was added to a stirred solution of benzyl alcohol (0.0029 g, 0.027 mmol) and ε-caprolactone (0.620 g, 5.4 mmol) in THF (4.1 mL). The reaction was stirred at room temperature. After predetermined time intervals, a small aliquot (<0.1 mL) of the reaction is quenched with a few drops of carbon disulfide which turns the reaction aliquot red-orange, characteristic of the formation of a zwitterionic carbon disulfide−imidazolyidene adduct.[52,53] The reaction aliquot is analyzed by ^{1}H NMR spectros-

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Table 1. Ring-Opening Polymerization of ε-CL in the Presence of Benzyl Alcohol (BnOH)[a]

entry	catalyst	[M] (M)	M/I	I/C	time	conversion[b] (%)	M_n[c,d] (g/mol)	PDI[c]
1	**1**	0.5	100	2	24 h	0		
2	**2**	0.5	100	2	24 h	0		
3	**1**	2	50	2	24 h	10		
4	**3**	1	100	2	2 min	18	2320 (1040)[d]	1.11
5	**3**	1	100	2	20 min	63	8630 (3880)[d]	1.14
6	**4**	0.9	200	1	10 min	21	5990 (2700)[d]	1.19
7	**4**	0.9	200	2	10 min	12	3430 (1540)[d]	1.2
8	**4**	0.9	200	2	93 min	47	16900 (7610)[d]	1.16
9	**4**	0.9	200	2	5 h	77	32300 (14500)[d]	1.3

[a] Initiated by BnOH in THF at room temperature. [b] Determined by ^{1}H NMR (see Experimental Section). [c] Determined by GPC versus polystyrene standards (PDI = M_w/M_n). [d] Corrected M_n using a correction factor of 0.45.[58]

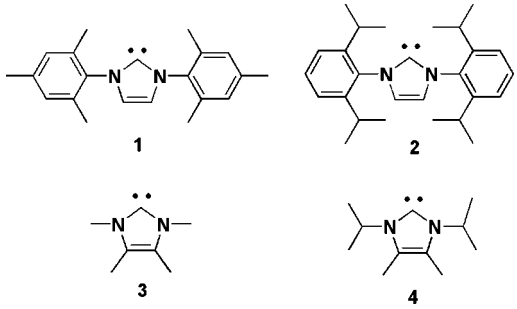


Figure 1. Structure of catalysts employed for the polymerization of ε-CL.

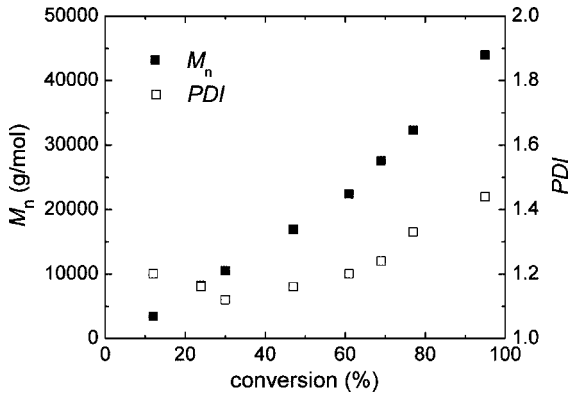
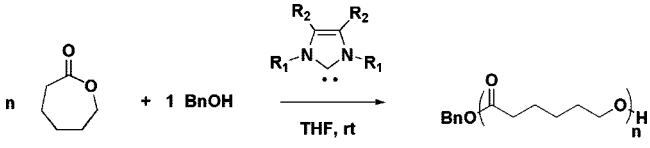


Figure 2. Polymerization of ε-CL initiated by benzyl alcohol using carbene**4** as the catalyst in THF at room temperature. Reaction conditions: $[\varepsilon\text{-CL}]_0 = 0.9$ M, $[\varepsilon\text{-CL}]_0/[I]_0 = 200$, $[I]_0/[C]_0 = 2$. M_n (■) and PDI (□) determined relative to polystyrene standards.

Scheme 1. General Synthesis for the ROP of ε-CL Using NHCs



copy to determine the percent conversion. Molecular weight and polydispersity data in Table 1 and Figure 3 were measured using reaction aliquots directly after quenching with carbon disulfide without further purification.

Polymerization of ε-Caprolactone with 1-Pyrenebutanol. A solution of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**4**) (0.0012 g, 0.0067 mmol) in THF (0.43 mL) was added to a stirred solution of 1-pyrenebutanol (0.0076 g, 0.0227 mmol) and ε-caprolactone (0.158 g, 1.38 mmol) in THF (0.79 mL). The reaction mixture was stirred for 40 min at room temperature. The reaction was terminated by addition of a few drops of carbon disulfide, turning the reaction mixture red-orange, characteristic of the formation of a zwitterionic carbon disulfide−imidazolylidene adduct.[52,53] A small aliquot is taken from the reaction mixture for conversion determination by

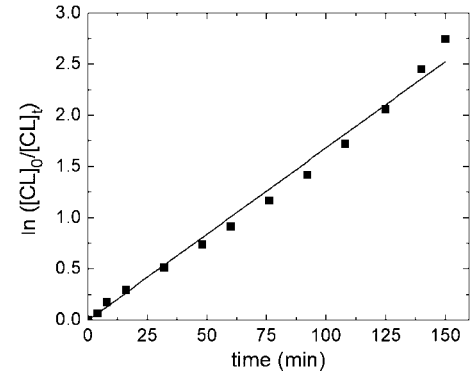


Figure 3. Plot of $\ln([\varepsilon\text{-CL}]_0/[\varepsilon\text{-CL}]_t)$ vs time for $[\varepsilon\text{-CL}]_0 = 0.25$ M and a targeted DP of 50.

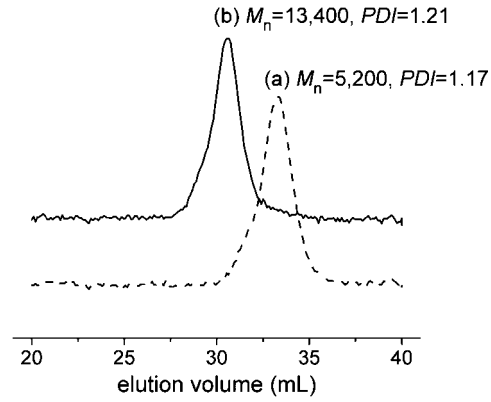


Figure 4. GPC traces of PCLs obtained by polymerization using **4** as the catalyst before (a) and after (b) chain extension experiment (results vs polystyrene standards).

^{1}H NMR spectroscopy. The crude polymer is isolated by removal of solvent. To purify, the crude polymer is dissolved in minimal dichloromethane, precipitated from methanol, and dried under vacuum to a constant weight. Percent conversion: 87%. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.85−8.27 (m, 9H, pyrene aromatic), 4.14 (t, 2H, pyrene−$CH_2CH_2CH_2CH_2OC(=O)$), 4.06 (t, 88H $C(=O)OCH_2$ PCL, 3.65 (m, 2H, −CH_2OH), 3.38 (t, 2H, pyrene−$CH_2CH_2CH_2CH_2OC(=O)$), 2.30 (t, 91H, $CH_2C(=O)O$ PCL backbone), 1.95 (m, 2H, pyrene−$CH_2CH_2CH_2CH_2OC(=O)$), 1.82 (m, 2H, pyrene−$CH_2CH_2CH_2CH_2OC(=O)$), 1.64 (m, 181H, $CH_2CH_2CH_2$ PCL), 1.38 ppm (m, 92H, $CH_2CH_2CH_2$ PCL). DP-(NMR) = 44; M_n(GPC vs PS standards) = 11 000, $M_w/M_n = 1.20$.

Polymerization of ε-Caprolactone with Multifunctional Alcohol. Polymerization is similar to the procedure described for ε-caprolactone polymerization with 1-pyrenebutanol. Polymerization with ethylene glycol initiator (**5**) for $[\varepsilon\text{-CL}]_0/[\text{initiator}] = 100$, >95% conversion in 60 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.27 (s, −OCH_2CH_2O−), 4.06 (t, −$CH_2O(C=O)$−, 3.65 (q, −CH_2OH), 2.31 (t, −$OCH(=O)CH_2$−), 1.65 (m, −$CH_2CH_2CH_2$−), 1.38 ppm

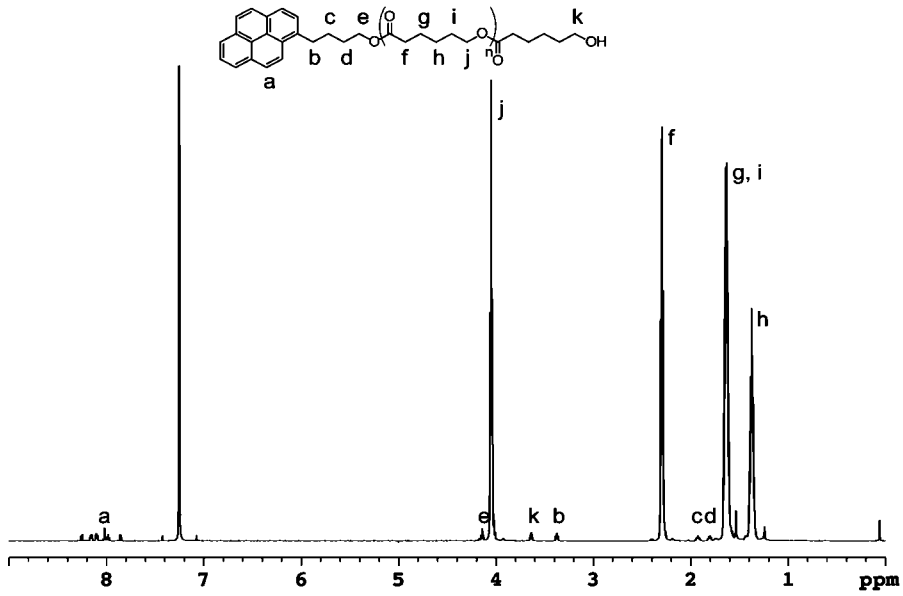


Figure 5. ^{1}H NMR spectrum of PCL in $CDCl_3$ as obtained by the ROP of ε-CL initiated from 1-pyrenebutanol in the presence of carbene **4** at room temperature.

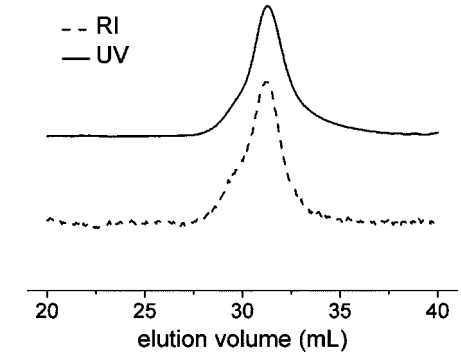


Figure 6. GPC traces of 1-pyrenebutanol initiated ROP of ε-CL using UV and RI detectors.

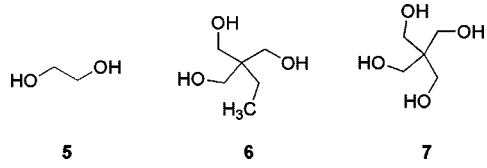


Figure 7. Multifunctional alcohol initiators for the polymerization of ε-CL.

(m, $-CH_2CH_2CH_2-$). DP(NMR) = 91; M_n(GPC vs PS standards) = 28 800, M_w/M_n = 1.37.

Polymerization with initiator (**6**) [ε-CL]$_0$/[initiator] = 100, 90% conversion in 1 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.06 (t, $-CH_2O(C{=}O)-$), 4.01 (s, $CH_3CH_2C(CH_2O-)_3$), 3.67 (q, $-CH_2OH$), 2.31 (t, $-O(C{=}O)CH_2-$), 1.65 (m, $-CH_2CH_2CH_2-$), 1.38 ppm (m, $-CH_2CH_2CH_2-$). DP(NMR) = 85, M_n(GPC vs PS standards) = 28 800, M_w/M_n = 1.15.

Polymerization with initiator (**7**) [ε-CL]$_0$/[initiator] = 100, >90% conversion in 1 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.10 (m, $C(CH_2O-)_3$), 4.05(t, $-C(=O)O-CH_2-$), 3.64 (t, $-CH_2OH$), 2.30 (t, $-O(C{=}O)CH_2-$), 1.64 (m, $-CH_2CH_2CH_2-$), 1.38 ppm (m, $-CH_2CH_2CH_2-$). DP(NMR) = 104, M_n(GPC vs PS standards) = 21 500, M_w/M_n = 1.24

Kinetics (^{1}H NMR). A solution containing ε-caprolactone (0.026 g, 0.228 mmol), benzyl alcohol (0.5 mg (4.6 μmol), and 7.2 mg (54 μmol) durene in d_8-THF (0.52 mL) was prepared and transferred to a J. Young NMR tube. A ^{1}H NMR spectrum was taken to determine the [ε-CL]$_0$ relative to the internal standard durene. A solution of carbene **3** (0.3 mg, 2.4 μmol) in d_8-THF (0.37 mL) was added to the NMR tube containing the d_8-THF solution of ε-CL, benzyl alcohol, and durene. A ^{1}H NMR spectrum was taken at t = 4 min, and 10 additional spectra were taken over time until t = 150 min (71% conversion). The [ε-CL]$_t$ was determined by integration of the methylene protons $-(O(C{=}O)CH_2)-$ of ε-CL at 2.59 ppm relative to the methyl groups of durene at 2.18 ppm at time t.

Results and Discussion

Four N-heterocyclic carbenes were investigated for the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) at room temperature (Scheme 1 and Figure 1). Polymerization data are summarized in Table 1. The efficiency of the ring-opening polymerization of ε-CL is sensitive to the steric and electronic nature of the carbene.[48] The sterically encumbered carbenes **1** and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**2**) are inactive for the polymerization of ε-CL ([ε-CL]$_0$ = 0.5−2.0 M) at room temperature in THF; after 24 h no polymer was obtained under these conditions (entries 1−3, Table 1). This behavior contrasts that observed for the ring-opening polymerization of lactide; previous studies have shown carbene **1** to be highly effective catalysts for lactide polymerization.[30,39,48] In neat monomer ([ε-CL]$_0$ = 9 M), the polymerization of ε-CL can be carried out with carbene **1** for a target DP = 50, reaching >90% conversion in 30 min to yield PCL with M_n = 11 500 (vs polystyrene)[54] and M_w/M_n = 1.3.

In contrast, the more electron-rich carbenes 1,3,4,5-tetramethylimidazol-2-ylidene (**3**) and 1,3,4,5-tetramethylimidazol-2-ylidene (**4**) were highly effective catalysts for polymerization of ε-CL (Table 1).[49] Controlled polymerizations were observed for reactions with up to target DP = 200 to generate poly(ε-caprolactone) with predictable molecular weights and narrow polydispersities. For lower molecular weight polymers (target DP = 25 or 50), low catalyst/monomer ratios were necessary in order to prevent undesired transesterification and formation of cyclic oligomers, which are known to form during metal−alkoxide-initiated anionic ROP[7,55,56] and lipase-catalyzed ROP.[57]

A plot of molecular weight vs conversion for the polymerization of ε-CL initiated from benzyl alcohol for a targeted DP of 200 shows a linear correlation up to ca. 70% conversion (Figure 2). At conversions higher than 70%, the number-average

Scheme 2. Synthesis of Four-Armed Star Polymer by Polymerization of ε-CL with Pentaerythritol in the Presence of NHC Catalyst

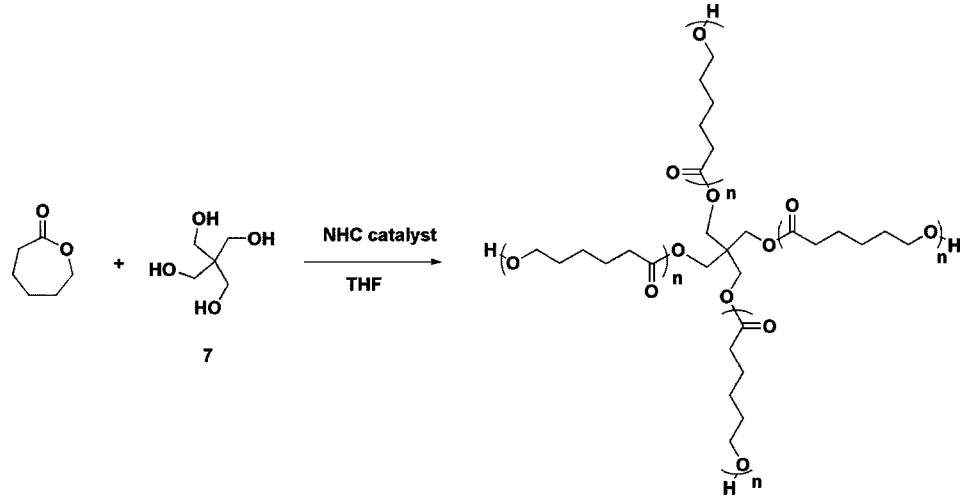
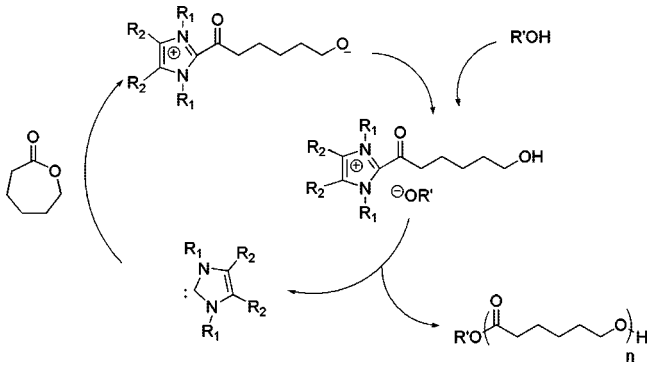


Table 2. Results of the ROP of ε-CL with Various Multifunctional Initiators at Room Temperature in THF Using Carbene 4

ROH	$[M]_0$ (M)	M/I	I/C	time (min)	conversion[a] (%)	M_n[b] (g/mol)	PDI[b]
5	1	100	2	60	95	28 800	1.37
6	0.5	100	2	100	90	28 800	1.15
7	0.5	100	2	45	90	21 500	1.24
7	0.5	100	8	45	60	14 600	1.09

[a] Determined by ^{1}H NMR. [b] Determined by GPC versus polystyrene standards.

Scheme 3. Proposed Mechanism for the NHC-Catalyzed ROP of ε-CL



molecular weights and the polydispersities increase (Table 1 and Figure 2),[59] implicating the onset of competitive transesterification reactions catalyzed by the NHC catalyst.[60−65]

To gain further insight on the polymerization mechanism, the kinetics of polymerization were studied using $[\varepsilon\text{-CL}]_0 = 0.25$ M initiated by benzyl alcohol, catalyzed by **3** in d_8-THF at room temperature. The polymerization of ε-CL with target DP = 50 and alcohol initiator/**3** = 2 was followed by ^{1}H NMR spectroscopy up to 71% conversion in the presence of durene as an internal standard. Under pseudo-first-order conditions, a plot of $\ln([\varepsilon\text{-CL}]_0/[\varepsilon\text{-CL}]_t)$ vs time is linear with time (Figure 3).[19] These data reveal a constant concentration of active species with time.

To probe the living character of this polymerization, a chain extension experiment was carried out. For this experiment polymerization of ε-CL at an initial $[\varepsilon\text{-CL}]_0/[\text{ROH}]_0 = 25$ with 5 mol % **4** was performed in THF and proceed to 80% conversion (^{1}H NMR) in 5 min to generate PCL with $M_n = 5200$ g/mol and $M_w/M_n = 1.17$. At this point, 100 equiv of ε-CL was added, and the resulting reaction mixture was quenched after 3 h with carbon disulfide to afford PCL with $M_n = 13\,400$ g/mol and $M_w/M_n = 1.21$ (Figure 4). The GPC curve completely shifted to a higher M_n, and a monomodal distribution was observed without any trace of dead polymer. This result demonstrates that the PCL generated from the ring-opening polymerization reactions mediated by carbenes retain their activities and function as efficient macromolecular initiators for further chain-growth reactions.

The initiation efficiency of the NHC-catalyzed ε-CL polymerization initiated from 1-pyrenebutanol was analyzed by ^{1}H NMR spectroscopy. A polymerization with a target DP of 50 using carbene **4** was terminated by quenching with carbon disulfide after 40 min at 87% conversion to yield a polymer with $M_n = 11\,000$ g/mol and PDI = 1.20 (vs polystyrene standards). The ^{1}H NMR spectrum of the crude reaction showed no evidence of unreacted 1-pyrenebutanol, indicating a high efficiency of initiation from the alcohol initiator. The only end groups observed in the ^{1}H NMR spectrum of the isolated polymer are the α-ester from the alcohol initiator and the ω-hydroxyl chain, indicating one initiator per alcohol chain end (Figure 5). ^{1}H NMR assignments were confirmed using two-dimensional NMR correlation techniques, ^{1}H−^{1}H COSY, and ^{1}H−^{13}C HMBC. GPC traces using the refractive index and UV detectors (410 and 350 nm, respectively), as displayed in Figure 6, show a statistical distribution of pyrene throughout the sample. Coupled with ^{1}H NMR analysis, the GPC data establish the fidelity of initiation from 1-pyrenebutanol.

To demonstrate the versatility of NHC-catalyzed ROP, several multifunctional alcohol initiators such as ethylene glycol (**5**), 1,1,1-tris(hydroxymethyl)propane (**6**), and pentaerythritol (**7**) were used to initiate polymerization of ε-CL (Figure 7).

Polymerization of ε-CL initiated from alcohol **5** forms two-arm linear PCL while initiation from alcohols **6** and **7** form three- and four-arm star-branched PCL, respectively (Scheme 2, four-arm PCL).

Star-branched polymers exhibit unique properties such as lower melt viscosities, lower crystallinity, and smaller hydrodynamic volume in solution relative to their linear analogues.[26,66,67] Among several methods to synthesize star polyesters, the use of multifunctional alcohol initiators is described as a core-first approach where the multifunctional alcohol provides the core from which the polymerization is initiated.[26] Star-shaped PCLs have been prepared from multifunctional initiators in the presence of stannous octoate,[68] $Bi(OAc)_3$,[69] or acid or base catalysts.[26,67] Table 2 summarizes the conditions and results of NHC-catalyzed polymerization of ε-CL with

various multifunctional alcohol initiators. High monomer conversion is achieved in short reaction time at room temperature for reactions with a target DP of 100 to give narrowly dispersed PCL with various branched architectures.

The proposed mechanism for the NHC-catalyzed ROP of ε-CL is through a monomer-activated pathway analogous to the proposed mechanism of NHC-catalyzed ROP of lactide and the ROP of cyclic esters with biocatalysts (Scheme 3). The NHC ring opens the ε-CL monomer to form a zwitterionic acylimidazole intermediate. The protonation of the intermediate by the alcohol initiator is followed by attack of the resulting alkoxide on the activated acyl intermediate and displacement of the NHC catalyst. The resultant hydroxyl-terminated monomer unit serves as the nucleophilic alcohol in subsequent propagation. The generated PCL bears the ester from the initiating alcohol as the α-chain end and a hydroxyl group as the ω-chain end.

Conclusion

In summary, NHCs are highly efficient organocatalysts for the living ring-opening polymerization of ε-CL. Polymerization conditions using less sterically demanding NHCs have been established to afford PCLs with controlled molecular weights and low polydispersities. High initiation efficiency and end-group fidelity were demonstrated for NHC-catalyzed ROP. Multifunctional initiators were used to generate PCLs with varying molecular architectures under mild conditions.

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