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Alcohol Adducts of *N*-Heterocyclic Carbenes: Latent Catalysts for the Thermally-Controlled Living Polymerization of Cyclic Esters

Olivier Coulembier,[†] Bas G. G. Lohmeijer,[‡] Andrew P. Dove,[‡] Russell C. Pratt,[‡] Laetitia Mespouille,[†] Darcy A. Culkin,[§] Stephanie J. Benight,[§] Philippe Dubois,*[,†] Robert M. Waymouth,*[,§] and James L. Hedrick*[,‡]

Laboratory of Polymeric and Composite Materials (LPCM), University of Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium, IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120, and Stanford University, Department of Chemistry, Stanford, California 94305

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ABSTRACT: Alcohol adducts of the *N*-heterocyclic carbene, 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2-triazol-5-ylidene (NHC), function as excellent single-component catalyst/initiators for the ring-opening polymerization of lactide and β-butyrolactone. Their reversible dissociation at elevated temperatures generates alcohol and triazolylidene carbene to provide a facile entry to polymerization of cyclic esters on demand. Under optimum conditions, adverse transesterification reactions are minimized, and importantly, upon complete consumption of monomer, a second monomer addition facilitates additional polymer growth, even after precipitation. Block copolymers were prepared by combining disparate polymerization techniques from the use of oligo-adducts and bifunctional initiators. Additionally, more complex polymer architectures were prepared from multifunctional or dendritic initiators, further demonstrating the versatility of the *N*-heterocyclic carbene platform.

Introduction

Aliphatic polyesters are an important class of biodegradable macromolecules derived from renewable resources.[1] These materials provide an attractive alternative to many petrochemical thermoplastics due to their attractive and improving cost/performance characteristics, their application as biomedical materials, and their potential to mitigate the environmental impact of discarded plastic waste in landfills. Poly(lactide) has recently been commercialized under the tradename NatureWorks.[1] Poly(hydroxyalkanoates) are another important class of biomacromolecules that are produced by a wide variety of microorganisms and used as metabolic storage materials.[2] Since poly[(*R*)-(−)-3-hydroxybutyrate] was discovered in 1926, this family of biopolymers has been significantly expanded by controlled fermentation experiments to include more than 70 different hydroxyacids.[3] From this work, a renewable and biodegradable poly(hydroxyalkanoate) copolymer, with properties comparable to those of poly(propylene), was commercialized.[4]

One of the most common synthetic routes to polyesters uses metal-containing compounds to catalyze the ring-opening polymerization (ROP) of cyclic ester monomers.[5] While these routes provide facile access to polyesters, removal of the metal contaminant bound to the chain end must be considered for application in resorbable biomaterials and microelectronics. The use of simple organic molecules as catalysts or promoters in asymmetric synthesis has provided an organocatalytic alternative to traditional organometallic reagents.[6]

The chemistry of *N*-heterocyclic carbenes (NHCs) has become a major area of research, as these compounds have been shown to be outstanding ligands for transition metals as well as potent nucleophilic organic catalysts for a wide variety of organic transformations.[7,8] In particular, the application of NHCs as catalysts for the ROP of cyclic esters has resulted in a highly active and versatile route for the metal-free living polymerization of cyclic esters.[9] We have proposed a monomer-activated mechanism in which the monomer is opened by the carbene to form an acyl imidazole zwitterion. Protonation of this zwitterion by an alcohol, followed by attack of the resultant alkoxide on the activated acyl imidazolium, generates a new chain-extended alcohol (Scheme 1), analogous to that proposed for the ROP of cyclic esters by enzymes.[10] The α-chain end of the polymer bears the ester from the initiating alcohol, and the ω-chain end is a hydroxyl group serving as the nucleophile for subsequent chain propagation.

It is worth noting that the isolation and application of NHCs is complicated by their air and moisture sensitivity. In an effort to develop more experimentally convenient procedures for the use of NHCs as catalysts, several strategies for generating these reactive nucleophiles in situ have been developed. Both unsaturated imidazolylidene and saturated imidazolinylidene carbenes can be generated by treatment of the corresponding imidazolium salts with *tert*-butoxide and used directly for the ring-opening polymerization of lactones.[9] Wanzlick, Arduengo, and others demonstrated that certain classes of NHCs undergo C−H insertion reactions with compounds containing an acidic C−H bond in high yields resulting in significantly more stable carbene precursors; these adducts often decompose upon heating.[11] We have exploited this behavior to generate saturated NHCs in situ for the ring-opening polymerization of lactones.[9b] More recently, Grubbs demonstrated that alcohol adducts of imidazolin-2-ylidenes can be used to generate the free carbene in situ to form NHC-coordinated transition metal complexes in a greatly simplified process.[12] Enders carried out analogous investigations on the methanol adduct of commercially available 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2-triazol-5-ylidene, **1**; thermolysis of this methanol adduct in vacuo removed methanol and cleanly

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* Corresponding authors. E-mail: hedrick@almaden.ibm.com (J.L.H.).

[†] Laboratory of Polymeric and Composite Materials (LPCM), University of Mons-Hainaut.

[‡] IBM Almaden Research Center.

[§] Stanford University, Department of Chemistry.

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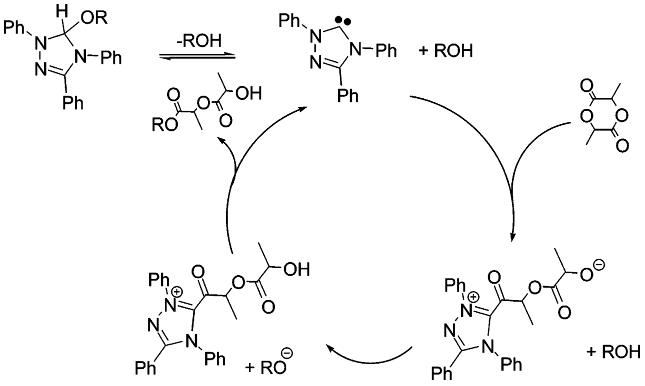
Scheme 1. Proposed Mechanism for the Polymerization of Lactide Using Triazole Carbenes



liberated the free carbene.[13] We have recently demonstrated that these alcohol adducts can be isolated and used directly as both catalysts and initiators for the ring-opening polymerization of lactones.[9e−f]

Here, we report more detailed results of our previous investigations into the living ROP of lactide using alcohol adducts of **1** and the important role of the reversible formation of alcohol adducts on the polymerization behavior of this class of NHC. A special emphasis dealing with the ROP of β-butyrolactone has also been investigated. Some aspects of this work have been previously communicated.[9f]

Results and Discussion

The ring-opening polymerization (ROP) of lactide by the unsaturated *N*-heterocyclic carbene (NHC) 1,3-dimesithylimidazol-2-ylidene (IMes) or the saturated carbene 1,3-dimesityl-imidazolin-2-ylidene (SIMes) in the presence of an alcohol initiator is generally accomplished within minutes at ambient temperature (10 min, $[\mathrm{LA}]_0 = 0.69$ M, [NHC] = 1%).[9] However, the polymerization of lactide with the commercially available 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2-triazol-5-ylidene carbene **1** was much slower at room temperature, affording less than 16% conversion after 100 hours.[9f] The attenuated reactivity of the triazole carbene **1** relative to IMes or SIMes could be due to an attenuated nucleophilicity or basicity of the triazole carbene **1** relative to the imidazolium carbenes. However, on the basis of our previous work[9f] and that of Enders,[13] we hypothesized that the reversible formation of the alcohol adducts and the higher stability of the alcohol adduct of **1** relative to that of the adduct from SIMes[9d] was responsible for this behavior. To address this latter hypothesis, we investigated the behavior of alkoxytriazoles **2** derived from the insertion of the carbene **1** into O−H bond of alcohols.

Triazolinylidene and Alkoxytriazoline: Reversible Adduct Dissociation. The dissociation of alkoxyimidazolyl-2-ylidenes has been shown to occur readily at room temperature, resulting in the generation of carbene and alcohol (Scheme 2A).[9e] In contrast, Enders had shown that the elimination of methanol from the methoxytriazole **2** only occurs at elevated temperature under vacuum (Scheme 2B).[13]

Scheme 2. Elimination of Methanol from Methoxyimidazolyl-2-ylidene (A) and Methoxytriazole (B)

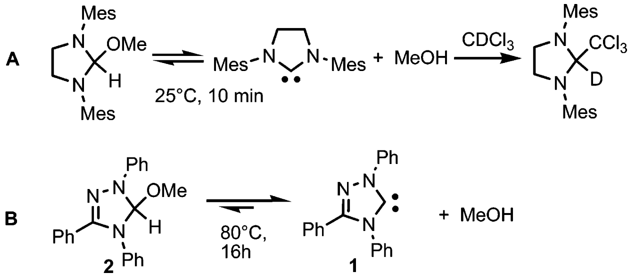


Table 1. Molecular Characteristics of Poly(L-lactide) (P(L-LA)) Synthesized Using 1[a]

entry	temp (°C)	time (h)	conversion[b] (%)	$M_{\mathrm{n\ theor}}$[c] (g/mol)	$M_{\mathrm{n\ GPC}}$[d] (g/mol)	M_w/M_n[d]
1	50	89.0	44	6600	2825	*f*
2	50	167.0	59	8800	2300	*f*
3	50	306.0	98	14 700	2400	*f*
4	90	2.6	15.5	2500	2750	1.08
5	90	17.7	67	9900	8400	1.17
6	90	44.2	80	11 800	10 000	1.08
7	90	94.8	85	12 000	10300	1.09
8[e]	90	4.3	97	6100	5900	1.13
9[e]	90	5.8	96	6100	5500	1.27
10[e]	90	17.5	98	6100	5400	1.29

[a] Initiated by 4-pyrene-1-butanol in THF at 50 °C, or toluene at 90 °C for $[\mathrm{L\text{-}LA}]_0 = 1$ M and $[\mathrm{M}]_0/[\mathrm{I}]_0 = 100$. [b] Determined by ^{1}H NMR (see text). [c] $M_{\mathrm{n\ theor}} = ([\mathrm{L\text{-}LA}]_0/[\mathrm{ROH}] \times \text{conversion } (\%) \times M_{\mathrm{wL-LA}})/100 + M_{\mathrm{w\ pyrenebutanol}}$. [d] Determined by GPC using PS as standards. [e] Initiated by methanol in toluene at 90 °C for $[\mathrm{L\text{-}LA}]_0 = 1$ M and $[\mathrm{M}]_0/[\mathrm{I}]_0 = 42$. [f] Multimodal distribution.

Treatment of **1** with methanol at room temperature readily generates the methoxytriazoline, **2**. The ^{1}H and ^{13}C NMR spectra (C_6D_6) display respectively characteristic resonances at $\delta = 3.1$ and 46.8 ppm (OCH_3); $\delta = 6.6$ and 101.0 ppm (MeO*C*-*H*); and $\delta = 142.9$ ppm (N−N=*C*(Ph)−N) (Figure S1i, Supporting Information). In a sealed NMR tube, the ^{13}C NMR spectrum of **2** was measured at 50 and 90 °C. Analysis of the ^{13}C NMR spectrum at 50 °C shows that **2** does not significantly dissociate at that temperature (Figure S1ii, Supporting Information). However, at 90 °C, a mixture of **2**, methanol and **1** was observed (Figure S1iii, Supporting Information). Cooling of the solution to 20 °C regenerates the spectra corresponding to **2**, clearly demonstrating the thermal reversibility of the adduct dissociation. From integration of the ^{1}H NMR spectra at 90 °C, an equilibrium constant (*K*) of 0.15 was determined, indicating that, even at 90 °C, the methoxytriazole is favored.

Polymerization of Lactide. The polymerization of L-lactide (L-LA) initiated by an equimolar combination of 4-pyrene-1-butanol as an initiator and **1** as a catalyst in dry THF at an initial monomer-to-initiator ratio ($[\mathrm{M}]_0/[\mathrm{I}]_0$) of 100 was investigated (Scheme 1). At room temperature, this system displays poor reactivity with only 16% conversion being observed after 100 h. Increasing the temperature to 50 °C results in complete monomer conversion within 300 h (Table 1, entries 1−3). Under these conditions, the polymerization is poorly controlled, with the resultant polymers displaying molecular weights much lower than predicted from the $[\mathrm{M}]_0/[\mathrm{I}]_0$ ratio and multimodal molecular weight distributions, irrespective of conversion (Figure S2, Supporting Information). On the basis of our equilibrium studies, we attribute the diminished reactivity of **1** for the polymerization of L-LA to be a consequence of the very low concentration of the free carbene **1** and the slow rate of alcohol elimination from **2** at this temperature. Hence, the initiation rate compared to the propagation rate is too slow in order to obtain well-defined polymers. As a significant concentration of the free carbene **1** was only observed at 90 °C, we carried out a series of lactide polymerizations at this temperature.

Polymerization of L-LA using equimolar 4-pyrene-1-butanol and **1** in toluene at 90 °C ($[\mathrm{L\text{-}LA}]_0 = 1$ M; $[\mathrm{M}]_0/[\mathrm{I}]_0 = 100$) resulted in 85% conversion after 95 h. Examination of the ^{1}H NMR spectrum of the as-obtained poly(L-lactide) (P(L-LA)) (Table 1, entry 7) shows resonances attributed to a 4-pyrene-

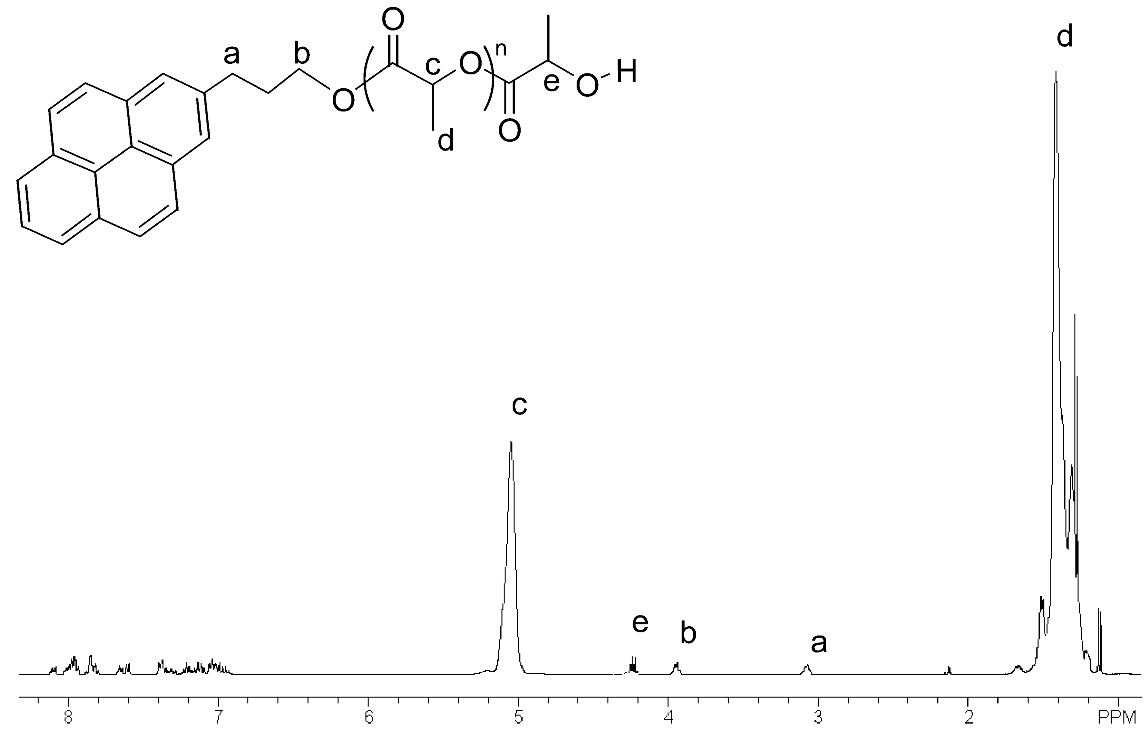


Figure 1. ^{1}H NMR spectrum in d_8-toluene of P(L-LA) as obtained by ROP of L-LA initiated from 4-pyrene-1-butanol in the presence of carbene **1** at 90 °C.

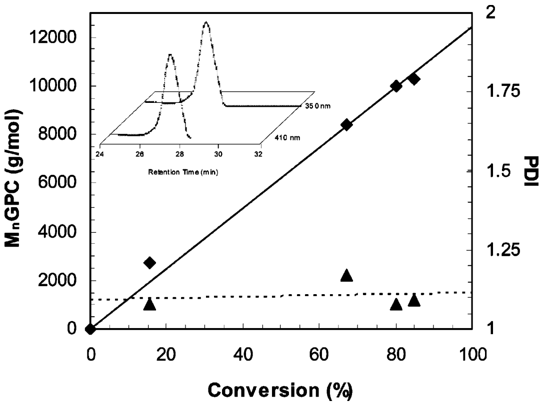


Figure 2. Chart of molecular weights (◆) and polydispersity indexes (▲) vs conversion for the synthesis of P(L-LA) by **1** at 90 °C, ([L-LA]$_0$ = 1 M, [M]$_0$/[I]$_0$ = 100). Inset: GPC traces of the polymer produced UV detectors (350 and 410 nm).[9f]

1-butyl ester at $\delta = 3.90$ ppm (Figure 1, H_b) as well as the methine α-hydroxyl chain ends at $\delta = 4.25$ ppm (H_e). GPC traces of P(L-LA) initiated from 4-pyrene-1-butanol using UV detectors (410 and 350 nm) clearly show distribution of pyrene throughout the sample (Figure 2), corroborating the ^{1}H NMR analysis of the polymer's end-group fidelity. The polymer M_ns, determined by GPC, show excellent agreement with those calculated from the target DP and expected conversion, with M_n increasing linearly with conversion and low polydispersities observed throughout the polymerization (Figure 2), consistent with a living polymerization. Examination of the microstructure of the P(L-LA) (Table 1, entry 7) produced using this catalyst system by ^{13}C NMR spectroscopy reveals a highly isotactic polymer with very low levels of stereoirregularity (Figure 3).

Further evidence of the living nature of this polymerization was provided by a chain extension experiment. A polylactide was prepared by the polymerization of 1.00 mmol of L-LA using 4-pyrene-1-butanol as initiator and **1** as catalyst in toluene at 90 °C ([M]$_0$/[I]$_0$ = 50); the polymerization was followed by ^{1}H NMR spectroscopy. After 24 h, nearly complete monomer conversion was observed. After cooling, a sample of the polymer was characterized, revealing that the polymer had an $M_n = 8000$ g·mol^{-1} and a $M_w/M_n = 1.10$. Additional L-LA (0.08 mmol) was added and the solution heated to 90 °C. After a further 17 h, approximately 70% of the monomer had been consumed, and analysis by GPC gave a polymer of $M_n = 11\,000$ g·mol^{-1} and $M_w/M_n = 1.10$. The ability to extend the polymer chains by the repeated addition of new monomer (Figure 4) clearly demonstrates the competence of this system for the preparation of poly(esters) in a controlled manner as well as the ability to generate block polymers (vide infra).

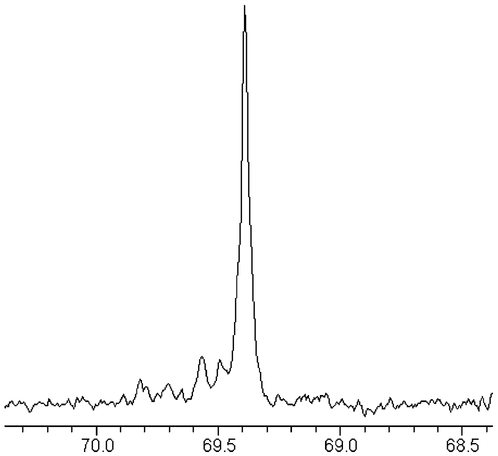


Figure 3. Methine region of the ^{13}C NMR spectrum of P(L-LA) obtained by ROP of L-LA initiated from 4-pyrene-1-butanol in the presence of carbene **1** at 90 °C. ([L-LA]$_0$ = 1 M, [M]$_0$/[I]$_0$ = 100).

To gain more information on the polymerization mechanism, the kinetics of the polymerization were studied using [L-LA]$_0$ = 1 M initiated by 4-pyrene-1-butanol, catalyzed by **1** in toluene at 90 °C and followed by ^{1}H NMR spectroscopy. Polymerizations were initially studied at a constant catalyst concentration ([**1**]$_0$ = 0.02 M) and varied concentrations of 4-pyrene-1-butanol

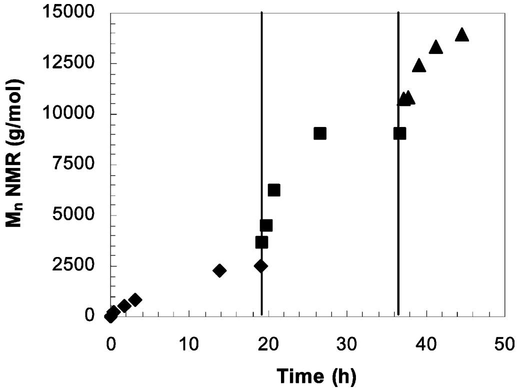


Figure 4. Time dependence of the P(L-LA) molecular weight (determined by ^{1}H NMR) for chain extension ([L-LA]/[4-pyrene-1-butanol]/[**1**] ratios = 25/1/0.5 (◆); 50/1/4 (■), and 100/1/4 (▲)).

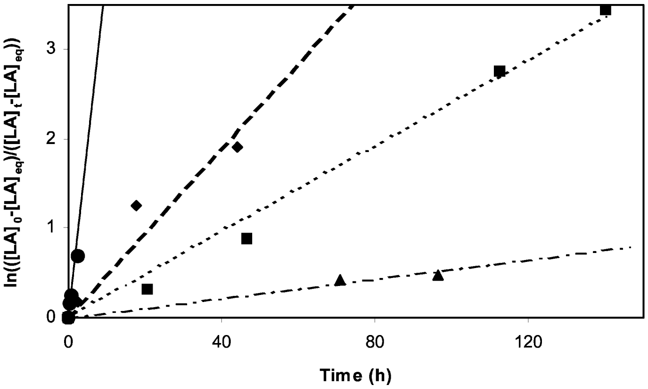


Figure 5. Semilogarithmic plot of time against monomer conversion for the polymerization of L-LA by 4-pyrene-1-butanol/**1** at 90 °C. $[\text{L-LA}]_0 = 1$ M; $[\mathbf{1}]_0 = 0.02$ M; [L-LA]$_0$/[4-pyrene-1-butanol] = 50 (●),100 (◆),150 (■), and 350 (▲).

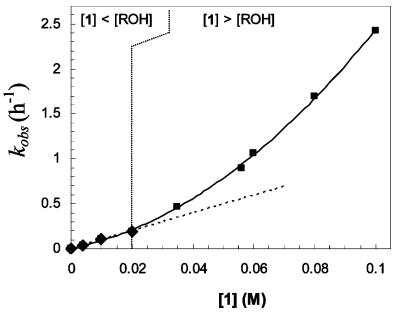


Figure 6. Plot of k_{obs} vs $[\mathbf{1}]_0$ for the polymerization of L-LA by 4-pyrene-1-butanol/**1** at 90 °C. $[\text{L-LA}]_0 = 1$ M; [4-pyrene-1-butanol]$_0$ = 0.02 M (◆), $[\mathbf{1}]_0$/[4-pyrene-1-butanol]$_0$ ≤ 1 (■), $[\mathbf{1}]_0$/[4-pyrene-1-butanol]$_0$ > 1.

([4-pyrene-1-butanol]$_0$ = 0.004−0.06 M). Under pseudo-first-order conditions, plots of $\ln(([\text{L-LA}]_0 - [\text{L-LA}]_{\text{eq}})/[\text{L-LA}]_t - [\text{L-LA}]_{\text{eq}}))$ against time are linear with zero intercepts (Figure 5), indicating a first-order dependence on L-LA concentration. Furthermore, these results indicate that initiation is fast, termination is absent, and the concentration of active species does not change appreciably with time. The observed rate constant for monomer consumption (k_{obs}) varies linearly with concentration of alcohol and with concentration of $[\mathbf{1}]_0$ ([4-pyrene-1-butanol]$_0$ = 0.02 M and $[\mathbf{1}]_0$ = 0.004−0.02 M), revealing a first-order dependence on both catalyst and initiator under these conditions (Figures S3−S5, Supporting Information). Thus, under these conditions, the L-LA monomer disappearing in the reaction with **1** (Scheme 3, pathway A) implies a rate law for the ROP given by eq 1:

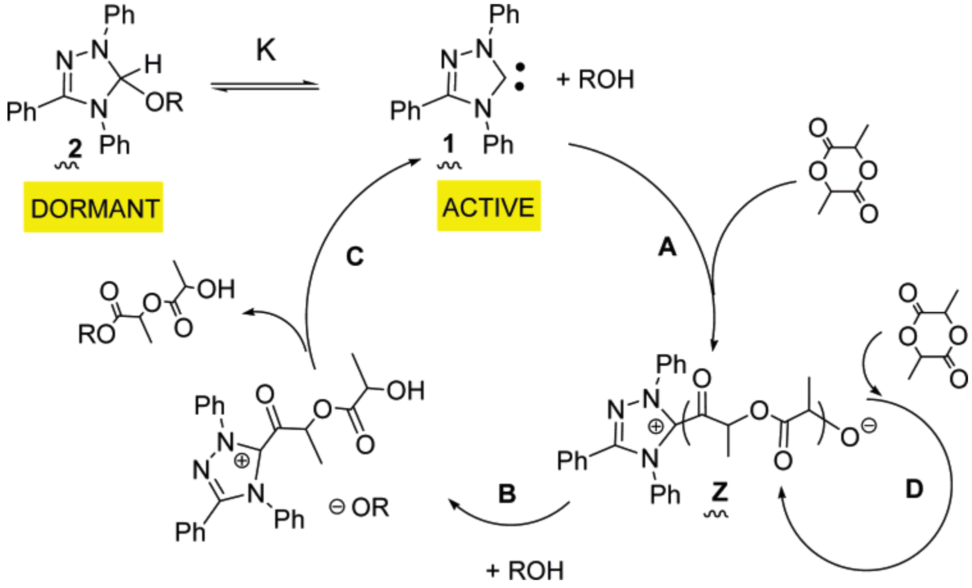
$$-\frac{\mathrm{d}[\text{LA}]}{\mathrm{d}t} = k_{\text{obs}}[\text{LA}] \tag{1}$$

where $k_{\text{obs}} = k'[\mathbf{1}]_0[\text{ROH}]_0$ is the observed rate constant; [LA] is the concentration of L-LA monomer; $[\mathbf{1}]_0$ is the initial concentration in **1**, and $[\text{ROH}]_0$ is the initial concentration of 4-pyrene-1-butanol.

The first-order dependence of the rate on alcohol, carbene, and monomer implies that the rate-limiting step occurs after the formation of the zwitterionic intermediate **Z** (Scheme 3), and as proton transfer from this intermediate is likely to be fast, we postulate that transesterification of the acyl imidazolium intermediate (step C) is rate limiting (Scheme 3). In addition, we propose that the concentration of the carbene **1** is controlled essentially by the reversible formation of the dormant alkoxytriazole **2**, defined by the equilibrium constant *K*.

Effect of Excess Catalyst. Different kinetic behavior was observed when the concentration of $[\mathbf{1}]_0$ exceeded the concentration of the alcohol initiator $[\text{ROH}]_0$. The plot of k_{obs} vs $[\mathbf{1}]_0$ (Figure 6) over the range $[\mathbf{1}]_0$ = 0.004−0.1 M reveals a presumably first-order dependence in $[\mathbf{1}]_0$ when $[\mathbf{1}]_0$/[4-pyrene-

Scheme 3. Proposed Mechanism for Ring-Opening Polymerization of Lactide with 1



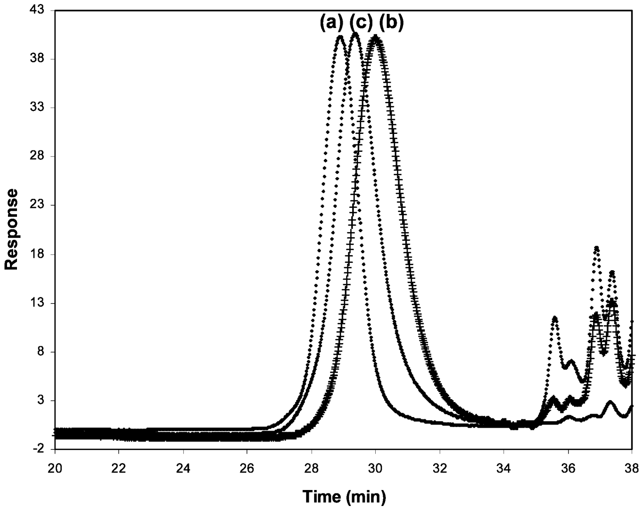


Figure 7. GPC traces of P(L-LA)s. $[\text{L-LA}]_0 = 1$ M; $[\text{MeOH}]_0 = 0.02$ M; for [**1**]: (a) 0.02 M, (b) 0.08M, (c) 0.1 M.

1-butanol$]_0 \leq 1.0$, but a nonlinear dependence when $[\mathbf{1}]_0$/[4-pyrene-1-butanol$]_0 > 1.0$. The deviation from first-order behavior under conditions where $[\mathbf{1}]_0$/[4-pyrene-1-butanol$]_0 > 1.0$ suggests that, under these conditions, an additional pathway for lactide enchainment becomes kinetically significant. These results are indicative of two kinetic regimes, where the second pathway (Step D) becomes significant when the concentration of $[\mathbf{1}]_0$ is higher than that of the alcohol $[\text{ROH}]_0$. One possibility is that, at low $[\text{ROH}]_0$, the direct addition of lactide to the zwitterion **Z** competes with proton transfer (Scheme 3, path D). According to this hypothesis, when $[\mathbf{1}]_0/[\text{ROH}]_0 \leq 1$, the relative concentration of $[\mathbf{1}]_0$ and $[\text{ROH}]_0$ is controlled by the equilibrium K and $[\mathbf{1}]_0 \leq [\text{ROH}]_0$. In the presence of excess [**1**], the relative rate of attack of the zwitterion on lactide (path D) becomes competitive with proton transfer to the zwitterion (path B), leading to a deviation in first-order behavior in $[\mathbf{1}]_0$.

To investigate this further, P(L-LA)s obtained at various $[\mathbf{1}]_0$/[4-pyrene-1-butanol$]_0$ ratios were analyzed by GPC. The appearance of new polymer populations at very high retention volume (i.e., low M_n) is observed when $[\mathbf{1}]_0$ exceeds $[\text{ROH}]_0$. Moreover, the relative proportion of these populations, in comparison to the P(L-LA) signal, increases dramatically when the ratio $[\mathbf{1}]_0$/[4-pyrene-1-butanol$]_0 > 4$ (Figure 7), which is suggestive of a second competing polymerization mechanism. Interestingly, regardless of the initial $[\mathbf{1}]_0$/[4-pyrene-1-butanol$]_0$ molar ratio, each of the P(L-LA) samples is characterized by low polydispersities ($M_w/M_n \leq 1.10$). To get more information on the low-molecular-weight population, the polymerization of 1 mol·L^{-1} of L-LA in toluene at 90 °C employing 4 equiv of **1** relative to methanol was surveyed ($[\text{L-LA}]_0/[\text{methanol}]_0 = 50$), cooled after 5 h (no quenching agent was added), and analyzed by electrospray ionization mass spectrometry (ESI-MS) (Figure 8). From the expanded portion of the spectrum between 1600 and 3600 *m*/*z*, two distinct species of periodically repeating peaks dominate. These are attributed to those corresponding to the mono- and doubly charged linear triazole-O−P(L-LA)−OMe (L) chains. This expansion of Figure 8 also shows the presence of other signals of lower intensity (represented in Figure 8, zoom) corresponding to HO−P(L-LA)−OMe, L′, and P(L-LA) macrocycles, C.

In the mass range below 1600 *m*/*z*, signals of P(L-LA) macrocycles (C), HO−P(L-LA)−OMe (L′), and triazole-O−P(L-LA)−OH (L″) were detectable, and the latter are likely to be generated from the presence of trace amounts of either water

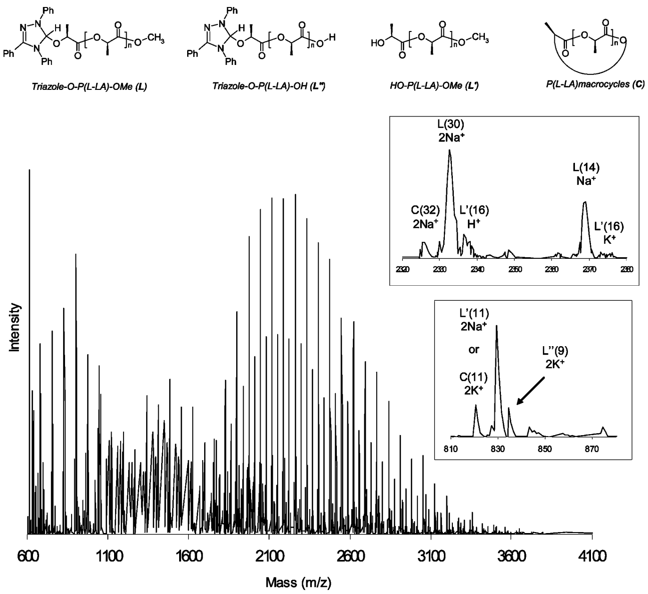


Figure 8. ESI mass spectrum of P(L-LA). $[\text{L-LA}]_0 = 1$ M; $[\text{L-LA}]_0/[\text{methanol}]/[\mathbf{1}] = 50/1/4$ (no termination by CS_2). DP$_n$ of the P(L-LA) chains and macrocycles in parentheses. See text for acronyms (L, L′, L″, and C) and definitions. The value "2" prior to some ions is referring to a doubly charged macromolecule.

or lactic acid. These data show that, when L-LA is polymerized with an excess of **1** compared to the alcohol, the polymerization is less well controlled, with competing mechanisms able to produce P(L-LA) without alcohol initiator, leading to the formation of linear and/or macrocyclic oligomers.

Thermal Control. The triazole carbene **1** exhibits several unique features as a ring-opening polymerization catalyst. In the presence of alcohols, **1** readily forms a dormant alkoxytriazole **2**, which is a very slow catalyst for ring opening (Table 1, entries 1−3). At elevated temperature (90 °C), the alkoxytriazole liberates the alcohol and free triazole, which catalyzes the ring opening of lactide in a controlled manner. This behavior is reminiscent of other living polymerization systems that involve equilibria between dormant and active species.[14] For example, in nitroxide-mediated radical polymerization (NMP), dormant alkoxyamines establish at elevated temperatures an equilibrium of persistent nitroxide radicals and transient carbon radicals, so monomers may add to the growing chain end in competition with the reformation of the alkoxyamine. We thus sought to exploit this fundamental behavior of the triazole carbene to reversibly activate the triazole carbene thermally.

The thermal control of the initiation and termination of the polymerization of racemic lactide (*rac*-LA) initiated by methanol adduct of **1** was monitored by ^{1}H NMR spectroscopy. Heating a toluene solution of lactide to 90 °C ($[rac\text{-LA}]_0 = 1$ M; $[\text{methanol}]_0 = [\mathbf{1}]_0 = 0.02$ M) initiated the polymerization. Upon cooling (20 °C), no further conversion was observed. The polymerization was reinitiated by reheating the solution to 90 °C and again deactivated upon cooling to 20 °C. This process was repeated successively four times, and the molecular weight followed with time (Figure 9). Upon completion of four successive heating and cooling cycles (∼95% conversion), GPC analysis of poly(*rac*-lactide) (P(*rac*-LA)) yielded a molecular weight $M_n = 5900$ g·mol^{-1} and $M_w/M_n = 1.13$. The exquisite control of this polymerization clearly demonstrates that the catalyst can be deactivated simply by cooling the reaction to room temperature. A portion of this polymer (point (1) in Figure 9) was heated to 90 °C for a further 17 h. This sample (point (2) in Figure 9) showed very little change in the molecular

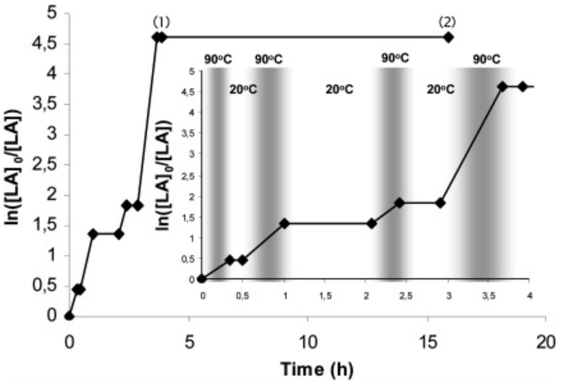


Figure 9. Time dependence of ln([LA]$_0$/[LA]) as a function of time ([LA]$_0$ = 1 M; [alcohol]$_0$ = 0.02 M; [alcohol]$_0$/[catalyst]$_0$ = 1/3) with alternation of high (90 °C) and low (20 °C) temperature. As determined by GPC, molecular weights and polydispersity index for (1) and (2) are 5900 (1.13) and 5400 (1.29), respectively. Inset: zoom representation of the first 4 h of reaction.

weight and only a slight broadening in polydispersity (M_n = 5400 g·mol^{-1} and PDI = 1.29). This behavior is quite distinct from that observed in the polymerization of lactide by the IMes carbene. For IMes, the rate of lactide polymerization is much faster (92% conversion after 10 s at 25 °C for [LA]$_0$ = 1 M, [IMes]$_0$ = 0.005 M, M_n = 21 000, PDI = 1.05), but for this catalyst, after 90% conversion of lactide, the polydispersities rapidly broaden to 1.67 as the conversion approaches 95% (15 min). The minimal change in the polydispersity of the lactide obtained from **1** after extended heating implies that, even after almost complete conversion of lactide, there is very little transesterification of the polylactide. This behavior can be rationalized in the context of the mechanism proposed in Scheme 3, where the reversible formation of the dormant alkoxytriazole **2** keeps the concentration of both the free triazole **1** and the alcohol chain ends [ROH] at a low concentration, thus presumably minimizing the rate of transesterification of the lactide polymer. While we have not measured the equilibrium constant K where ROH = polylactide, the small equilibrium constant observed for ROH = MeOH (K = 0.15) would imply that equilibrium concentration of both free carbene **1** and lactide chain ends ROH are low.

Finally, further evidence of adduct formation from a hydroxyl-terminated polymer and free carbene was provided by an NMR-scale single-turnover experiment. A solution of **1**, methanol, and L-LA in dry d_8-THF ([**1**]$_0$ = [MeOH]$_0$ = [L-LA]$_0$ = 0.5 M) was heated to 60 °C overnight. Upon cooling, the NMR spectrum of the product revealed that the L-LA had been completely consumed with the major product assigned as a stable carbene adduct of the methyl ester of ring-opened lactide (Figure 10). These observations provide excellent evidence to suggest the formation of carbene/alcohol adducts during and after the polymerization and, in combination with the end-group analysis, confirm that polymerization occurs by acyl−oxygen cleavage.

Block Copolymers and Complex Macromolecular Architectures. The ability to form alcohol adducts of **1** leads to interesting and simple methods of generating well-defined macromolecular structures through extremely well-controlled polymerization. Primary or secondary alcohols are effective initiators and form alkoxytriazoles readily at room temperature. This behavior provides a means of forming a stable catalyst precursor that contains both the catalyst and the initiator. Simply heating this adduct to 90 °C initiates polymerization of lactide in a controlled manner. To demonstrate the versatility of **1** in

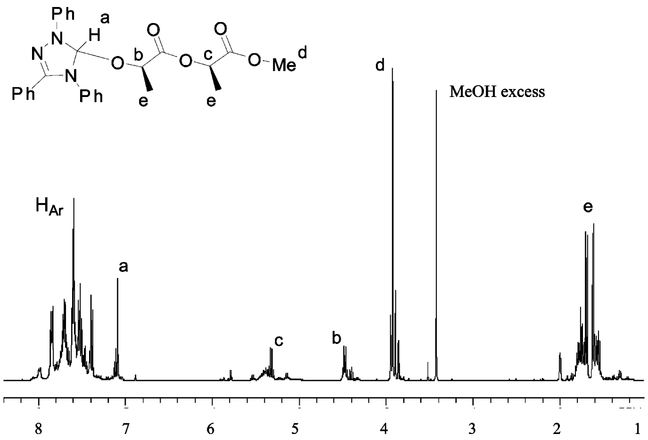


Figure 10. Single-turnover experiment realized between **1**, methanol, and LA in dry d_8-THF ([**1**] = [MeOH] = [L-LA]$_0$ = 0.5 M) at 60 °C.

the preparation of block copolymers and complex macromolecular architectures, several adducts of hydroxyfunctional oligomers and multifunctional alcohols were synthesized, isolated, and used in a one-step polymerization process. For example, a monohydroxypoly(ethylene oxide) oligomer (PEO-OH) (M_n = 2000 g·mol^{-1}, M_w/M_n = 1.05) was reacted with **1** in toluene at room temperature for 12 h to yield the corresponding alkoxytriazoline quantitatively. The oligo-alkoxytriazoline is stable at room temperature, but readily polymerizes LA at 90 °C to yield a narrowly dispersed diblock copolymer in near quantitative yields (~90%) (Table 2, entry 1).

Polystyrene−polylactide block copolymers were prepared from a bifunctional initiator containing both alkoxyamine and alcohol functional groups[14c] via the controlled radical polymerization of styrene and ROP of lactide (Scheme 4). Hydroxyl-functionalized poly(styrene) was synthesized by bulk polymerization of styrene at 125 °C using this initiator with target DPs of 50 and 100. The polymerizations were stopped before 80% of styrene was consumed to prevent adverse radical termination reactions;[14] the resulting polymers were isolated by precipitation and used as macroinitiators (after reaction with **1**) for the ROP of *rac*-LA at 90 °C in toluene ([*rac*-LA)] = 1 M). Analysis of the resultant polymers by GPC show that clean chain extension was observed in each case, generating narrowly dispersed block copolymers (Table 2, entries 2−4). These examples clearly demonstrate the end-group fidelity of the polystyrene macroinitiators together with the exemplary polymerization control that the triazole adducts provide for the ROP of lactide. The DPs of the individual blocks were determined from the ^{1}H NMR spectra with respect to the benzylic protons of the starting initiator fragment.

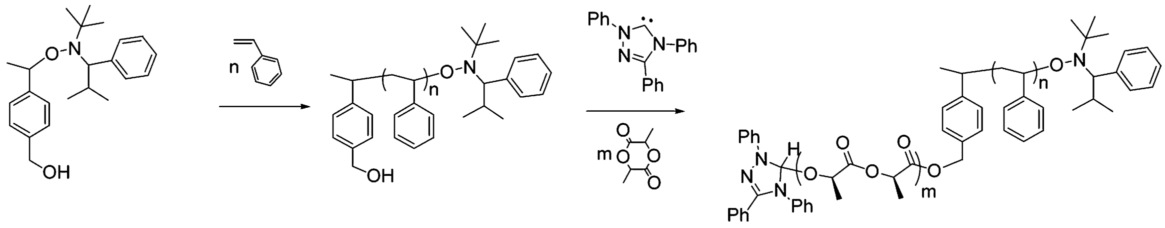
In a second example of combining disparate polymerization techniques, the compatibility of the triazole carbene with RAFT polymerization was investigated. A hydroxyl-functionalized RAFT agent was prepared according to literature procedures[15] and subsequently used for the polymerization of methyl methacrylate and *N*,*N*-dimethylaminoethyl methacrylate using 4,4′-bisazo(4-cyanopentan-1-ol) as initiator to ensure end-group fidelity (Scheme 5).[15] This macroinitiator was used for the ROP of (D,L)-lactide. Narrowly dispersed, monomodal block copolymers of predictable molecular weights were obtained, and the polylactide block was characterized by NMR spectroscopy (Table 2, entries 5 and 6). The presence of the esters in the polymer backbone were largely unaffected by the triazole; however, the characteristic red color of the dithioester of the macroinitiators disappeared, indicating the loss of this end group. This means that the RAFT polymerization must be conducted

Table 2. Molecular Characteristics of Diverse Block Copolymers Based on Poly(L-lactide) as Synthesized Using 1[a]

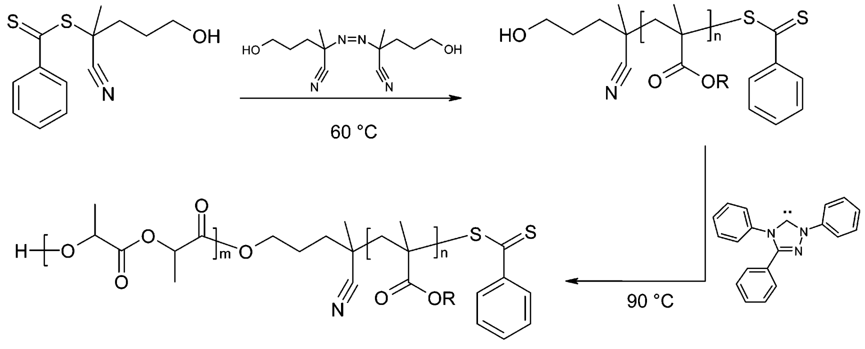
entry	ROH	$[\text{L-LA}]_0/[\text{ROH}]_0$	time (h)	conversion[b] (%)	$M_{n\ \text{theor}}$ (g/mol)	$M_{n\ \text{GPC}}$[d] (g/mol)	M_w/M_n[d]
1	PEO−OH	100	63	88	14 600	16 000	1.17
2	PS_{40}−OH	25	15	93	7400	7300	1.14
3	PS_{40}−OH	50	15	89	10 400	9700	1.09
4	PS_{70}−OH	25	15	92	10 300	9400	1.05
5	$PMMA_{140}$−OH	100	14	25	19 400	21 200	1.15
6	$PDMAEMA_{100}$−OH	100	14	27	21 000	21 400	1.30

[a] Initiated by ROH in toluene at 90 °C for $[\text{L-LA}]_0 = 1$ M. [b] Determined by ^{1}H NMR. [c] $M_{n\,\text{theor}} = ([\text{L-LA}]_0/[\text{ROH}] \times \text{conversion}(\%) \times M_{w\,\text{L-LA}})/100 + M_{w\,\text{ROH}}$. [d] Determined by GPC using PS as standards.

Scheme 4. Synthesis of Poly(styrene)-*b*-poly(lactide) Using Both NMP and ROP Processes

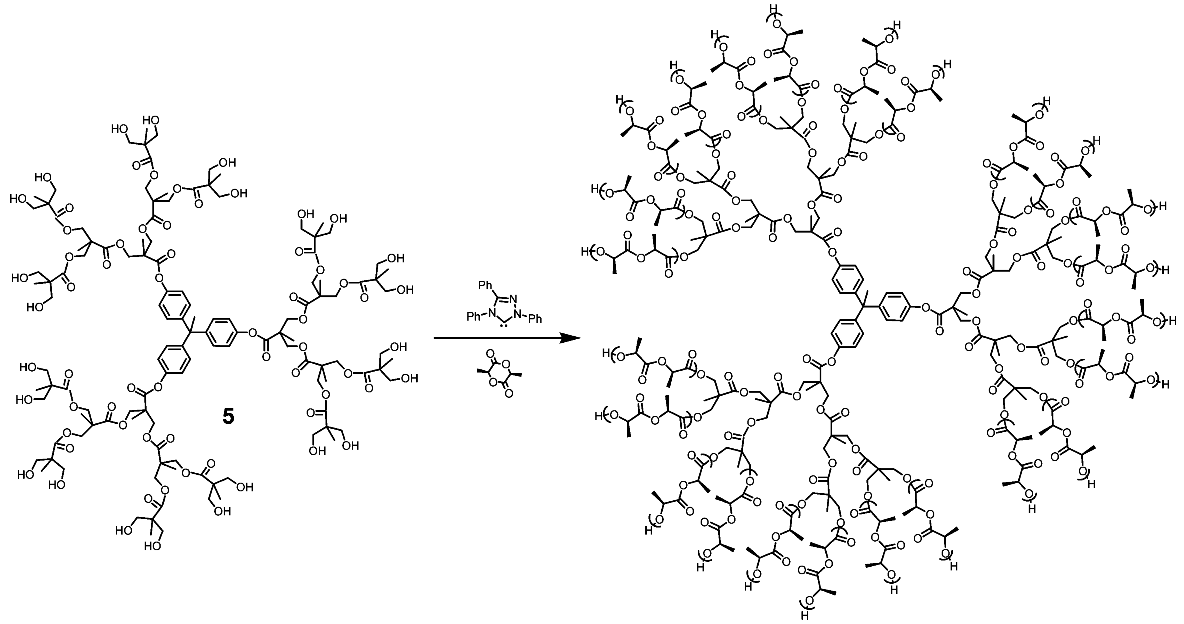


Scheme 5. Synthesis of Poly(methacrylate)-*b*-poly(lactide) Using Both RAFT and ROP Processes



R = CH_3, $CH_2CH_2N(CH_3)_2$

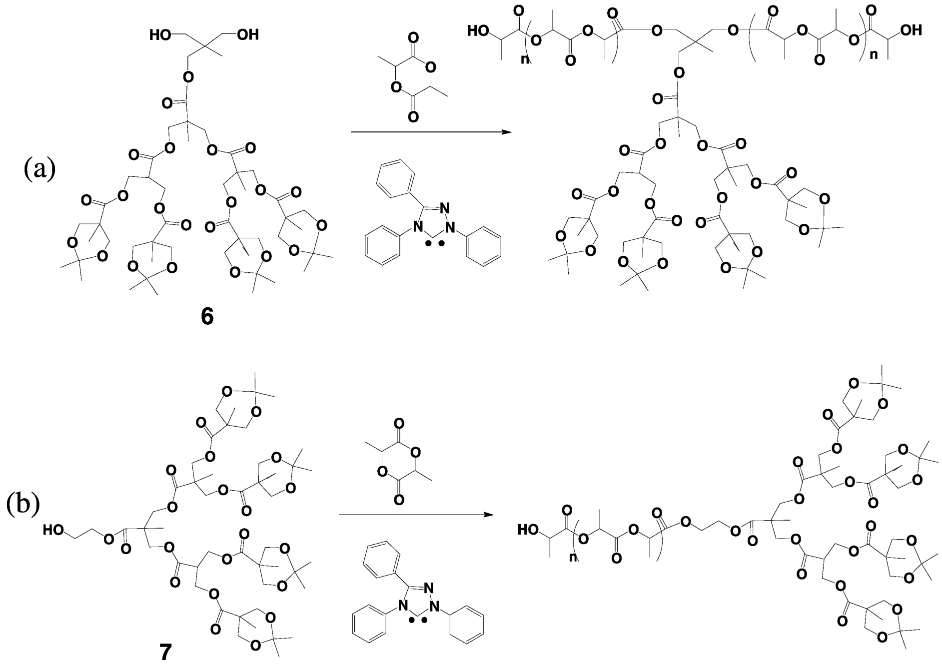
Scheme 6. Synthesis of Star-Shaped Polymers Initiated from a 24-Arm Hydroxyl-Functional Dendrimer (G-3)



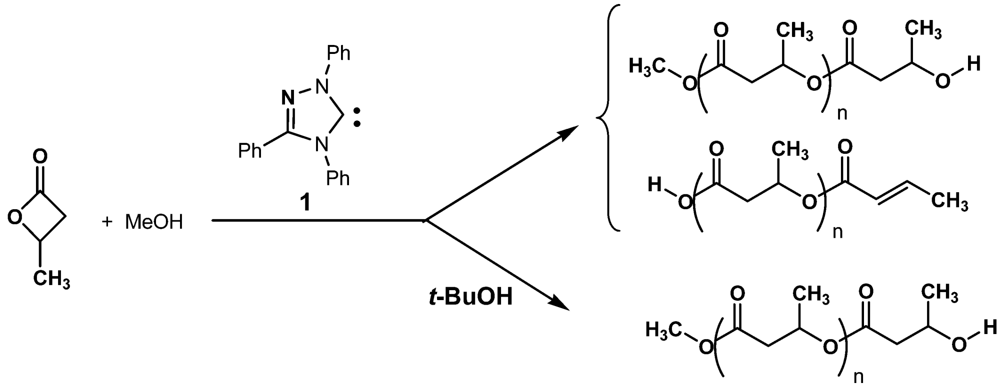
first, followed by ROP. In the case of NMP, the polymerization sequence was shown not to make a difference.

As previously communicated,[9f] we have also synthesized star-shaped polymers initiated from a 24-arm hydroxyl-functional dendrimer (G-3) derived from 2,2′-(bis-hydroxymethyl)propionic acid (bis-MPA) using procedures developed by Hult and others (Scheme 6).[15] The G-3 dendrimer, lactide, and **1** were suspended in toluene, and upon adduct formation (~2 h), the solution became homogeneous. Polymerization was initiated by increasing the temperature to 90 °C, and after 40 h, the polymerization was stopped by cooling to 20 °C. Two star-shaped polymers were prepared with target DPs of 15 and 40 per arm. NMR analysis indicated that ~96% of the monomer had been consumed in each case to generate polymers with DPs of 14

Scheme 7. Synthesis of Dendritic-linear, Di-, and Triblock Copolymers



Scheme 8. Effect of *t*-BuOH Co-solvent on the Polymerization of *β*-BL Initiated from Methanol and Triazole Carbene as Initiator and Catalyst, Respectively[a]



[a] Polymerization performed at 80 °C in toluene.

and 38, respectively. The molecular weights by GPC were 43 000 and 75 000 g·mol^{-1}, respectively, and each had a polydispersity of 1.14. NMR analysis of the quartenary carbon and protons of the methylene group of the neighboring hydroxyl group on the dendritic initiator allows the efficiency of initiation to be assessed, and this analysis demonstrated that polylactide was initiated from each of the 24 hydroxyl functionalities of the dendrimer. Furthermore, the reversible adduct formation, essentially eliminating transesterification reactions, resulted in the poly(ester) dendritic core remaining intact, evidenced by the quartenary carbon and the protons on the methylene group of the bis-MPA repeating units.

To further demonstrate the versatility and tolerance to functional groups, dendritic-linear, di-, and triblock copolymers were prepared (Scheme 7). An orthogonal protecting group strategy was used to prepare third-generation dendrons containing either one or two primary hydroxyl groups. ROP of lactide in the presence of 1 equiv of the triazole carbene in toluene at 90 °C gave either a di- or triblock copolymer with molecular weights of 9000 g·mol^{-1} ($M_w/M_n = 1.07$) and 10 000 g·mol^{-1} ($M_w/M_n = 1.20$), respectively (Scheme 7a and b).

Investigation of the *β*-Butyrolactone Ring-Opening Polymerization. Poly(hydroxyalkanoates) are an important class of biomacromolecules that are produced by a wide variety of microorganisms and used as metabolic storage materials.[16] Since poly[(*R*)-(−)-3-hydroxybutyrate] (PHB) was discovered in 1926, this family of biopolymers has been significantly expanded, and a family of biodegradable poly(hydroxyalkanoate) copolymers with properties comparable to those of poly(propylene) were recently commercialized by a fermentation process.[17,18]

An alternative entry to PHBs involves the ROP of *β*-butyrolactone (*β*-BL). Crystalline, isotactic PHB thermoplastics can be prepared from the enantiomerically pure monomer and amorphous atactic PHB from the racemic monomer.[19] Nevertheless, the ROP of *β*-BL is challenging in that ring-opening can proceed by bond breaking either between the carbonyl carbon and oxygen atom of the *β*-lactone ring (O−acyl cleavage), resulting in retention in stereochemistry, or between the *β*-carbon and oxygen atom (O−alkyl cleavage), leading to inversion of configuration.[20] An additional complication is that poly(hydroxyalkanoates) are extraordinary base-sensitive and are readily deprotonated by bases to eliminate crotonates and carboxylates.[21,22] The resultant carboxylates are themselves initiators for polymerization of *β*-BL by alkyl cleavage, leading to loss of control and end-group fidelity. Although there is a considerable number of reports on the ROP of *β*-BL, only a few recent

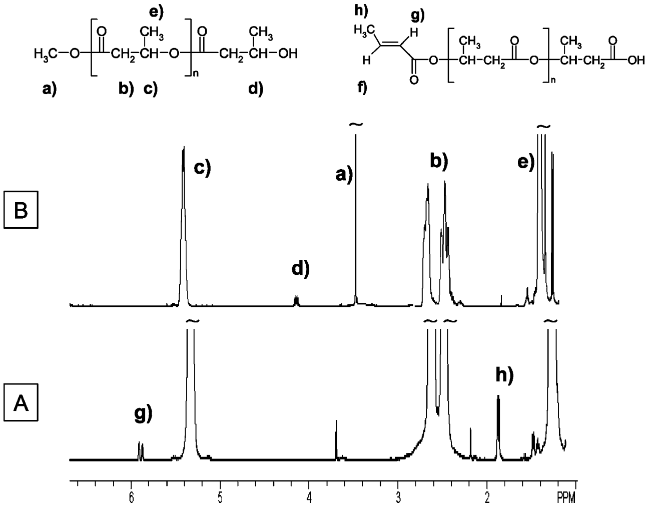


Figure 11. ^{1}H NMR spectra of poly([*R*,*S*]-β-butyrolactone) as obtained by ROP of (*R*,*S*)β-BL initiated by MeOH and catalyzed by **1** at 80 °C in toluene without (**A**) and with *t*-BuOH (**B**) ($[\beta\text{-BL}]_0/[\text{MeOH}]_0 = 25$; $[\beta\text{-BL}]_0 = 1$ M) (solvent = $CDCl_3$).

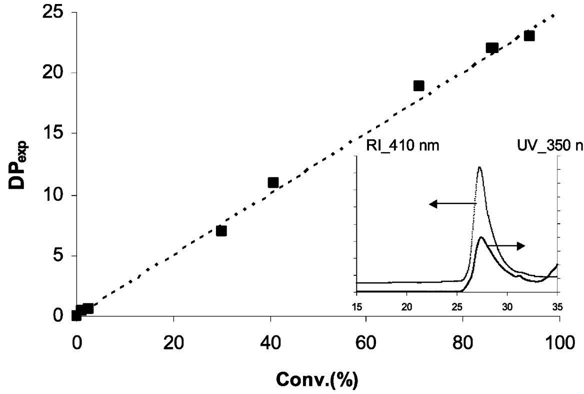
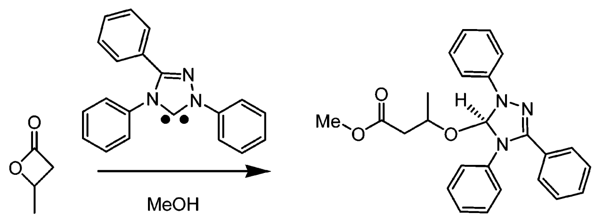


Figure 12. Evolution of the experimental degree of polymerization vs conversion in the ROP of β-BL as initiated by 4-pyrene-1-butanol added with 1 equiv of **1** in toluene/*t*-BuOH (8/2 v/v) at 80 °C for a $[\text{BL}]_0$ of 7.7 M and $[\text{M}]_0/[\text{I}]_0$ of 25, together with GPC traces using both RI (410 nm) and UV (350 nm) detectors.

Scheme 9. Exclusive Formation of Alkoxytriazole Methyl Ester from Treatment of β-BL with Methanol, Triazole Carbene, and *t*-BuOH



examples using either distannoxane or zinc complexes as organometallic promoters have demonstrated the synthesis of narrowly dispersed PHB of high molecular weight.[21] However, crotonate formation and hence end-group fidelity still remain a problem for these catalyst systems.

The selectivity of the triazole carbene **1** for the ROP of lactide prompted us to investigate its reactivity for the ROP of β-BL. The polymerization of *rac*-β-BL initiated from methanol and **1** was performed at 80 °C in toluene (Scheme 8). Shown in Figure 11A is the ^{1}H NMR spectrum of the resulting product in which α-methoxy chain-end protons (H_a) are clearly observed together with crotonate byproducts (H_g), indicating uncontrolled polymerization by both alkoxide (O−acyl) and carboxylate (O−alkyl) pathways. Reasoning that the basicity of free **1** might lead to undesired elimination reactions with unreacted β-BL, generating crotonate initiators, we added *tert*-butyl alcohol as a cosolvent to favor adduct formation and minimize the concentration of free **1**. *tert*-Butyl alcohol cannot initiate the polymerization of β-BL, however, it does react reversibly with the triazole to form the corresponding adduct. Under these conditions, PHB polymers were obtained having molecular weights matching those predicted from the monomer-to-initiator ratios and narrow polydispersities (Table 3, entries 1−3). Importantly, for molecular weights having DPs below 200, the ^{1}H NMR spectra show only α-methoxy and β-hydroxyl chain ends and no crotonate end groups (Figure 11B). For such small DP, the plot of the molecular weight versus conversion for **1**-catalyzed ROP is linear, consistent with a living polymerization (Figure 12).

Gel permeation chromatography (GPC) traces of PHB initiated from 4-pyrene-1-butanol using both refractive index and UV detectors (410 and 350 nm, respectively) clearly show distribution of pyrene throughout the sample (inset Figure 12), corroborating the end-group fidelity shown by ^{1}H NMR. These observations were substantiated with a single-turnover experiment. Treatment of β-BL with 1 equiv of **1** in the presence of a slight excess of methanol at 80 °C using *t*-BuOH as cosolvent yielded the alkoxytriazole methyl ester **3** (Scheme 9). This result demonstrates that the ring-opening of β-BL with MeOH cleanly generates the methyl ester. In addition, the formation of the alkoxytriazole implies that, as in the case of lactide, the reversible formation of alkoxytriazole also occurs for the ROP of β-BL.

Further evidence of end-group fidelity was provided by the synthesis of PEO-*b*-PBL diblock copolymers. Polymerization of β-BL with **1**/*t*-BuOH in the presence of a PEO-OH macroinitiator ($M_n = 2000$ g·mol^{-1}, $M_w/M_n = 1.05$) yielded a block copolymer with a M_n of 7900 g·mol^{-1} and a polydispersity of 1.02.

These combined data demonstrate end-group fidelity and predictable molecular weights, particularly for targeted DPs of 200 or less. However, polymerization targeting higher molecular weights (DPs ranging from 250 to 450), generally accompanied by long reaction times, tended to show some broadening in the polydispersity (1.10−1.15) (Table 3, entries 3−5). Moreover, for these molecular weights, a small amount of crotonate was observed (~25% of total chain ends), consistent with a second mode of polymerization. The loss of control and end-group fidelity at the high molecular weights is consistent with that

Table 3. Molecular Characteristics of Poly(β-butyrolactone) (P(β-BL)) Polymers Using 1[a]

entry	$[\text{BL}]_0/[\text{ROH}]_0$	$[t\text{-BuOH}]_0/[\mathbf{1}]_0$	time (h)	conversion[b] (%)	$M_{n\ theor}$[c]	$M_{n\ GPC}$[d]	M_w/M_n[d]
1	37	25	3.0	95	3000	4400	1.19
2	75	50	4.5	92	5900	9300	1.09
3	150	100	5.4	81	10 400	13 700	1.11
4	300	200	14.0	89	23 000	14 300	1.15
5	450	300	24.0	92	35 600	15 500	1.10

[a] Initiated by 4-pyrene-1-butanol in toluene at 80 °C using *tert*-BuOH as co-solvent and for $[\text{BL}]_0 = 1$ M. [b] Determined by ^{1}H NMR. [c] $M_{n\ theor} = ([\text{BL}]_0/[\text{4-pyrene-1-butanol}] \times \text{conversion (\%)} \times M_{w\ BL})/100 + M_{w\ pyrenebutanol}$. [d] Determined by GPC using PS as standards.

observed by Coates.[21h] Clearly, the use of the triazole carbene with *tert*-butyl alcohol as a cosolvent, intended to enhance nucleophilic attack over detrimental deprotonation side reactions and to minimize crotonate formation, was successful for the polymerization of β-BL for molecular weight targets below 200, but the control (i.e., end-group fidelity) was compromised for the higher molecular weights.

Conclusion

Alcohol adducts of 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2-triazol-5-ylidene function as excellent single-component catalyst/initiators for the ring-opening polymerization of lactide and β-butyrolactone. Their reversible dissociation at elevated temperatures generates alcohol and triazolylidene carbene to provide a facile entry to polymerization of cyclic esters while minimizing adverse transesterification reactions. Block copolymers were prepared by combining disparate polymerization techniques from the use of oligo-adducts and bifunctional initiators, and a variety of macromolecular architectures were prepared from multifunctional or dendritic initiators. All of these examples demonstrate the versatility of the *N*-heterocyclic carbene-platform. Our future work will focus on the extension of this system to other cyclic ester monomers.

Experimental Section

Characterization. ^{1}H NMR spectra were recorded with a Bruker Avance 2000 (400 MHz) spectrometer and referenced to the residual solvent proton signal. ^{13}C NMR spectra were recorded at 100 MHz on a Bruker Avance 2000 spectrometer and referenced to the residual solvent carbon signal. Gel permeation chromatography (GPC) was carried out on a Waters chromatography instrument connected to a Waters 410 differential refractometer. Polystyrene samples of known molecular weight were used as calibration standards. Four 5 μm Waters columns (300 mm × 7.7 mm) connected in series in order of increasing pore size (100, 1000, 105, 106) were used with THF as a solvent. The molecular weights were corrected using the Mark−Houwink relationship $[\eta] = KM^a$ for PS and P(L-LA) ($K_{PS} = 1.25 \times 10^{-4}$ dL^{-1}g, $a_{PS} = 0.707$, $K_{PLLA} = 3.08 \times 10^{-4}$ dL^{-1}g, $a_{PLLA} = 0.628$).

Materials. An inert atmosphere glovebox was used for chemical storage and manipulations. l-Lactide was purchased from Purac and recrystallized from toluene three times prior to use. 4-Pyrene-1-butanol was dried by three successive azeotropic distillations. Solvents were dried using standard methods and stored over 3 Å molecular sieves. Poly(ethylene glycol monomethyl ether) with an average molecular weight of 2000 gmol^{-1} was purchased from Polysciences, Inc., recrystallized from toluene three times prior to use, and stored in a glovebox. 2,2-Bis(hydroxymethyl) propionic acid (bis-MPA) was obtained from Aldrich and used without further purification. Dowex 50W-X2 ion-exchange resin was obtained from Aldrich and used after a simple methanol rinse, and DMAP (Aldrich) was used as received. The 4-(Dimethylamino)pyridinium *p*-toluensulfonate (DPTS) was prepared according to literature procedure. Hydroxyl-functional dendrimer (bis-MPA) was synthesized according to a procedure developed by Ihre et al. and stored inside a glovebox.[23] Deuterated NMR solvents were purchased from Aldrich. The triazole **1** was purchased from Acros and used without any further purification. Methoxytriazole **2** was prepared in a glovebox by an equimolar addition of dried methanol and triazole carbene, **1**, dissolved in dry THF. 4,4′-Azobis(4-cyanopentan-1-ol) was bought from Langfang Hawk (China) and dissolved into methylene chloride, which was subsequently dried over $MgSO_4$, then filtered and evaporated under reduced pressure. The resulting solid was recrystallized twice from methylene chloride/hexanes, yielding off-white crystals. The bifunctional initiators with the alcohol group for ring-opening polymerization and an alkoxyamine moiety for nitroxide-mediated radical polymerization (NMP) or a dithioester for reversible addition fragmentation and chain-transfer polymerization (RAFT) were synthesized according to literature procedures.[14,15] Styrene, methyl methacrylate, *N*,*N*-dimethylaminoethyl methacrylate, and ethyl acetate were distilled over CaH_2 prior to use.

Equilibrium Measurements of Triazolinylidene and Alkoxytriazoline. *(i) ^{1}H NMR Calibration with Ethylene Glycol.* A sealed NMR tube containing ethylene glycol was placed in the NMR apparatus. The machine was then set to the desired temperature and the lock/shim turned off. After choosing $CDCl_3$ as the solvent, a spectrum was recorded. The distance between the two peaks determines the NMR probe temperature. Once the probe is adjusted accordingly and the distance between ethylene glycol peaks gives the desired temperature, the ethylene glycol sample is removed and the experimental sample placed in the probe to be heated.

(ii) Preparation of Hexamethylbenzene Stock Solution. A hexamethylbenzene stock solution was made to be $^1/_6$ the concentration of alkoxytriazoline in solution. Alkoxytriazoline (0.01 g) was used in experiments. A typical NMR sample has a volume of 0.7 mL. $[\text{Alkoxytriazoline}]_0$ in NMR sample was calculated to be 0.0434 M, and the desired [hexamethylbenzene] to be 0.0072 M. Stock solution (0.010 L) was made.

(iii) Determination of the Equilibrium Constant between Triazolinylidene and Alkoxytriazoline. In the spectrum where alkoxytriazoline and triazolinylidene are at equilibrium, the adduct proton has an integration of 3.70. The alkoxytriazoline is represented in a doublet at 8.6 ppm with an integration of 1.71. Because this doublet represents 2 protons, one alkoxytriazoline proton has a value of 0.855 (1.71/2). Taking the integration value for the peak representing the mixture and subtracting the proposed integration value pertaining to the adduct methyl group gives the integration value representative of free methanol in solution, allowing the determination of the equilibrium constant (K) to be 0.15.

Synthesis of Polystyrene Macroinitiators by NMP. 2,2,5-Trimethyl-3-(4′-*p*-hydroxymethylphenylethoxy)-4-phenyl-3-azahexane (34.2 mg, 0.096 mmol and 17.1 mg, 0.048 mmol)[20] and styrene (0.500 g, 4.8 mmol) were transferred to two polymerization vessels, targeting DPs of 50 and 100. Oxygen was removed by three freeze−pump−thaw cycles. The reaction flasks were sealed under nitrogen and heated to 125 °C for 5.5 and 6.5 h respectively. Conversions were measured by ^{1}H NMR and found to be 75% and 70% for targeted DP = 50 and 100, respectively. The reaction mixture was diluted with methylene chloride and precipitated into methanol, filtered, and washed with methanol and hexanes. The resulting white powder was dried in a vacuum oven at 40 °C for two days and then stored in a glovebox. The yield was 310 mg (65%) for PS_{40} and 270 mg (55%) for PS_{70}. ^{1}H NMR ($CDCl_3$, δ): 0.42−0.94 (nitroxide), 1.21−2.06 (CH PS, CH_2 PS, CH_3 PLA), 2.65−2.82 (nitroxide), 3.68 (CH alcohol end group), 4.28 ($PhCH_2O$), 5.07−5.16 (CH PLA), 6.32−7.19 (C_6H_5 PS, nitroxide). GPC (RI): M_n (PDI) = 3900 g/mol (1.05); 6700 g/mol (1.06).

Synthesis of Poly(methyl methacrylate) Macroinitiator by RAFT. 4-Cyano-1-hydroxypent-4-yl-dithiobenzoate (14.9 mg, 56.2 μmol),[21] 4,4′-bisazo(4-cyanopentan-1-ol) (3.2 mg, 12.7 μmol), and methyl methacrylate (1.5 g, 15 mmol) were dissolved in dry toluene (0.5 g). The reaction flask was degassed by three freeze−pump−thaw cycles, sealed under nitrogen, and heated for 8 h at 60 °C. Conversion was measured by ^{1}H NMR, and the reaction mixture was precipitated into methanol. Filtering off the solids and washing with pentane yielded a pink solid that was dried in a vacuum oven. The yield was 715 mg (47%). Before transferring to a glovebox, the polymer was dried by azeotropic distillation of toluene (3×). ^{1}H NMR ($CDCl_3$, δ): 0.78−0.95 (CH_3 PMMA), 1.14−1.91 (CH_3 PLA, CH_2 PMMA), 3.53 (OCH_3 PMMA), 3.72 (CH−OH), 4.16 (OCH_2 ester initiating), 5.07−5.16 (CH PLA), 7.13−7.44 (aromatic). GPC (RI): M_n (PDI) = 14 100 g·mol^{-1} (1.08).

Synthesis of Poly(*N*,*N*-dimethylaminoethyl methacrylate) Macroinitiator by RAFT. 4-Cyano-1-hydroxypent-4-yl-dithiobenzoate (9.6 mg, 36.2 μmol),[21] 4,4′-bisazo(4-cyanopentan-1-ol) (2.2 mg, 8.7 μmol), and *N*,*N*-dimethylaminoethyl methacrylate (1.5 g, 9.5 mmol) were dissolved in dry ethyl acetate (2.5 g). The reaction flask was degassed by three freeze−pump−thaw cycles, sealed under nitrogen, and heated for 22 h at 60 °C. Conversion was measured by ^{1}H NMR, and the reaction mixture was precipitated into pentane. Filtering off the solids and washing with pentane yielded a red solid that was dried in a vacuum oven. The yield was 932 mg (61%). Before transferring to a glovebox, the polymer was dried by azeotropic distillation of toluene (3×). ^{1}H NMR ($CDCl_3$, δ): 0.83−0.99 (CH_3 PDMAEMA), 1.34−1.84 (CH_3 PLA, CH_2 PDMAEMA), 2.22 ($N(CH_3)_2$ PDMAEMA), 2.51 (CH_2N PDMAEMA), 4.00 (OCH_2 PDMAEMA, CH−OH), 4.14 (CH_2O ester initiating), 5.07−5.15 (CH PLA), 7.11−7.41 (aromatic). GPC (RI): M_n (PDI) = 15 700 g/mol (1.24).

Synthesis of Polystyrene-*block*-poly(DL-lactide), Poly(methyl methacrylate)-*block*-poly(DL-lactide), and Poly(*N*,*N*-dimethylaminoethyl methacrylate)-*block*-poly(DL-lactide). PS_{40}−OH (80 mg), PS_{40}−OH (40 mg), PS_{70}−OH (70 mg), $PMMA_{140}$−OH (100 mg), and $PDMAEMA_{100}$−OH (100 mg) were first transferred to vials containing 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2-triazol-5-ylidene (5.0, 2.5, 2.5, 2.0, and 2.0 mg, respectively) in dry toluene (0.5, 0.5, 0.25, 0.25, and 0.25 mL, respectively). After complete dissolution, DL-lactide (36, 72, 36, 100, and 100 mg, respectively) was added, resulting in a light-yellow suspension. The reaction flask was sealed and subsequently heated to 90 °C for 14, 24, 14, 48, and 48 h, respectively. A drop of CS_2 was added under inert atmosphere, and the reaction mixture was dialyzed against acetone. The copolymers were isolated by precipitation in hexane and dried in a vacuum oven. See Table 3 for results.

Dendritic Building Blocks: General Procedures. *[g-1] Acetonide-Protected bis-MPA.* Bis-MPA (50.0 g, 373 mmol), 2,2-dimethoxypropane (58.0 g, 557 mmol), and *p*-toluenesulfonic acid monohydrate (*p*-TSA; 1.4 g, 7 mmol) were mixed together in 200 mL of acetone. The mixture was stirred for 1 h and neutralized with NH_3/EtOH. After evaporation of the acetone, the mixture was dissolved in CH_2Cl_2 and washed three times with 75 mL of water. The combined organic phases were dried over $MgSO_4$, and the organic solvents were distilled off to yield 55.0 g (316 mmol, 85%) of acetonide-protected bis-MPA **(xx1)**. ^{1}H NMR ($CDCl_3$, δ): 1.18 (s, 3H, $-CH_3$), 1.38 (s, 3H, $-CH_3$), 1.41 (s, 3H, $-CH_3$), 3.64 (d, 2H, $-COCH_2-$, $J = 11.9$ Hz), 4.16 (d, 2H, $-COCH_2-$, $J = 11.9$ Hz). ^{13}C NMR ($CDCl_3$, δ): 18.4, 22.3, 24.9, 41.7, 65.8, 98.3, 180.1.

(g-1)$_p$ Benzyl-Protected bis-MPA. Bis-MPA (75.0 g, 521 mmol) and KOH (31.8 g, 567 mmol) were dissolved in 100 mL of dimethylformamide (DMF). After 1 h at 110 °C, benzyl chloride (75.1 g, 592 mmol) was slowly added. The mixture was allowed to react for 14 h. DMF was distilled off, and the residue was dissolved in CH_2Cl_2 and three times extracted with 75 mL of water. The crude product was purified by recrystallization from toluene. After evaporation of the toluene, the product was purified by column chromatography on silica gel with ethyl acetate/hexane to yield a total of 68.8 g (307 mmol, 59%) of **xx2** in the form of white crystals. ^{1}H NMR ($CDCl_3$, δ): 1.06 (s, 3H, $-CH_3$), 3.70 (d, 2H, $-CH_2OH$, $J = 11.3$ Hz), 4.90 (d, 2H, $-CH_2OH$, $J = 11.3$ Hz), 5.18 (s, 2H, $-COOCH_2Ph$), 7.27−7.39 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 17.1, 49.3, 66.7, 68.1, 127.8, 128.3, 128.6, 135.7, 175.7.

[g-2]$_p$ Acetonide- and Benzyl-Protected Second-Generation Dendron and a General Procedure for DCC/DPTS Coupling. (g-1)p **(xx2)** (22.4 g, 100 mmol) and [g-1] **(xx1)** (40.0 g, 230 mmol) were dissolved in 500 mL of CH_2Cl_2 and 5 mL of dried pyridine and heated until totally dissolved. 1,3-Dicyclohexylcarbodiimide (DCC; 47.4 g, 230 mmol) and 4-(dimethylamino)pyridinum-4-toluenesulfonate (DPTS; 21.5 g, 69 mmol) were added and stirred for 16 h. The solution was filtered, diluted with CH_2Cl_2, and washed three times with 300 mL of saturated NH_4Cl solution. The combined organic phases were dried over $MgSO_4$ and evaporated. The viscous oil was redissolved in ethyl acetate, cooled in liquid nitrogen, and then cold filtered. Evaporation of the organic solvent yielded 54.0 g of a transparent, slightly yellow oil. The crude product was purified by column chromatography on silica gel with ethyl acetate/hexane. The column was neutralized with 10% triethylamine/hexane in order to prevent the cleavage of the acetonide protection group. Yield: 45.4 g (85 mmol, 85%) as a clear oil that crystallized after several days. ^{1}H NMR ($CDCl_3$, δ): 1.07 (s, 6H, $-CH_3$), 1.23 (s, 3H, $-CH_3$), 1.32 (s, 6H, $-CH_3$), 1.38 (s, 6H, $-CH_3$), 3.55 (d, 4H, $-COCH_2-$, $J = 11.8$ Hz), 4.08 (d, 4H, $-COCH_2-$, $J = 11.9$ Hz), 4.36 (s, 4H, $-COOCH_2-$), 5.13 (s, 2H, $-COOCH_2Ph$), 7.23−7.31 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 17.7, 18.5, 22.4, 24.8, 42.0, 46.8, 65.4, 65.9, 66.9, 98.1, 128.2, 128.4, 128.6, 135.5, 172.4, 173.5.

[g-2] Acetonide-Protected Second-Generation Dendron (xx10) and a General Procedure for Deprotection of the Benzyl Protection Group. [g-2]$_p$ **(xx9)** (13.6 g, 25 mmol) was dissolved in 100 mL of THF and 100 mL of ethyl acetate. Under N_2 (g) flow, 1.0 g Pd/C (10 wt %) was added to the reaction flask. The apparatus for catalytic hydrogenolysis was filled with H_2 (g) at 30 PSI, and the reaction mixture was shaken for 6 h. The Pd/C was filtered off and the solvents evaporated to yield 11.5 g (25 mmol, 100%) of a clear viscous oil that crystallized after several days. No further purification was necessary. ^{1}H NMR ($CDCl_3$, δ): 1.13 (s, 6H, $-CH_3$), 1.26 (s, 3H, $-CH_3$), 1.33 (s, 6H, $-CH_3$), 1.39 (s, 6H, $-CH_3$), 3.60 (d, 4H, $-COCH_2-$, $J = 11.9$ Hz), 4.14 (d, 4H, $-COCH_2-$, $J = 11.8$ Hz), 4.31 (s, 4H, $-COOCH_2-$). ^{13}C NMR ($CDCl_3$, δ): 17.6, 18.5, 22.3, 24.9, 42.1, 46.5, 65.1, 65.9, 98.2, 173.5, 176.8.

Dendritic Initiator Synthesis. Initiators [g-3]-M, [g-1]-d, [g-2]-d, and [g-3]-d were prepared according to literature procedures.

[g-3]-M. ^{1}H NMR ($CDCl_3$, δ): 1.11 (s, 12H, $-CH_3$), 1.25 (s, 6H, $-CH_3$), 1.27 (s, 3H, $-CH_3$), 1.32 (s, 12H, $-CH_3$), 1.39 (s, 12H, $-CH_3$), 3.59 (d, 8H, $-COCH_2-$, $J = 12.0$ Hz), 3.80 (t, 2H, $-OCH_2CH_2OH$), 4.12 (d, 8H, $-COCH_2-$, $J = 11.8$ Hz), 4.19 (t, 2H, $-OCH_2CH_2OH$), 4.29 (s, 12H, $-COOCH_2-$). ^{13}C NMR ($CDCl_3$, δ): 17.6, 18.5, 22.0, 25.2, 42.1, 46.7, 46.9, 60.7, 65.0, 65.9, 66.2, 98.1, 171.9, 172.4, 173.6.

[g-3]-D. ^{1}H NMR ($CDCl_3$, δ): 0.85 (s, 3H, $-CH_3$), 1.11 (s, 12H, $-CH_3$), 1.26 (s, 6H, $-CH_3$), 1.27 (s, 3H, $-CH_3$), 1.33 (s, 12H, $-CH_3$), 1.39 (s, 12H, $-CH_3$), 3.56 (s, 4H, $-CH_2OH$), 3.60 (d, 8H, $-COCH_2-$, $J = 12.0$ Hz), 4.13 (d, 8H, $-COCH_2-$, $J = 11.8$ Hz), 4.19 (s, 2H, $-COOCH_2-$), 4.30 (s, 12H, $-COOCH_2-$). ^{13}C NMR ($CDCl_3$, δ): 16.9, 17.7, 18.5, 22.0, 25.2, 40.5, 42.1, 46.9, 65.0, 65.9, 66.2, 67.4, 98.2, 171.9, 172.4, 173.6..

General Polymerization Procedure for Lactide. Table 1, entry 5. In a glovebox, a vial equipped with a stir bar was charged with L-lactide (0.2 g, 1.39 mmol), 4-pyrene-1-butanol (2.6 mg, 9.5 μmol), **1** (2.8 mg, 9.5 μmol), and toluene (1.4 mL). The sealed vial was stirred at 90 °C in an oil bath. After 113 h, the reaction was cooled to room temperature and quenched with a few drops of carbon disulfide.

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Supporting Information Available: Adduct thermal stability and kinetic studies are provided. This material is available free of charge via the Internet at http://pubs.acs/org.

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