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Synthesis of Polybutadiene−Polylactide Diblock Copolymers Using Aluminum Alkoxide Macroinitiators. Kinetics and Mechanism

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ABSTRACT: Polybutadiene−polylactide block copolymers were prepared using well-defined hydroxy-terminated polybutadiene (PBD-OH). PBD-OH samples were reacted with $AlEt_3$ at various $[PBD\text{-}OH]_0/[AlEt_3]_0$ ratios to form the corresponding aluminum alkoxide macroinitiators. Controlled polymerization of lactide was performed using these macroinitiators. The polylactide molecular weight grows linearly with lactide conversion at $[PBD\text{-}OH]_0/[AlEt_3]_0$ ratios between 1 and 6 and polymerization temperatures between 70 and 120 °C. Narrow molecular weight distribution block copolymers were obtained under all conditions investigated if the conversion of lactide was kept below 90%. The kinetics of lactide polymerization were investigated at various $[PBD\text{-}OH]_0/[AlEt_3]_0$ ratios. At fixed $[PBD\text{-}OH]_0$ using less $AlEt_3$ resulted in significant enhancement in the lactide polymerization rate. We attributed this behavior to the aggregation of active species in the polymerization. While the absolute propagation rate constants for the lactide polymerization using monoalkylaluminum bisalkoxide and the aluminum trisalkoxide were similar, increased aggregation of the former lowered the instantaneous concentration of active species and thus lowered polymerization rates.

Introduction

The preparation of block copolymers generally requires the use of living or controlled polymerizations if narrow molecular weight distributions, prescribed molecular weights, and control over the component volume fractions are desired. For fundamental studies on block copolymer self-assembly,[1] control of these molecular parameters is critical. Although many block copolymer systems have been prepared using living or controlled polymerizations, the range of block copolymers available using these techniques is limited. This is because most block copolymers are prepared by sequential addition of monomers to a single type of active species. For example, polystyrene−polybutadiene block copolymers are routinely synthesized by first the anionic polymerization of styrene followed by the anionic polymerization of butadiene.[2] Styrene and butadiene are a “mechanistically compatible” pair of monomers. The same is true for isobutylene and vinyl ethers in cationic polymerization[3] and substituted norbornene pairs in ring-opening metathesis polymerization.[4]

The combination of “mechanistically incompatible” monomers into a single block copolymer increases the variety of synthetically accessible block copolymers. Transformation of one type active center to another allows the linking of polymeric segments that have been traditionally restricted to one class of materials. For example, the combination of living ring-opening metathesis polymerization and aldol group transfer polymerization led to the formation of polynorbornene−poly(vinyl alcohol) block copolymers, materials that are not accessible using just one polymerization technique.[5] Since these types of transformation reactions were reviewed in 1989,[6] there have been many examples that combine two chemically distinct polymerization mechanisms, either sequentially[7] or simultaneously,[8] for the preparation of one block copolymer. We recently reported the preparation of polyisoprene−polylactide block copolymers using a combination of living anionic polymerization (isoprene) and controlled “coordination-insertion” polymerization (lactide) sequentially.[9,10]

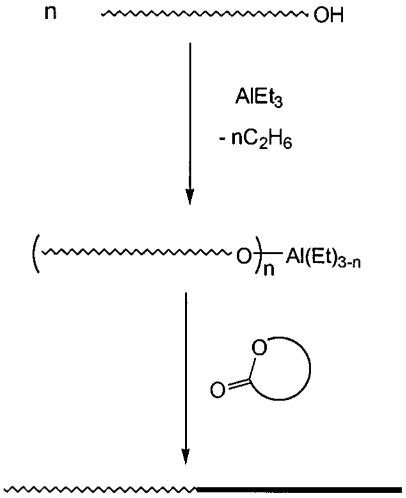

Figure 1. Synthetic protocol for the preparation of block copolymers using hydroxyl functionalized polymers and the aluminum alkoxide-initiated polymerization of cyclic esters.

The synthesis of the polyisoprene−polylactide block copolymers required the preparation of hydroxyl-terminated polyisoprene (PI-OH). A corresponding aluminum alkoxide-terminated species, prepared by the reaction with triethylaluminum, was employed as a macroinitiator for the polymerization of lactide. The use of hydroxyl end-functionalized polymers as precursors to aluminum alkoxide macromolecular initiators for the ring-opening polymerization of cyclic esters is an established technique.[11] The generic protocol we used is shown in Figure 1. A critical feature of this synthetic scheme is the use of an aluminum reagent that reacts cleanly and efficiently with the hydroxyl-functionalized polymer. Any byproducts should not interfere with the subsequent polymerization, and there should be no

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impurities in either the hydroxyl-functionalized polymer or the aluminum reagent that will be detrimental to the overall synthetic scheme. Alkylaluminum compounds will react with alcohols to yield the corresponding aluminum alkoxides and innocuous alkane byproducts.[12] Either one, two, or three polymeric aluminum alkoxide arms should initiate the cyclic ester polymerization, and any excess aluminum alkyl groups will not under anhydrous conditions.[13,14] Therefore, the reaction of triethylaluminum ($AlEt_3$) with hydroxyl end-functionalized polymers is an ideal system for the formation of discrete block copolymers containing polymers derived from cyclic esters such as lactide or caprolactone.

In our work with PI−OH, we showed evidence for the formation of the diethylaluminum monoalkoxide (PI−O−$AlEt_2$) in the equimolar reaction of $AlEt_3$ and PI−OH.[9] Using this protocol, 1 mol of $AlEt_3$ is required for 1 mol of block copolymer. Since there are three potential reactive sites in $AlEt_3$, 1 mol of $AlEt_3$ could potentially be used for the preparation of at least 3 mol of block copolymer. In addition, the polymerization of lactide using these PI−O−$AlEt_2$ macroinitiators was carried out at 70 °C for 4−6 days. Higher reaction temperatures were avoided because of possible transesterification reactions,[15] but we did not investigate the effect of temperature on the rate and control of the polymerization in these systems. Although the synthetic protocol we reported was successful for the formation of model block copolymers, there are deficiencies that prompted us to investigate the kinetics and mechanism for the general preparation of polydiene−polylactide block copolymers.

We have shifted our efforts toward the use of hydroxyl-terminated polybutadiene (PBD-OH) as the precursor for the formation of polybutadiene−polylactide block copolymers using the protocol shown in Figure 1. Since the glass transition (T_g) temperature of PBD is about −100 °C, 40 °C lower than the T_g of PI,[16] and PBD has been used in a variety of toughening applications (e.g., HIPS, ABS, and SBS), we are exploring the use of PBD for the toughening of PLA. After preparing and characterizing PBD-OH, we synthesized a variety of block copolymers using macroinitiators prepared at several $[\text{PBD-OH}]_0/[AlEt_3]_0$ ratios. The control of these polymerizations along with the kinetics was then investigated. From this work we have uncovered significant improvements in the synthesis of polydiene−polylactide block copolymers.

Experimental Section

Materials. 1,3-Butadiene (Aldrich, 99+%) was distilled twice from *n*-butyllithium (Aldrich) under reduced pressure. Ethylene oxide (Aldrich, 99.5+%) was purified by sequential reduced pressure distillations from calcium hydride (Aldrich, powder/40 mesh, 90−95%) and dibutylmagnesium (Aldrich). *sec*-Butyllithium (Aldrich, 1.3 M in cyclohexane) was used as received, and the concentration was determined by the Gilman double-titration method.[17] DL-Lactide (Aldrich) was recrystallized from ethyl acetate and dried at room temperature for 24 h under reduced pressure and was stored in drybox. Triethylaluminum ($AlEt_3$, Aldrich, 1.9 M solution in toluene) was used as received, and the concentration was verified by ^1H NMR analysis of the reaction product between equimolar $AlEt_3$ and 1-propanol. Degassed cyclohexane for the anionic polymerization of butadiene and toluene for the ring-opening polymerization of DL-lactide were rigorously purified by passing through an activated alumina column and through a supported copper catalyst.[18] The solvent system was interfaced with a Schlenk manifold for anhydrous/anaerobic collection. Toluene-d_8 (Aldrich 99.6%) was dried over CaH_2, distilled under N_2, and stored in a drybox prior to use.

Measurements. ^1H NMR spectra were recorded on a Varian INOVA 500 MHz NMR spectrometer. Samples of the prepolymer and macroinitiator were prepared by dissolving approximately 30 mg of polymer in 1 mL of toluene-d_8. Samples of block copolymer were prepared by dissolving approximately 30 mg of polymer in 1 mL of deuterated chloroform (Cambridge Isotope Laboratories). Size exclusion chromatography analyses were performed on a Hewlett-Packard 1100 series liquid chromatograph equipped with a Hewlett-Packard 1047A refractive index detector and three Jordi poly(divinylbenzene) columns of 10^4,10^3, and 500 Å pore sizes. THF was used as the mobile phase (40 °C and 1 mL/min), and column calibration was performed with polystyrene standards (Polymer Laboratories).

Synthesis of PBD-OH Prepolymer. A general polymerization following previously reported procedure is described as follows: A 3L glass reactor was equipped with five internal ACE-THREDS threaded glass connectors and a Teflon-coated magnetic stir bar. Using Ace Glass bushings and FETFE O-rings, the reactor was fitted with three glass plugs, one glass thermowell, and one Y-connector. The Y-connector was equipped with three ports: one capped with a Teflon-coated septum and two with Teflon-capped valves interfaced to a vacuum/argon manifold and a pressure guage. The sealed reactor was evacuated to 10^{-3} Torr and heated overnight to 270 °C. After cooling the glass plugs were replaced (under a positive pressure of argon) with pretared burets of purified butadiene (92.5 g, 1.71 mol), purified ethylene oxide (30.0 g, 0.68 mol), and an air-free flask containing approximately 1 L of dry cyclohexane ($[\text{butadiene}]_0 \approx 1.7$ M). The reactor was evacuated and backfilled with argon five times, after which the pressure was set to 2 psig and the reactor was isolated from the manifold. The pressure was monitored to ensure the absence of leaks. Cyclohexane (≈1 L) was added to the reactor, followed by the addition of *sec*-butyllithium (14 mL of a 1.33 M cyclohexane solution, 18.6 mmol) through the Teflon-coated septum using a syringe. The butadiene was slowly added to the reaction flask. The flask was immersed in a water bath which was heated to 45 °C over 30 min. The reaction solution was stirred for 5 h at 45 °C. The temperature of the water bath was lowered to 25 °C over 30 min, and then ethylene oxide was added at a steady rate. The reaction was allowed to stir overnight at room temperature. The reaction was quenched with acidic methanol (3 mL of concentrated HCl in 50 mL of methanol). The product was precipitated in 3 L of a 50/50 mixture (by volume) of methanol/2-propanol; the precipitated product was washed with distilled water until the washings were neutral and subsequently dried under vacuum at 80 °C overnight. The isolated yield of polymer was 88.8 g (94.6%). From ^1H NMR spectroscopy end group analysis, the $M_n = 5.3$ kg/mol. This value compared favorably with the targeted molecular weight predicted from the reaction stoichiometry ($M_n = 5.1$ kg/mol). SEC analysis: $M_n = 9.0$ kg/mol and $M_w/M_n = 1.02$. ^1H NMR δ ppm (multiplicity, identity, integration): 5.4 (m, $CH_2{-}C\mathbf{H}{=}C\mathbf{H}{-}CH_2{-}$ and $CH_2{=}C\mathbf{H}{-}CH{-}$, 3146), 4.9 (m, $C\mathbf{H_2}{=}CH{-}CH{-}$, 270), 2.0 (b, $C\mathbf{H_2}{-}CH{=}CH{-}C\mathbf{H_2}{-}$ and $CH_2{=}CH{-}C\mathbf{H}{-}$, 6086), 1.2 (m, $CH_2{=}CH{-}C(R)H{-}C\mathbf{H_2}{-}$, 344; includes intensity from initiator), 0.9 (m, $-C\mathbf{H_3}$ resonances from initiator, 103), 3.3−3.5 (m, $-C\mathbf{H_2}{-}OH$, 34.3), 0.5 (m, $-CH_2{-}O\mathbf{H}$, 15.8) (this resonance disappeared after adding D_2O or trifluoroacetic anhydride to the NMR tube). The resonances between 3.3 and 3.5 ppm shifted to 3.8−4.0 ppm after adding trifluoroacetic anhydride ($-C\mathbf{H_2}{-}OCOCF_3$).

Formation of Aluminum Alkoxide Macroinitiator. A typical reaction is described as follows: In a glovebox, a Teflon-coated stir bar, previously prepared 5.3 kg/mol PBD-OH (0.32 g, 0.06 mmol), and toluene (9.3 mL) were added to a dry 48 mL Chemglass high-pressure vessel equipped with an internal thread. A 1.9 M solution of $AlEt_3$ in toluene (15.8 μL, 0.03 mmol) was slowly added to the flask using a syringe, and the mixture was allowed to stir for 2 h at room temperature.

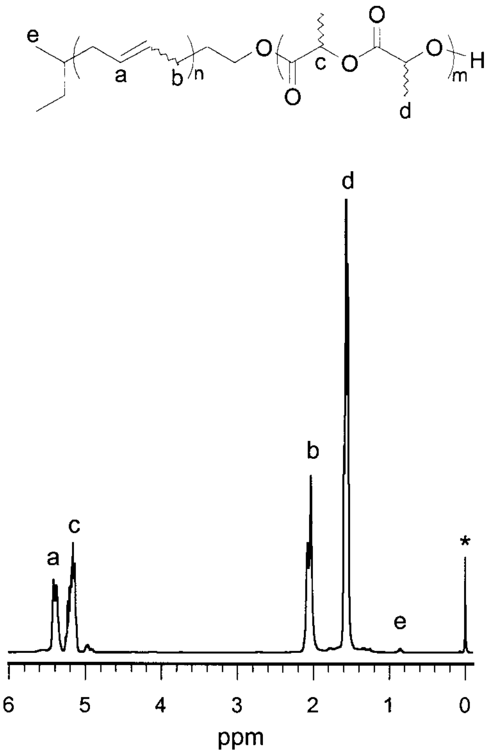


Figure 2. ^{1}H NMR spectrum (CDCl$_3$, RT) of a PBD−PLA diblock copolymer (see Experimental Section). The * denotes reference resonance from TMS.

Ring-Opening Polymerization of Lactide. A typical polymerization process is as follows: After formation of the above macroinitiator, DL-lactide (1.34 g, 9.3 mmol) was added to the flask in drybox. The flask was sealed with a Teflon bushing fitted with a Viton O-ring, removed from the glovebox, and immersed into an oil bath at 90 °C. After 6 h the reaction was quenched with 0.25 mL of 2 N HCl (8-fold molar excess with respect to aluminum), and the block copolymer was precipitated in cold (0 °C) methanol and subsequently dried under vacuum at 80 °C for about 24 h. The yield of dried block copolymer was 1.55 g (91.8% conversion of DL-lactide assuming complete recovery of polybutadiene). SEC analysis $M_n = 34.3$ kg/mol and $M_w/M_n = 1.15$. ^{1}H NMR δ ppm (multiplicity, identity, integration): 5.2 (m, $-C(O)-C(\mathbf{H})(CH_3)-O-$, 1665), 1.6 (m, $-C(O)-C(H)(C\mathbf{H}_3)-O-$, 5000) for the PLA block; 5.4 (m, $-CH_2-C\mathbf{H}{=}C\mathbf{H}-CH_2-$ and $CH_2{=}C\mathbf{H}-CH-$, 1109), 4.9 (m, $C\mathbf{H}_2{=}CH-CH-$, 99), 2.0 (b, $C\mathbf{H}_2-CH{=}CH-C\mathbf{H}_2-$ and $CH_2{=}CH-C\mathbf{H}-$, 2089) for the PBD block (see Figure 2).

Results

Synthesis of PBD-OH. The anionic polymerization of butadiene followed by the reaction with ethylene oxide is an established method for the preparation of hydroxyl-terminated polybutadiene PBD-OH in high yield, with near quantitative functionalization (i.e., one hydroxyl group per chain) and with narrow molecular weight distributions.[19−22] We have prepared a variety of PBD-OH samples using this technique (Table 1). The number-average degree of polymerization (X_n) calculated by reaction stoichiometry compared favorably with the molecular weight determined by ^{1}H NMR spectroscopy end group analysis. The average molecular weight (M_n) of the PBD-OH samples was calculated using the X_n value from NMR spectroscopy, the molecular weight of the butadiene repeat unit, the molecular weight of the initiator fragment, and the molecular weight of the hydroxyl end group ($-CH_2CH_2OH$). A combination of an alkyllithium initiator with a nonpolar solvent yields PBD containing over 90% of the 1,4 regioisomer, and all the samples we prepared contained between 91% and 93% of the 1,4 regioisomer by ^{1}H NMR spectroscopy. The PBD-OH samples also exhibited narrow molecular weight distributions ($M_w/M_n \leq 1.04$) by SEC. The PBD-OH used for most of the studies below (unless noted) was the material with an overall molecular weight of 5.3 kg/mol (entry 2, Table 1).

Table 1. Characterization of PBD-OH Samples[a]

entry	$[M]_0/[I]_0$	X_n[b]	$M_n \times 10^{-3}$ [b]	$M_n \times 10^{-3}$ [c]	PDI[c]	[OH]/[*s*-Bu][d]	% 1,4[d]
1	45	47	2.6	4.7	1.03	0.99	91.0
2	92	97	5.3	9.0	1.02	1.00	91.9
3	184	184	10.0	15.2	1.02	0.98	92.1
4	351	350	19.0	34.7	1.02	1.00	92.9
5	527	533	28.9	53.0	1.04	0.98	92.5

[a] Polymerization of butadiene in cyclohexane at 45 °C for 5 h using *sec*-butylithium as initiator, end-capped with EO, and quenched with acidic methanol. All samples were isolated in greater than 94% yield (See Expermental Section). [b] Calculated using *sec*-butylithium end group analysis from ^{1}H NMR spectroscopy. [c] SEC vs polystyrene standards. [d] Determined by ^{1}H NMR spectroscopy.

Ring-Opening Polymerization of DL-Lactide. With the PBD-OH prepared above, we used triethylaluminum (AlEt$_3$) to form the macroinitiator for the polymerization of DL-lactide (**L**).[23] Alcohols are effective chain transfer agents in aluminum alkoxide-catalyzed polymerizations of cyclic esters, and [R−OH]/[Al] ratios as high as 1000 can be used without broadening of the molecular weight distribution,[24,25] although the polymerization is extremely slow. Anticipating that any excess (unreacted) PBD-OH would act as a chain transfer agent and still be effective for block copolymer formation, we investigated $[\text{PBD-OH}]_0/[\text{AlEt}_3]_0$ (ξ) ratios between 1 and 6. In a typical polymerization, the selected concentrations of PBD-OH and AlEt$_3$ were allowed to react in toluene for a set time and temperature, and then **L** was added to the reaction flask and allowed to polymerize for a set time. After the polymerization, the reaction was quenched with dilute HCl, and the polymer was precipitated in methanol and dried under vacuum. Figure 2 shows a ^{1}H NMR spectrum of a representative PBD-PLA block copolymer.

In a typical polymerization, $[\mathbf{L}]_0 = 1$ M, $[\text{PBD-OH}]_0 = 6.5 \times 10^{-3}$ M, $[\mathbf{L}]_0/[\text{PBD-OH}]_0 = 154$, and $T = 90$ °C. Using these conditions, the number-average degree of polymerization for the PLA block (X_n) and the polydispersity index (PDI) for the block copolymer as a function of conversion for various ξ ratios are shown in Figure 3 and Figure 4, respectively. For all of the ξ ratios examined we observed a linear relationship between the X_n for the PLA block and the **L** conversion (Figure 3), and the slope of this line compared favorably with the predicted relationship for a controlled polymerization in which all of the PBD-OH chains initiate the **L** polymerization. The PDIs for the block copolymers are narrow (<1.15) at conversions less than 90%, but as the conversion increases, the PDIs begin to broaden (Figure 4). Figure 5 shows the SEC results for block copolymers prepared using $\xi = 2$. At low conversions there was no PBD-OH contamination by SEC, indicating that nonfunctional PBD was virtually nonexistent and the initiation efficiency at $\xi = 2$ was excellent.[26] At conversions greater than 90% depolymerization and transesterification compete effectively with polymerization, and the molecular weight distribution broadens.[15,27,28] We

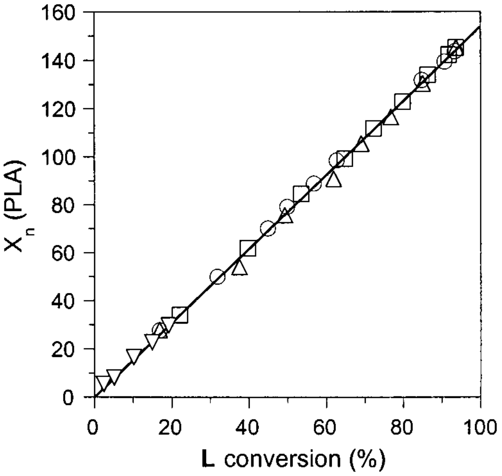


Figure 3. Relationship between degree of **L** polymerization (X_n) and **L** conversion. X_n was calculated from ^{1}H NMR spectroscopy. Conversion of lactide was obtained from mass of recovered polymer. Polymerization conditions: toluene, $[\mathbf{L}]_0/[\text{PBD-OH}]_0 = 154$, $M_n(\text{PBD-OH}) = 5.3 \times 10^3$ g/mol (entry 2 in Table 1), $[\text{PBD-OH}]_0 = 6.5 \times 10^{-3}$M, $[\mathbf{L}]_0 = 1$ M, temperature = 90 °C, $[\text{PBD-OH}]_0/[\text{AlEt}_3]_0 = 1$ (○), 2 (□), 3 (△), 6 (▽).The solid line is the theoretical relationship between X_n and conversion assuming 100% initiator efficiency.

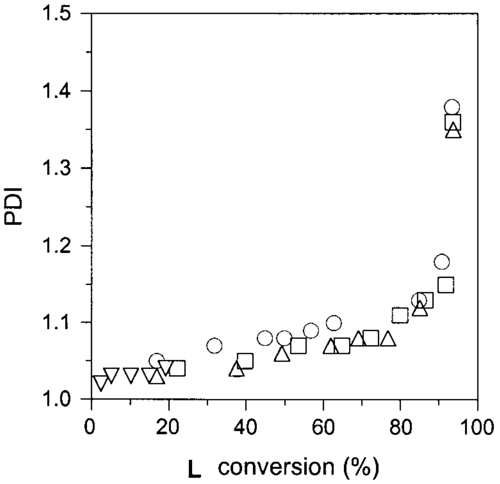


Figure 4. Relationship between molecular weight distribution (PDI) and **L** conversion. PDI was calculated from SEC, and conversion of lactide was obtained from mass of recovered polymer. Polymerization conditions are given in the caption for Figure 3.

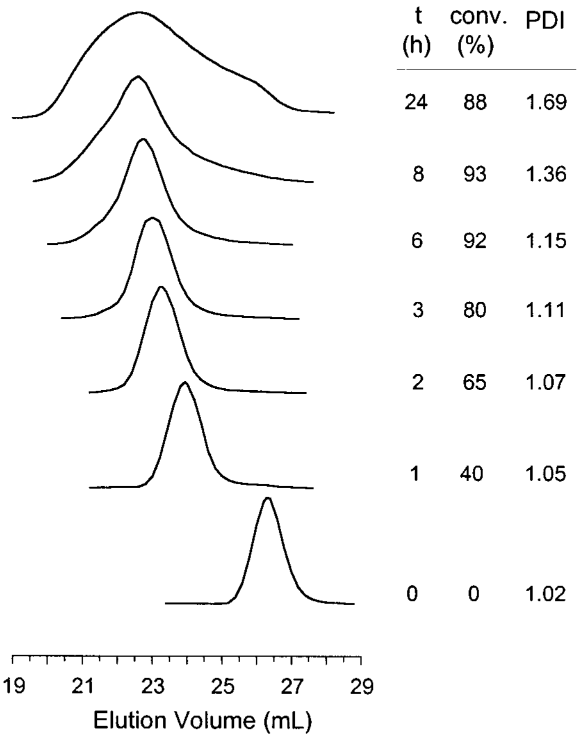


Figure 5. SEC traces of **L** polymerization at different times. Polymerization conditions: toluene, $[\mathbf{L}]_0/[\text{PBD-OH}]_0 = 154$, $M_n(\text{PBD-OH}) = 5.3 \times 10^3$ g/mol (entry 2 in Table 1), $[\mathbf{L}]_0 = 1$ M, temperature = 90 °C, $[\text{PBD-OH}]_0/[\text{AlEt}_3]_0 = 2$.

Table 2. Ring-Opening Polymerization of Lactide with Macroinitiators Derived from Various PBD-OH Samples[a]

$M_n \times 10^{-3}$ (PBD-OH)	conversion[b] (%)	$M_n \times 10^{-3}$ (PLA)[c]	$M_n \times 10^{-3}$ (total)[c]	PDI[d]
2.6	58	13.0	15.6	1.09
5.3	54	12.1	17.4	1.09
10.0	63	14.2	24.2	1.10
19.0[e]	82	3.6	22.6	1.08
28.9	50	11.0	39.9	1.10

[a] Polymerization conditions: toluene, $[\text{PBD-OH}]_0/[\text{AlEt}_3]_0 \approx 1$, 105 °C, 1.5 h, $[\mathbf{L}]_0 = 1$ M, $[\text{PBD-OH}]_0 = 6.5 \times 10^{-3}$ M. [b] Calculated from mass. [c] Calculated from ^{1}H NMR spectroscopy using ratio of integration values from the main chain of the block copolymer. [d] Calculated from SEC. [e] $[\text{PBD-OH}]_0/[\text{AlEt}_3]_0 \approx 2$, $[\mathbf{L}]_0 = 0.2$ M, $[\text{PBD-OH}]_0 = 6.5 \times 10^{-3}$ M, 90 °C, 4 h.

have also prepared PBD-PLA block copolymers using other PBD-OH starting materials, and Table 2 gives representative results for these block copolymers.

PBD-PLA block copolymers can be easily prepared at a variety of ξ ratios. Even at $\xi = 6$ (Figures 3 and 4) all of the PBD-OH chains initiated polymerization, there was linear growth of the PLA molecular weight, and the PDIs of the resultant block copolymers were below 1.05 at low conversion. Invoking the coordination insertion mechanism generally accepted for the polymerization of **L** with aluminum alkoxide initiators,[29] equilibration between growing aluminum alkoxide species and unreacted PBD-OH (eq 1) is fast relative to polymerization.

$$\rangle\mathrm{Al{-}OP} + \mathrm{HO}\mathbf{P} \rightleftharpoons \rangle\mathrm{Al{-}O}\mathbf{P} + \mathrm{HOP} \qquad (1)$$

In other literature reports using polymeric alcohols and AlEt_3 to prepare macroinitiators for the polymerization of cyclic esters, the ξ ratio has almost exclusively been 1.[11,29,30] Since purification of the PBD−PLA copolymers is necessary for many structure/property relationship studies, using less AlEt_3 in the block copolymerizations described here is beneficial and is clearly effective for the formation of pure block copolymers. However, using less AlEt_3 can lead to differences in the polymerization kinetics.

Kinetics of DL-Lactide Polymerization. Although the generally accepted protocol for aluminum alkoxide initiated polymerizations of **L** is to perform the polymerization below 70 °C to avoid transesterifcation side reactions,[31] our results suggest that at 90 °C the polymerization is well-behaved and the PDI can be kept below 1.15 if the conversion of **L** is controlled. Therefore, we examined the kinetics of the polymerization at a variety of temperatures using $\xi = 1$.

Depolymerization competes with polymerization at high monomer conversions, and determination of the equilibrium **L** concentration ($[\mathbf{L}]_{eq}$) is necessary for evaluation of the polymerization kinetics. The equilibrium concentration of lactide as a function of temper-

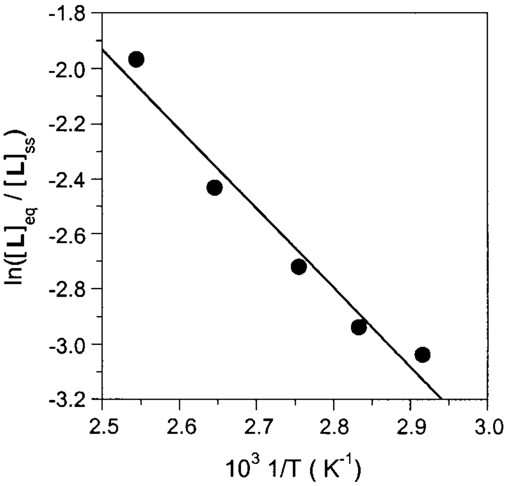


Figure 6. Equilibrium monomer concentration for the polymerization of **L** in toluene at various temperatures ($[\mathbf{L}]_{ss}$ = 1 M).

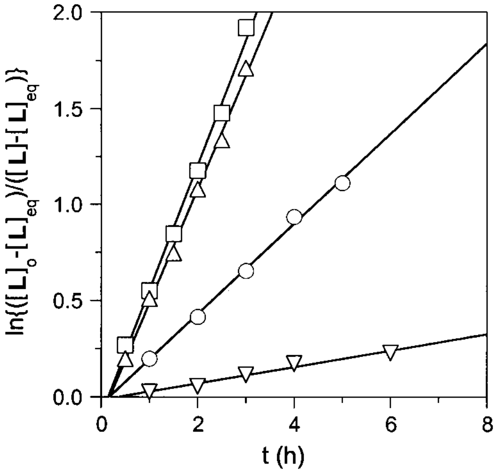


Figure 7. Kinetics of **L** ring-opening polymerization initiated with PBD macroinitiators at various $[\text{PBD-OH}]_0/[\text{AlEt}_3]_0$ ratios. Polymerization conditions are given in the caption for Figure 3.

ature for the polymerization of **L** in 1,4-dioxane has been measured by Penczek.[27] All the polymerizations reported here were performed in toluene so we measured $[\mathbf{L}]_{eq}$ as a function of temperature (Figure 6). Using a standard state lactide concentration $[\mathbf{L}]_{ss}$ of 1 M and the following equation

$$\ln([\mathbf{L}]_{eq}/[\mathbf{L}]_{ss}) = \frac{\Delta H°}{RT} - \frac{\Delta S°}{R} \qquad (2)$$

where $\Delta H°$ and $\Delta S°$ are the standard state polymerization enthalpy and entropy, respectively. We calculated $\Delta H° = -23.9$ kJ mol^{-1} and $\Delta S° = -43.8$ J mol^{-1} K^{-1}. These values are in excellent agreement with the values calculated by Duda and Penczek for the polymerization of lactide in dioxane ($\Delta H° = -22.9$ kJ mol^{-1} and $\Delta S° = -41.1$ J mol^{-1} K^{-1}). The calculated enthalpy and entropy led to a $[\mathbf{L}]_{eq}$ of 0.011 M at 20 °C, 0.045 M at 70 °C, and 0.129 M at 120 °C. We calculated a ceiling temperature of 273 °C for $[\mathbf{L}]_0$ = 1 M and 355 °C for $[\mathbf{L}]_0$ = 2 M.[32]

Table 3. Apparent Propagation Rate Constants for L Polymerizations[a]

entry	$[\text{PBD-OH}]_0/[\text{AlEt}_3]_0$	$[\text{AlEt}_3]_0 \times 10^3$ (M)	T (°C)	$k_{app} \times 10^5$ (s^{-1})[b]	$t_{0.5}$ (h)[c]
1	1	6.5	70	2.2	9.5
2	1	6.5	80	3.2	6.5
3	1	6.5	90	6.6	3.2
4	1	6.5	105	21.5	1.0
5	1.5	4.3	90	17.6	1.2
6	2	3.3	90	18.1	1.1
7	2[d]	6.5	120	116.1	0.2
8	3	2.2	90	16.4	1.3
9	6	1.1	90	1.2	17.8

[a] Polymerization conditions: toluene solvent, $[\mathbf{L}]_0$ = 1 M, $[\mathbf{L}]_0/[\text{PBD-OH}]_0$ = 154, M_n of PBD-OH = 5.3 × 10^3 (entry 2 in Table 1), [PBD-OH] = 6.5 × 10^{-3} M. [b] $k_{app} = \ln[([\mathbf{L}]_0 - [\mathbf{L}]_{eq})/([\mathbf{L}] - [\mathbf{L}]_{eq})]/t$. [c] Calculated assuming $[\mathbf{L}]_0$ = 1 M. [d] $[\mathbf{L}]_0$ = 2 M, $[\text{PBD-OH}]_0$ = 1.3 × 10^{-2} M.

Figure 7 shows the appropriate first-order kinetic plots[27] for representative polymerizations using various ξ ratios at 90 °C. Although there appears to be a short induction period,[33] all of our kinetic analyses gave similar linear relationships. For $\xi = 1$ we also investigated the polymerization kinetics at 70, 80, and 105 °C (not shown). Ignoring the initiation process and using the generally accepted kinetic form for the polymerization of **L** with aluminum alkoxides, the linearity of these plots is consistent with polymerization process that is first order in **L** and can be described by

$$R_p = -\frac{d[\mathbf{L}]}{dt} = k_p[P^*]([\mathbf{L}] - [\mathbf{L}]_{eq}) \qquad (3)$$

where R_p is the rate of polymerization, k_p is the absolute propagation rate constant, and [P*] is the concentration of the active propagating species (presumably an unaggregated aluminum alkoxide species). At $\xi = 1$ and $[\mathbf{L}]_0$ of 0.5, 1.0, and 2.0 M, we observed the same relative conversion after 1.5 h (54.2, 53.6, and 53.8%), further confirming first-order behavior in **L**. Since the relationships shown in Figure 7 are linear, [P*] is effectively constant throughout the polymerization, and the slopes of these plots are equal to the product k_p[P*]. The evaluation of k_p, however, is not straightforward. Potential aggregation of [P*] to an inactive form, a situation observed in many other polymerizations using aluminum alkoxides,[14,34−36] complicates the determination of [P*] (i.e., $[P^*] \neq [\text{AlEt}_3]_0$). For ease of comparison we define an apparent first-order rate constant as $k_{app} = k_p[P^*]$. The apparent rate constant (k_{app}) for the polymerizations at $\xi = 1$ increases by a factor of 10 upon increasing the polymerization temperature from 70 to 105 °C (entries 1−4, Table 3), and an Arrhenius analysis gives the following relationship between k_{app} and polymerization temperature at $\xi = 1$,

$$k_{app} = 1.3 \times 10^6\ \text{s}^{-1}\ e^{-8580(\text{K})/T} \qquad (4)$$

Practically, at 105 °C ($[\mathbf{L}]_{eq}$ = 0.097 M) and $[\text{AlEt}_3]_0 = [\text{PBD-OH}]_0$ = 6.5 × 10^{-3} M, approximately 90% conversion of **L** can be achieved in about 3 h. Like the polymerizations shown in Figures 3 and 4, the polymerization of **L** at 105 °C showed a linear increase in X_n with conversion of **L**, and the PDI of the block copolymers was below 1.15 at **L** conversions below 90%. This represents a significant improvement over the polymerization protocol used in our recent report on the preparation of PI−PLA block copolymers at 70 °C.[9]

The k_{app} for lactide polymerization at 90 °C with $[\text{PBD-OH}]_0 = [\text{AlEt}_3]_0$ = 6.5 × 10^{-3} M *increased* by a

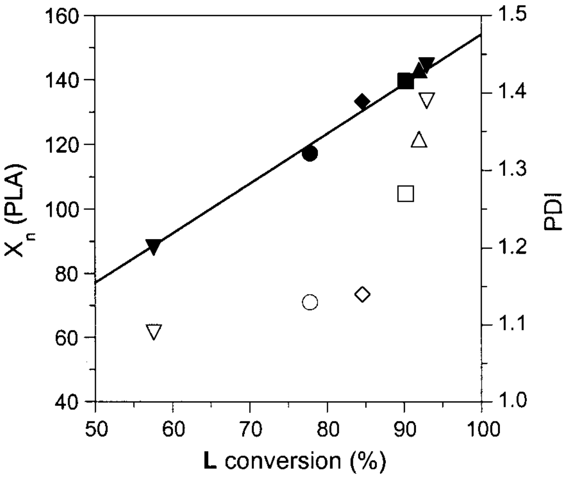


Figure 8. Dependence of the degree of polymerization (X_n) and molecular weight distribution (PDI) on **L** conversion at 120 °C. Polymerization conditions: toluene, $[\mathbf{L}]_0/[\text{PBD-OH}]_0 = 154$, $M_n(\text{PBD-OH}) = 5.3 \times 10^3$ g/mol (entry 2 in Table 1), $[\mathbf{L}]_0 = 2$ M, $[\text{PBD-OH}]_0/[\text{AlEt}_3]_0 = 2$. Polymerization time ($X_n$, PDI): 10 (▼, ▽), 20 (●, ○), 30 (◆, ◇), 40 (■, □), 50 (▲, △), and 60 min (▼, ▽). The solid line is the theoretical relationship between X_n and conversion assuming 100% initiator efficiency.

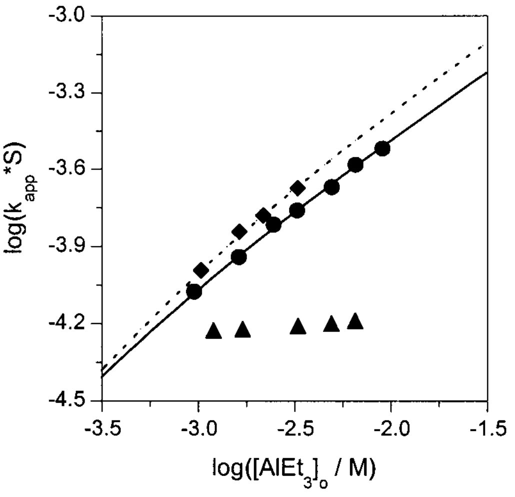


Figure 9. Determination of order in initiator concentration at various $[\text{PBD-OH}]_0/[\text{AlEt}_3]_0$ ratios. Polymerization conditions: toluene, $M_n(\text{PBD-OH}) = 5.3 \times 10^3$ g/mol (entry 2 in Table 1), $[\mathbf{L}]_0 = 1$ M, temperature = 90 °C, $[\text{PBD-OH}]_0/[\text{AlEt}_3]_0 = 1$ (▲), 2 (●), 3 (◆). Solid line: theoretical plot of $\ln(k_{app})$ versus $\ln([\text{AlEt}_3]_0)$ when $[\text{PBD-OH}]_0/[\text{AlEt}_3]_0 = 2$ using $m = 2$, $k_p = 0.21$ M^{-1} s^{-1}, $K_a = 1700$ M^{-1}. Dotted line: theoretical plot of $\ln(k_{app})$ versus $\ln([\text{AlEt}_3]_0)$ when $[\text{PBD-OH}]_0/[\text{AlEt}_3]_0 = 3$ assuming $m = 2$, $k_p = 0.18$ M^{-1} s^{-1}, $K_a = 670$ M^{-1}.

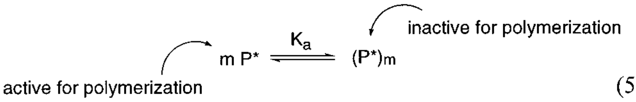
factor of approximately 3 when we *decreased* $[\text{AlEt}_3]_0$ by a factor of 2 (entries 3 and 6, Table 3). At $\xi = 1$ the macroinitiator is predominantly the aluminum monoalkoxide ($\text{Et}_2\text{Al-OPBD}$), and at $\xi = 2$, the macroinitiator is predominantly the aluminum dialkoxide (EtAl(OPBD)_2). The rate of **L** polymerization by the dialkoxide appears to be much faster than the rate of polymerization of **L** polymerization by the monoalkoxide. Consistent with this, other experimental reports[14,35,36] and recent theoretical work[37] suggests that aluminum trialkoxide species are more active than dialkylaluminum monoalkoxide species for the polymerization of **L**. However, we must consider the possibility of aggregation of the active species as a possible source of the observed rate difference (see below).

Since using less AlEt_3 led to an increase in polymerization rate, we decided to investigate the polymerization using $\xi = 2$ at an even higher temperature than the 105 °C used in the $\xi = 1$ case (entry 7, Table 3). At 120 °C with $[\mathbf{L}]_0 = 2$ M, $[\text{AlEt}_3]_0 = 6.5 \times 10^{-3}$ M, and $[\text{PBD-OH}]_0 = 1.3 \times 10^{-2}$ M ($\xi = 2$) approximately 90% conversion of **L** was achieved in about 30 min. Furthermore, the features observed in Figures 3 and 4 are retained in this high-temperature polymerization (Figure 8). We prepared 1.45 g of a PBD-PLA block copolymer in 9.3 mL of toluene using 0.8 mg of Al in 30 min (15 wt % solids).

At fixed $[\text{PBD-OH}]_0 = 6.5 \times 10^{-3}$ M, the k_{app} at $\xi = 3$ was only slightly smaller than for $\xi = 2$ (entry 8, Table 3). The macroinitiator at $\xi = 3$ is predominantly the aluminum trisalkoxide. We also studied the kinetics of the $\xi = 6$ case, and the polymerization rate is very slow (entry 9, Table 3). From these kinetic experiments, at fixed $[\text{PBD-OH}]_0$ and temperature, the fastest rates (in terms of k_{app}) were observed at $\xi = 2$, and comparable k_{app} values were obtained at $\xi = 3$.

Although the ξ ratios utilized in these block copolymerizations clearly affect the polymerization kinetics, the requirements of a block copolymer synthesis will vary since the desired volume fraction of one of the components and the overall molecular weight of the block copolymer changes from sample to sample. Therefore, the $[\text{AlEt}_3]_0$ can change between samples at fixed ξ. To uncover the kinetic order in $[\text{AlEt}_3]_0$, we investigated the effect of $[\text{AlEt}_3]_0$ on the polymerization rate (k_{app}) at 90 °C using ξ ratios of 1, 2, and 3.

The k_{app} values at 90 °C as a function of $[\text{AlEt}_3]_0$ using ξ ratios of 1, 2, and 3 are shown in Figure 9. In all cases the largest k_{app} at fixed $[\text{AlEt}_3]_0$ was observed at $\xi = 3$. The data in Figure 9 demonstrate a fractional order in AlEt_3 and are consistent with active site aggregation, a kinetic situation explored by Duda and Penczek.[14] If there is aggregation according to the equilibrium shown in eq 5,



(5)

where P* is the active species and $(\text{P}^*)_m$ is the aggregated inactive species with an aggregation number m, then the instantaneous concentration of P* will depend on K_a, the aggregation equilibrium constant, and $[\text{AlEt}_3]_0$. If K_a is large, then the instantaneous concentration of P* will be small. Duda and Penczek have shown that using $i\text{-Bu}_2\text{AlOMe}$ as an initiator in the polymerization of **L** in tetrahydrofuran $m = 2$ and $K_a = 77$ mol^{-1} L, and using Et_2AlOEt as an initiator in the polymerization of **L** in tetrahydrofuran, $m = 3$ and $K_a = 4 \times 10^4$ mol^{-2} L^2. In both of these cases, the instantaneous concentration of P* is extremely small. We can reasonably assume that the macromolecular propagating species used in this work also aggregate.[38] Therefore, assuming that all of the AlEt_3 is transformed into some macroinitiator species, eq 6 can be applied.

$$[\text{AlEt}_3]_0 = [\text{P}^*] + m[(\text{P}^*)_m] \qquad (6)$$

Assuming that [P*] can be neglected as compared to $[(\text{P}^*)_m]$ (which is the case if K_a is large and $[\text{AlEt}_3]_0$ is relatively large), then the expression relating the total

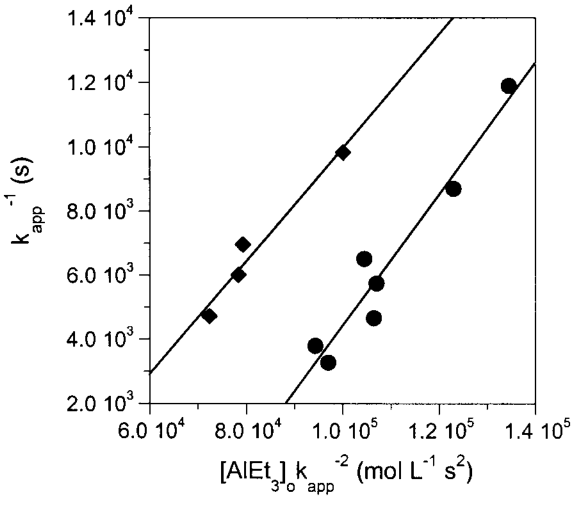


Figure 10. Determination of the aggregation equilibrium constant (K_a) and the propagrarion rate constants (k_p) in the ring-opening polymerization of **L** with PBD macroinitiators at different ratio of $[PBD\text{-}OH]_0/[AlEt_3]_0$. Polymerization conditions: toluene solvent, M_n(PBD-OH) = 5.3 × 10^3 g/mol (entry 2 in Table 1), $[\mathbf{L}]_0$ = 1 M, temperature = 90 °C, $[PBD\text{-}OH]_0/[AlEt_3]_0$ = 2 (●), 3 (◆).

Table 4. K_a and k_p for the Polymerization of L at 90 °C[a]

$[PBD\text{-}OH]_0/[AlEt_3]_0$	K_a (M^{-1})	k_p ($M^{-1}\,s^{-1}$)
2	1700	0.21
3	670	0.18

[a] Toluene, $[L]_0$ = 1 M.

concentration of the starting initiator and the apparent rate constant is given by eq 7.[36]

$$\ln(k_{app}) = \ln[k_p(mK_a)^{-1/m}] + \frac{1}{m}\ln[AlEt_3]_0 \qquad (7)$$

With the above assumptions, the data in Figure 9 should be linear with a slope that is the inverse of the degree of aggregation, m. For $\xi = 2$ and 3 the slopes are 0.58 and 0.64, respectively, and lead to noninteger values of m, 1.7 and 1.6. However, for $\xi = 1$ the slope is 0.05, suggesting that at $\xi = 1$ the polymerization is essentially zero order in $[AlEt_3]$.

From this analysis at $\xi = 2$ or 3, m is noninteger value. This may be a result of the assumptions used in the derivation of eq 7, where $[P^*]$ is assumed to be much smaller than $m[(P^*)_m]$. Without this assumption, Duda and Penczek have show that $k_p[P^*]$ (k_{app}) is related to $[AlEt_3]_0$ by eq 8.[36]

$${k_{app}}^{1-m} = (k_p[P^*])^{1-m} = k_p\left(\frac{[AlEt_3]_0}{(k_p[P^*])^m}\right) - \frac{K_a m}{{k_p}^{m-1}} \qquad (8)$$

The data for the polymerizations performed at $\xi = 2$ and 3 are shown in Figure 10 using the form according to eq 8 with $m = 2$. We used $m = 2$ since analysis of the data in Figure 9 gave a value of m close to 2, and related aluminum alkoxides have been shown to aggregate into dimers.[34] Using a linear fit of the data in Figure 10, the slope and intercept give K_a and k_p values (Table 4) for the two $[PBD\text{-}OH]_0/[AlEt_3]_0$ ratios. The aggregation equilibrium constant for the initiator $\xi = 2$ is almost 3 times as large as for the $\xi = 3$ case, while the propagation rate constants for these two cases differ by only 15%. Although the propagation rate constant for the $\xi = 2$ is slightly larger than for $\xi = 3$, the higher degree of aggregation leads to an overall smaller observed rate of propagation (k_{app}).

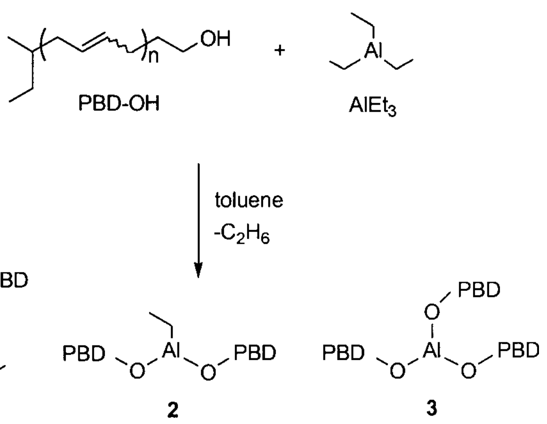


Figure 11. Possible macroinitaitor structures from the reaction of PBD-OH and $AlEt_3$.

Discussion

The kinetics of **L** polymerization using these polybutadiene macroinitiators is quite dependent on ξ. In block copolymer syntheses using $AlEt_3$ in combination with hydroxy-terminated polymers, a 1 to 1 ratio of hydroxy-terminated polymer and $AlEt_3$ has typically been employed. While effective for the formation of block copolymers, the rate of polymerization using $\xi = 1$ suffers dramatically compared to $\xi > 1$. In fact, at 90 °C using a fixed $[PBD\text{-}OH]_0$ the calculated $t_{0.5}$ for the polymerization of **L** at $\xi = 1$ is almost a factor of 3 larger than at $\xi = 2$ and 2.5 times larger than at $\xi = 3$ (Table 3). From both a rate of PLA production and a lower aluminum impurities in the system, using less $AlEt_3$ is beneficial. In the extreme, at $\xi = 6$ the rate enhancement is lost (entry 9, Table 3), but block copolymers can still be effectively prepared (i.e., no homopolymer contamination).

Aggregation of the polymerization active centers (P*) is responsible for the observed kinetic behavior. In this work, we prepared the macroinitiators for the polymerization of lactide by the reaction of PBD-OH and $AlEt_3$ at different $[PBD\text{-}OH]_0/[AlEt_3]_0$ ratios, and these reaction mixtures were directly used for the polymerization of lactide. The structure of the initiating (and propagating) species is dictated by the reaction stoichiometry (Figure 11). In previous work by our group[9] and others,[29−31] an equal molar ratio of hydroxyl terminal polymer to $AlEt_3$ was employed for the block copolymer synthesis, and the proposed structure of the macroinitiator, and the corresponding propagating species, was the dialkylaluminum monoalkoxide analogous to **1** in Figure 11. Similarly, **2** would be formed at $\xi = 2$, and **3** would be formed at $\xi = 3$. At higher ξ values, **3** would exist with excess PBD-OH. However, this idealized analysis is too simple. In a detailed NMR study[39] we investigated the reactivity of $AlEt_3$ with PBD-OH in toluene. There are three reactive alkyl groups in $AlEt_3$, and each could potentially react with PBD-OH to form the corresponding alkoxide and ethane. The reaction of $AlEt_3$ with 1 equiv of PBD-OH is rapid. The reaction of **1** with a second molecule of PBD-OH is somewhat diminished; therefore, at $\xi = 1$ the reaction mixture contains **1** and small amounts of **2** and unreacted $AlEt_3$. On the other hand, at $\xi = 2$, while we cannot completely rule out the presence of **3** in the macroinitiator solution at this time, **2** is the predominant species. This is due to the extremely slow reaction of **2** with a third molecule of PBD-OH. This diminished reactivity was also observed using 1-propanol as a model nonpolymeric alcohol. Therefore, at $\xi = 3$, care must be taken to ensure the complete formation of the aluminum trisalkoxide **3**.[40] Increasing ξ to values greater than 3 (i.e., using excess PBD-OH) led to the more facile formation of **3**. We propose that, during the polymerization of **L**, the propagating species derived from these macroinitiators are structurally analogous to the macroinitiators shown in Figure 11.

The detailed kinetics analysis of polymerizations performed at $\xi = 2$ and 3 (Figure 9) are consistent with the proposed structures of the initiating species **2** and **3**, respectively. Since **2** is more electrophilic than **3**, the observed increase in the aggregation equilibrium constant (K_a) is expected. While the K_a values for **2** and **3** are significantly different, the absolute rate constants (k_p) are essentially identical within the error of our measurements (Table 4). At $\xi = 6$ we believe that the active species for polymerization is **3**, and the excess PBD-OH in the reaction solution is undergoing rapid exchange with the alkoxides arms in **3** (eq 1) and may decrease the aggregation of **3** through coordination. This would presumably lead to a decrease in the aggregation equilibrium constant, although the reduced levels of Al offset any rate enhancement related to decreased aggregation of the active species.

In the case of $\xi = 1$, the reaction mixture contains **1**, **2**, and excess $AlEt_3$. From the dependence of the polymerization rate on the $[AlEt]_0$ at $\xi = 1$, there is clearly aggregation of the active polymerization species. Detailed analysis of the kinetic data to extract k_p and K_a for these polymerizations was not performed. Excess $AlEt_3$ in the polymerization solution may play a significant role in inhibition of lactide polymerization rate. This highly Lewis acidic species may lead to mixed multicomponent aggregates during the polymerization that are thermodynamically favored over unaggregated species ($K_a \gg 10^3$). While this situation is similar to the case for $\xi = 2$ and 3, the rate of aggregation/deaggregation in the case where $\xi = 1$ may be slower than the rate of **L** polymerization. If this is the case, then eq 7 is not appropriate for treating the dependence of the apparent rate constant on $[AlEt_3]_0$.[41] Furthermore, $[PBD\text{-}OH]_0$ in the polymerizations shown in Figure 9 is highest for the $\xi = 1$ case. This may lead to mass transfer limitations in the polymerization of lactide due to the high concentration of polymer in the reaction.

Conclusions

We have developed a facile synthesis of polybutadiene–polylactide block copolymers starting from well-defined hydroxy-terminated polybutadiene (PBD-OH). Using $AlEt_3$, a readily available aluminum reagent, we generated polybutadiene macroinitiators at various $[PBD\text{-}OH]_0/[AlEt_3]_0$ ratios. Controlled polymerization of lactide was performed using these macroinititors as seen by linear growth of polylactide molecular weight with lactide conversion and narrow molecular weight distribution block copolymers. $[PBD\text{-}OH]_0/[AlEt_3]_0$ ratios as large as 6 could be used without sacrificing the controlled nature of the polymerization (Figures 3 and 4). Furthermore, polymerization temperatures as high as 120 °C were not detrimental to the preparation of model block copolymers (Figure 8). Model polybutadiene–polylactide block copolymers can be prepared in as little as 30 min.

At fixed $[PBD\text{-}OH]_0$ using less $AlEt_3$ resulted in significant rate enhancements. We attributed this behavior to the aggregation of active species in the polymerization. While the absolute propagation rate constants for the monoalkyl aluminum bisalkoxide and the aluminum trisalkoxide were similar, increased aggregation of the former resulted in a lower equilibrium concentration of active species and thus lower polymerization rates. From these detailed kinetics studies we have made significant improvements in the preparation of polydiene–polylactide block copolymers in terms of polymerization rate and levels of aluminum necessary for the synthesis of these interesting hybrid materials.

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(41) Fast reversible deactivation by aggregation of active centers is a necessary requirement for the kinetic analysis given in eq 7 (rapid preequilibrium).

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