Phosphazene Bases: A New Category of Organocatalysts for the Living Ring-Opening Polymerization of Cyclic Esters

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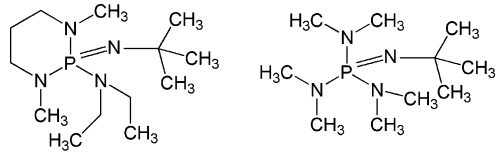
ABSTRACT: We demonstrate that phosphazene bases, such as 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) and *N*′-*tert*-butyl-*N*,*N*,*N*′,*N*′,*N*′′,*N*′′-hexamethylphosphorimidic triamide (P_1-*t*-Bu), are active organocatalysts for the living ring-opening polymerization (ROP) of cyclic esters. Polyesters prepared through this organocatalytic route possess predictable molecular weights, narrow polydispersities, and high end-group fidelity. Mechanistic studies suggest that the intermolecular hydrogen bonding of the alcohol initiator to phosphazene bases activates the alcohol for ROP of cyclic esters.

Introduction

Because of their outstanding materials properties and facile degradation, aliphatic polyesters have been investigated for a wide range of applications such as textiles, packaging, and biodegradable materials.[1−4] Catalytic ring-opening polymerization (ROP) of cyclic esters by transition metal complexes is one of the most effective and versatile strategies.[5] Although organometallic catalysts provide facile and direct access to aliphatic polyesters with exquisite control, this synthetic route may have limited applications in microelectronics and resorbable biomedical areas due to the heavy metal residue trapped within the polymer chains. Therefore, our group has focused on metal-free, organocatalytic synthetic approaches to well-defined macromolecules. Successful organocatalysts for living ROP of cyclic esters include 4-(dimethylamino)pyridine (DMAP),[6] phosphines,[7] N-heterocyclic carbenes,[8−13] bifunctional thiourea−amines,[14,15] and guanidines and amidines,[16,17] such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), *N*-methyl-TBD (MTBD), and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU).

Analogous to guanidine and amidine bases, phosphazene bases developed by Schwesinger are another category of potent, nonionic bases of a general structure $(R_2N)_3P{=}N{-}R$.[18−20] The phosphazene base 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP, Scheme 1, ${}^{MeCN}pK_{BH^+}$ 27.6) is more basic than DBU (${}^{MeCN}pK_{BH^+}$ 24.3) and MTBD (${}^{MeCN}pK_{BH^+}$ 25.4)[20] by approximately 2−3 pK_a units. BEMP has been used as a powerful nucleophilic reagent for a variety of reactions, including the Michael addition,[21,22] alkylation,[23,24] ketene generation,[25,26] and transesterification reactions.[27] Herein, we describe the use of BEMP as an organic catalyst for the living ROP of cyclic esters. Polyesters were obtained using mild polymerization conditions and exhibit high end-group fidelity, narrow polydispersities, and a linear relationship between conversion and molecular weight. Another structurally similar phosphazene base, *N*′-*tert*-butyl-*N*,*N*,*N*′,*N*′,*N*′′,*N*′′-hexamethylphosphorimidic triamide (P_1-*t*-Bu, Scheme 1, ${}^{MeCN}pK_{BH^+}$ 26.9), was also investigated for the ROP of L-lactide (L-LA) and *δ*-valerolactone (VL).

Scheme 1. Phosphazene Bases Used in This Study: (1) BEMP and (2) P_1-*t*-Bu



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Results and Discussion

The catalytic activity of BEMP for the ROP of L-LA was studied in dry toluene at room temperature using 1-pyrenebutanol (PB) as the initiator. The monomer-to-initiator molar ratio was fixed at 100 (targeted degree of polymerization (DP) = 100), while the amount of BEMP added to the solution was varied. At a 1 mol % catalyst to monomer ratio, L-lactide was converted to poly(L-lactide) (PLLA) with 78% conversion after 23 h with a number-average molecular weight (M_n) of 13 100 g/mol and a polydispersity index (PDI = M_w/M_n) of 1.08 (Table 1, entry 2). A plot of M_n (measured by gel permeation chromatography, GPC) vs monomer conversion (measured by ^{1}H NMR spectroscopy) for the ROP of L-LA shows a linear correlation (Figure 1A, ●), which is characteristic of a living polymerization. The polydispersity decreases slightly as the conversion approaches 70% and then increases. The increase of molecular weight distribution at high conversion is likely due to the transesterification of the produced PLLA catalyzed by BEMP. BEMP can be quenched by the addition of benzoic acid in order to minimize adverse transesterification reactions. GPC traces (Figure 2, inset) using both refractive index (RI) and UV detectors (at 254 nm) show the complete incorporation of UV-active 1-pyrenebutanol initiator into the polymer chain, demonstrating the high end-group fidelity. This conclusion is further confirmed from the two-dimensional heteronuclear multibond correlation (HMBC) NMR spectrum, for which a cross-peak between the α-H of 1-pyrenebutanol and the carbonyl carbon at 170.1 ppm verifies the connectivity between the initiator and the polymer chain (Figure 2).

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Table 1. ROP of Cyclic Esters (L-LA, VL, and CL) Using BEMP or P_1-*t*-Bu Catalyst at Room Temperature

	catalyst	monomer	initiator	solvent	$[M]_0/[I]_0$	catalyst (%)	time (h)	conv[a] (%)	DP[a]	M_n[b] (g mol^{-1})	PDI[b]
1	BEMP	LLA	PB	Tol	100	0.5	36	48	47	10700	1.06
2	BEMP	LLA	PB	Tol	100	1	23	76	68	13100	1.08
3	BEMP	LLA	PB	Tol	100	2	33	95	92	18000	1.14
4	BEMP	*rac*-LA	BAol	Tol	100	1	66	97	101	15000	1.05
5	BEMP	VL	BAol	none	100	0.5	97	61	56	8400	1.08
6	BEMP	VL	PB	none	100	1	73	69	68	9200	1.12
7	BEMP	VL	BAol	none	100	2	45	93	101	8500	1.23
8	BEMP	CL	PB	none	100	1	240[c]	14	15	3600	1.08
9	P_1-*t*-Bu	LLA	PB	Tol	100	1	70	82	71	16000	1.06
10	P_1-*t*-Bu	VL	PB	none	100	1	70	56	68	8200	1.11

[a] Determined by ^{1}H NMR. [b] Determined by GPC in THF using a RI detector. [c] At 80 °C.

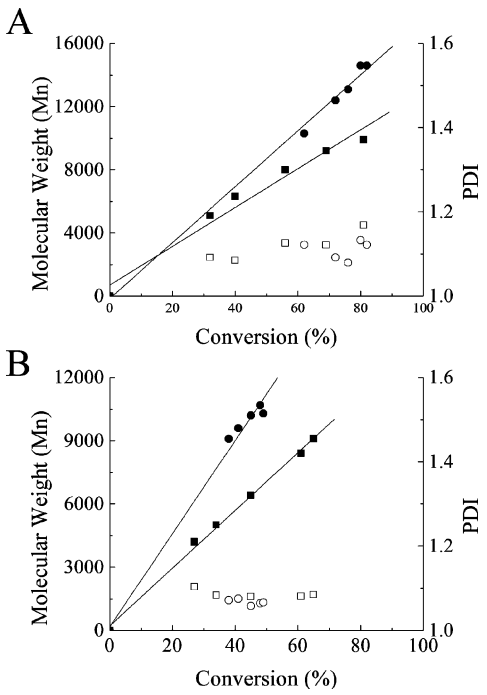


Figure 1. M_n (filled circles (●) and filled squares (■)) and PDI (open circles (○) and open squares (□)) vs % monomer conversion for ROP of L-LA (circles) and VL (squares) using A) 1 mol % (to monomer) and B) 0.5 mol % (to monomer) BEMP as catalyst.

The ^{13}C NMR spectra of the PLLA methine resonances (Figure 3) indicate a highly isotactic structure, suggesting that epimerization of either L-LA monomer or the PLLA polymer is minimal. Polymerization of *rac*-lactide (*rac*-LA) yields isotactic-enriched poly(lactide) (Figure 3) with the probability of isotactic propagation (P_i) equal to 0.70 (determined from the homonuclear decoupled ^{1}H NMR spectrum, Figure S1).[28−32] This latter result is consistent with the isotactic enchainment of the monomer by a chain-end control mechanism as seen for other ROP organocatalysts.[15]

BEMP can also promote the ROP of δ-valerolactone (VL). At a monomer-to-initiator-to-catalyst ratio of 100:1:1, neat VL was converted to polyvalerolactone (PVL) with 70% conversion in 73 h. The produced PVL exhibited a M_n of 9200 g/mol and a PDI of 1.12 (Table 1, entry 6). Higher conversions were possible even though the reaction mixture solidified, but the PDI increased slightly. The molecular weight of polymer is again linearly related to the conversion of the monomer (Figure 1A, ■). The ROP of ϵ-caprolactone (CL) is very slow even at elevated temperatures. Polycaprolactone (PCL) with a molecular weight of 3600 at 14% conversion of monomer was obtained by polymerization at 80 °C for 10 days (of a neat reaction mixture with the molecular ratio of CL to PB to BEMP at 100:1:1).

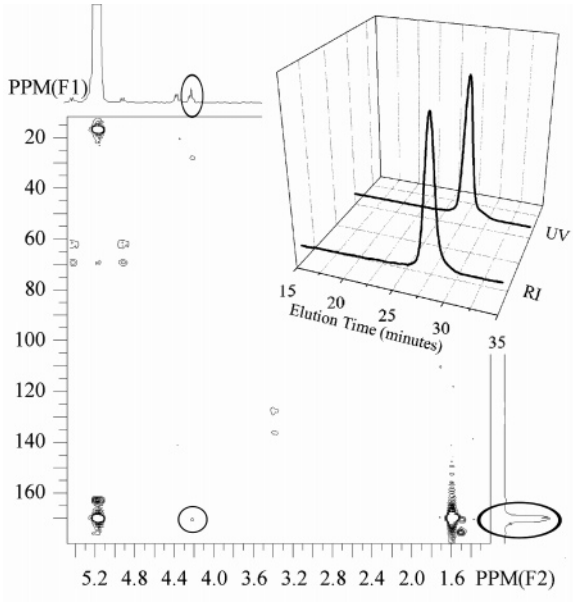


Figure 2. 2-D HMBC NMR spectrum of PLLA initiated by 1-pyrenebutanol using BEMP catalyst (Table 1, entry 2). Inset: GPC traces from RI and UV (254 nm) detectors showing incorporation of UV-active 1-pyrenebutanol initiator into PLLA.

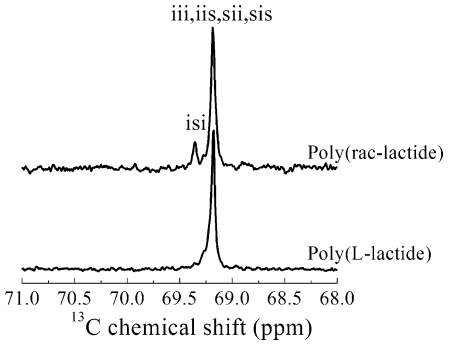


Figure 3. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, methine carbon range) of the PLLA (Table 1, entry 2) and poly(*rac*-LA) (Table 1, entry 4).

The effect of the catalyst on ROP of cyclic esters was studied by changing the concentration of BEMP in the starting mixture at a fixed monomer-to-initiator ratio (100:1) (Table 1). Lower polydispersities are observed at lower concentrations of BEMP: at 0.5 mol % of BEMP catalyst to monomer, the PDI is less than 1.07 for L-LA (until 48% conversion) and 1.10 for VL (until 61% conversion) throughout the reaction with a linear correlation between the molecular weight and conversion (Figure 1B). Higher concentrations of BEMP catalyst provide faster reactions and higher conversions. For example, conversions as high as 95% and 93% were achieved in 33 and 45 h when using 2 mol % of catalyst for L-LA and VL, respectively. However, under these conditions, the polydispersities are higher, implicat-

Scheme 2. Synthesis of a Variety of Poly(*rac*-LA) Block Copolymers Using the BEMP Catalyst

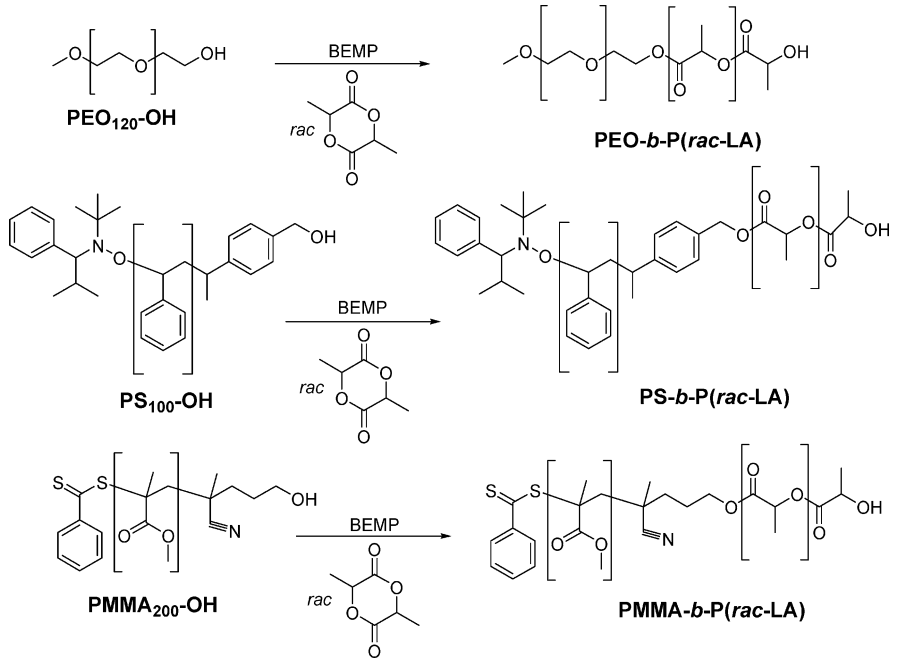


Table 2. Characterization of Poly(*rac*-LA)-Based Block Copolymers Prepared Using Hydroxyl Functional Macroinitiator and BEMP Catalyst at Room Temperature

	macroinitiator	monomer	DP	time (h)	conv[a] (%)	M_n[b] (g mol^{-1})	PDI[b]	T_g[c] (°C)
1	PEO_{120}-OH	*rac*-LA	35	5	>99	14 300	1.07	38 °C P(*rac*-LA) 50 °C PEO(T_m)
2	PS_{100}-OH	*rac*-LA	70	5	>99	20 000	1.07	35 °C P(*rac*-LA) 80 °C PS
3	$PMMA_{200}$-OH	*rac*-LA	140	16	>99	38 600	1.17	33°C P(*rac*-LA) 79 °C PMMA

[a] Determined by ^{1}H NMR. [b] Determined by GPC in THF using a RI detector. [c] Determined using DSC.

ing a higher degree of transesterification of the polyesters with higher BEMP concentrations at high conversions.

The efficiency and versatility of the BEMP catalyst was further demonstrated by a series of chain extension block copolymerizations. Hydroxyl functional macroinitiators including hydroxyl-terminated poly(ethylene oxide) monomethyl ether (PEO-OH), poly(styrene) (PS-OH),[33,34] and poly(methyl methacrylate) (PMMA-OH)[35,36] were used for the ROP of *rac*-lactide (Scheme 2). All polymerizations were performed in dichloromethane at room temperature using a catalyst concentration of 1 mol % to monomer. GPC analysis confirmed clean chain-extended block copolymers free from unreacted macroinitiator contamination and indicated excellent control of molecular weights and correspondingly low polydispersities (Table 2).

Structurally similar phosphazene base,P_1-*t*-Bu, can also promote the ROP of L-LA and VL (Table 1, entries 9 and 10) with the reaction rate a little slower than that with BEMP. Preliminary mechanistic studies support an activated alcohol mechanism for these ROP reactions.[37] As illustrated in Figure 4, the chemical shift of −OH in benzyl alcohol shifts from 1.13 to 2.50 ppm upon the addition of BEMP in toluene-d_8. The downfield shift of −OH is indicative of an intermolecular hydrogen bond between BEMP and the alcohol initiator. The ^{1}H NMR spectra of mixtures of BEMP and L-LA or VL provide no evidence for an interaction in solution. These data suggest that BEMP activates the alcohol for the nucleophilic attack on the carbonyl group of cyclic esters without the activation of cyclic esters (Scheme 3).

The polymerization activity of BEMP relative to the guanidines and amidines[16,17] is illuminating. BEMP is more basic than the

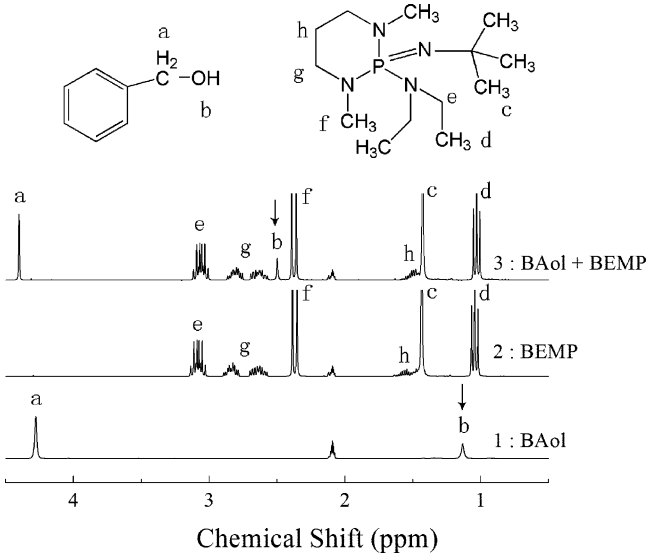
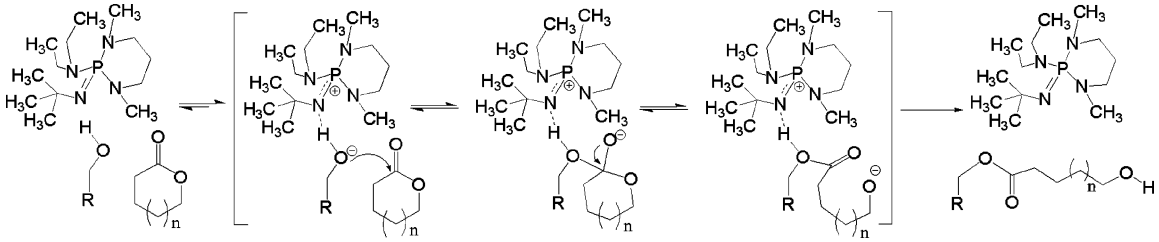


Figure 4. ^{1}H NMR spectra (75 MHz, $C_6D_5CD_3$) of (1) BAol, (2) BEMP, and (3) BAol with BEMP.

amidine DBU or the methylated guanidine MTBD but shows comparable catalytic activity to these strong nonionic bases. In contrast, the guanidine TBD ($^{MeCN}pK_{BH^+}$ 26.0)[38] has a basicity intermediate to that of BEMP and DBU/MTBD but is much more active for the ROP of cyclic esters. We have previously suggested that the higher rate of ROP for TBD (relative to MTBD, DBU,[16] and in the present case BEMP) is due to the accessibility of a bifunctional mechanism[17] that is inaccessible

Scheme 3. Postulated Mechanism for the ROP of Cyclic Esters Using BEMP as Catalyst



to monofunctional DBU, MTBD, and BEMP, which catalyze ROP solely by interactions with the alcohol chain end.

Conclusion

Commercially available phosphazene bases are found to be a new category of efficient organocatalysts for ROP of cyclic esters. Polyesters with narrow distributed molecular weight and high end-group fidelity can be prepared through the organocatalytic living polymerization route. Further studies on the polymerization dynamics and intermediate are under investigation.

Experimental Section

Materials. L-Lactide (L-LA, 99%, Purac) and *rac*-lactide (*rac*-LA, 99%, Purac) were recrystallized three times from toluene and dried in vacuum prior to use. δ-Valerolactone (VL, technical, Aldrich) and ϵ-caprolactone (CL, >99%, Aldrich) were distilled twice over calcium hydride (CaH_2, Mallinckrodt Chemical). 1-Pyrenebutanol (PB, 99%, Aldrich) was dissolved in THF over CaH_2, filtered after an overnight stir, and collected by evaporation of the solvent. 2-*tert*-Butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP, 98%, Aldrich), *N*′-*tert*-butyl-*N*,*N*,*N*′,*N*′,*N*″,*N*″-hexamethylphosphorimidic triamide (P_1-*t*-Bu, 98%, Fluka), benzyl alcohol (BAol, 99.9%, J.T. Baker), and toluene-d_8 ($C_6D_5CD_3$, D 99.6%, Aldrich) were stirred over CaH_2 overnight and filtered prior to use. Toluene and dichloromethane solvent were dried using an Innovative Technology PureSolv System (model SPS-400-5) equipped with alumina drying columns. Chloroform-*d* ($CDCl_3$, D 99.8%, Cambridge Isotope Laboratories, Inc.), methanol (100.0%, J.T. Baker), and benzoic acid (99.5%, Aldrich) were used as received. α-Methoxy-ω-hydroxypoly(ethylene oxide) (PEO_{120}-OH, Fluka, M_n = 5000 g mol^{-1}, PDI = 1.03), hydroxyl functional poly(styrene) (PS_{100}-OH, M_n = 10 000 g mol^{-1}, PDI = 1.07, polymerized using nitroxide-mediated polymerization techniques)[33,34] and hydroxyl functional poly(methyl methacrylate) ($PMMA_{200}$-OH, M_n = 20 000 g mol^{-1}, PDI = 1.09, polymerized using reversible addition−fragmentation chain-transfer techniques)[35,36] were dried by azeotropic distillation with toluene prior of use.

Instruments. One-dimensional ^{1}H (300 MHz) and ^{13}C (75 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 instrument using a deuterated solvent ($CDCl_3$ or $C_6D_5CD_3$) as an internal standard. Gel permeation chromatography (GPC) was carried out with a Waters chromatograph calibrated with polystyrene standards (750−2 × 10^6 g mol^{-1}) using THF as solvent. A Waters 410 differential refractometer and a 996 photodiode array detector were installed for detection. Four 5 μm Waters columns (300 mm × 7.7 mm) with pore sizes of 10, 100, 1000, 10^5, and 10^6 Å were connected in series in the chromatograph. Differential scanning calorimetry (DSC) was performed using a TA differential scanning calorimeter 1000.

Polymerization of L-LA Using BEMP as Catalyst (Table 1, entry 2). In a glovebox, L-LA (430 mg, 3.0 mmol) and 1-pyrenebutanol (8.2 mg, 0.03 mmol) were dissolved in toluene (7 g). BEMP (8.2 mg, 0.03 mmol) was added to initiate the polymerization. After continuously stirring at room temperature for the desired time, an aliquot of the reacted solution was removed and quenched with benzoic acid. Thereafter, part of the aliquot was diluted with chloroform-*d* for NMR analysis to determine the conversion. The balance of the aliquot was poured into methanol to precipitate PLLA, which was then isolated by filtration. The obtained polymer was characterized by GPC (for molecular weight and polydispersity) and NMR (for degree of polymerization). ^{1}H NMR ($CDCl_3$): 8.28−7.83 (m, 9H, aromatic), 5.27−5.07 (m, C*H* PLLA backbone), 4.36 (m, 1H, C*H*−OH), 4.21 (t, 2H, pyrene-$CH_2CH_2CH_2CH_2OC(=O)$), 3.38 (t, 2H, pyrene−CH_2−), 1.70−1.40 (m, CH_3 PLLA backbone, pyrene−$CH_2CH_2CH_2$). GPC (RI): M_n = 13 100 g mol^{-1}, PDI = 1.08.

Polymerization of *rac*-LA Using BEMP as Catalyst (Table 1, entry 4). In a glovebox, *rac*-LA (530 mg, 3.7 mmol) and benzyl alcohol (4.0 mg, 0.37 mmol) were mixed in toluene (7 g) (some *rac*-LA was not dissolved). BEMP (10.1 mg, 0.37 mmol) was added to initiate the polymerization. After continuously stirring at room temperature for 66 h, benzoic acid was added to quench the reaction. ^{1}H NMR ($CDCl_3$): 7.40−7.29 (m, 5H, aromatic), 5.28−5.07 (m, C*H* poly(*rac*-LA) backbone), 4.36 (m, 1H, C*H*−OH), 1.74−1.30 (m, CH_3 poly(*rac*-LA) backbone). GPC (RI): M_n = 15 000 g mol^{-1}, PDI = 1.05.

Polymerization of VL Using BEMP as Catalyst (Table 1, entry 6). In a glovebox, 1-pyrenebutanol (54.8 mg, 0.2 mmol) was dissolved in VL (2 g, 20 mmol). BEMP (54.8 mg, 0.2 mmol) was added to initiate the polymerization. After continuously stirring at room temperature for the desired time, an aliquot of the reacted solution was removed and quenched with benzoic acid. ^{1}H NMR ($CDCl_3$): 8.30−7.84 (m, 9H, aromatic), 4.21 (t, 2H, pyrene−CH_2-$CH_2CH_2CH_2OC(=O)$), 4.16−3.99 (m, C(=O)OCH_2 PVL backbone), 3.65 (t, 2H, CH_2OH), 3.39 (t, 2H, pyrene−CH_2−), 2.45−2.24 (m, CH_2C(=O)O PVL backbone), 2.00−1.54 (m, CH_2CH_2 PVL backbone, pyrene−$CH_2CH_2CH_2$). GPC (RI): M_n = 9200 g mol^{-1}, PDI = 1.12.

Polymerization of CL Using BEMP as Catalyst (Table 1, entry 8). In a glovebox, 1-pyrenebutanol (55 mg, 0.2 mmol) were dissolved in ϵ-caprolactone (2.4 g, 20 mmol). BEMP (55 mg, 0.2 mmol) was added to initiate the polymerization. After continuously stirring for at 80 °C for 10 days, benzoic acid was added to quench the reaction. ^{1}H NMR ($CDCl_3$): 8.29−7.83 (m, 9H, aromatic), 4.15 (t, 2H, pyrene−$CH_2CH_2CH_2CH_2OC(=O)$), 4.11−3.99 (m, C(=O)-OCH_2 PCL backbone), 3.64 (t, 2H, CH_2OH), 3.39 (t, 2H, pyrene−CH_2−), 2.38−2.23 (m, CH_2C(=O)O PCL backbone), 2.00−1.53 (m, C$H_2CH_2CH_2$ PCL backbone, pyrene−$CH_2CH_2CH_2$), 1.46−1.29 (m, $CH_2CH_2CH_2$ PCL backbone). GPC (RI): M_n = 3600 g mol^{-1}, PDI = 1.08.

Synthesis of Poly(ethylene oxide)-*block*-poly(*rac*-lactide) (Table 2, entry 1). In a glovebox, α-methoxy-ω-hydroxypoly(ethylene oxide) (0.2 g, 40 μmol, M_n = 5000 g mol^{-1}, PDI = 1.03), BEMP (3.8 mg, 14 μmol), and *rac*-LA (0.2 g, 1.4 mmol) were dissolved in 3 mL of dry dichloromethane and stirred at room temperature for 5 h. Benzoic acid was added to quench the polymerization, and the viscous solution was precipitated in cold methanol. ^{1}H NMR ($CDCl_3$): δ = 5.30−5.15 (m, H, CH_{PLA}), 4.40−4,35 (q, H, C*H*−OH), 3.63 (s, 4H, OCH_2CH_2 $_{PEG}$), 1.65−1.50 (3H, CH_3 $_{PLA}$). GPC (RI): M_n = 14 300 g mol^{-1}, PDI = 1.07.

Synthesis of Poly(styrene)-*block*-poly(*rac*-lactide) (Table 2, entry 2). In a glovebox, hydroxyl functional poly(styrene) (0.2 g, 20 μmol, M_n = 10 000 g mol^{-1}, PDI = 1.07), BEMP (3.8 mg, 14 μmol), and *rac*-LA (0.2 g, 1.4 mmol) were dissolved in 3 mL of dry dichloromethane and stirred at room temperature for 5 h.

Benzoic acid was added to quench the polymerization, and the viscous solution was precipitated in methanol. ^{1}H NMR ($CDCl_3$): δ = 7.20−6.20 (m, 5H, ArH_{PS}), 5.30−5.15 (m, H, CH_{PLA}), 4.40−4,35 (q, H, CH−OH), 2.20−1.20 (m, H: CH_{PS}, C$H_{2\ PS}$, C$H_{3\ PLA}$). GPC (RI): M_n = 20 000 g mol^{-1}, PDI = 1.07.

Synthesis of Poly(methyl methacrylate)-*block*-poly(*rac*-lactide) (Table 2, entry 3). In a glovebox, hydroxyl functional poly(methyl methacrylate) (0.3 g, 15 μmol, M_n = 20 000 g mol^{-1}, PDI = 1.09), BEMP (5.8 mg, 21 μmol), and *rac*-LA (0.3 g, 2.1 mmol) were dissolved in 4 mL of dry dichloromethane and stirred at room temperature for 16 h. Benzoic acid was added to quench the polymerization, and the viscous solution was precipitated in methanol. ^{1}H NMR ($CDCl_3$): δ = 5.30−5.15 (m, H, CH_{PLA}), 3.60 (s, 3H, C$H_{3\ PMMA}$), 2.10−0.70 (m, H: C$H_{3\ PMMA}$, C$H_{2\ PMMA}$, C$H_{3\ PLA}$). GPC (RI): M_n = 38 600 g mol^{-1}, PDI = 1.17.

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Supporting Information Available: Figure S1 showing the methine region of the homonuclear decoupled ^{1}H NMR spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Publication. This article was published ASAP on May 19, 2007, without a Supporting Information paragraph. This article was reposted on May 29, 2007.

References and Notes

(1) Scheirs, J.; Long, T. E. *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*; John Wiley and Sons Ltd.: Chichester, UK, 2003.
(2) Ree, M.; Yoon, J.; Heo, K. *J. Mater. Chem.* **2006**, *16*, 685−697.
(3) Li, M.; Coenjarts, C. A.; Ober, C. K. *Adv. Polym. Sci.* **2005**, *190*, 183−226.
(4) Ueda, H.; Tabata, Y. *Adv. Drug Delivery Rev.* **2003**, *55*, 501−518.
(5) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147−6176.
(6) Nederberg, F.; Connor, E. F.; Moller, M.; Glauser, T.; Hedrick, J. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 2712−2715.
(7) Myers, M.; Connor, E. F.; Glauser, T.; Mock, A.; Nyce, G.; Hedrick, J. L. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 844−851.
(8) Connor, E. F.; Nyce, G. W.; Myers, M.; Mock, A.; Hedrick, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 914−915.
(9) Nyce, G. W.; Glauser, T.; Connor, E. F.; Mock, A.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 3046−3056.
(10) Coulembier, O.; Dove, A. P.; Pratt, R. C.; Sentman, A. C.; Culkin, D. A.; Mespouille, L.; Dubois, P.; Waymouth, R. M.; Hedrick, J. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4964−4968.
(11) Coulembier, O.; Lohmeijer, B. G. G.; Dove, A. P.; Pratt, R. C.; Mespouille, L.; Culkin, D. A.; Benight, S. J.; Dubois, P.; Waymouth, R. M.; Hedrick, J. L. *Macromolecules* **2006**, *39*, 5617−5628.
(12) Coulembier, O.; Mespouille, L.; Hedrick, J. L.; Waymouth, R. M.; Dubois, P. *Macromolecules* **2006**, *39*, 4001−4008.
(13) Csihony, S.; Culkin, D. A.; Sentman, A. C.; Dove, A. P.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 9079−9084.
(14) Dove, A. P.; Pratt, R. C.; Lohmeijer, B. G. G.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 13798−13799.
(15) Pratt, R. C.; Lohmeijer, B. G. G.; Long, D. A.; Lundberg, P. N. P.; Dove, A. P.; Li, H.; Wade, C. G.; Waymouth, R. M.; Hedrick, J. L. *Macromolecules* **2006**, *39*, 7863−7871.
(16) Lohmeijer, B. G. G.; Pratt, R. C.; Leibfarth, F.; Logan, J. W.; Long, D. A.; Dove, A. P.; Nederberg, F.; Choi, J.; Wade, C.; Waymouth, R. M.; Hedrick, J. L. *Macromolecules* **2006**, *39*, 8574−8583.
(17) Pratt, R. C.; Lohmeijer, B. G. G.; Long, D. A.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2006**, *128*, 4556−4557.
(18) Schwesinger, R. *Chimia* **1985**, *39*, 269−272.
(19) Schwesinger, R.; Schlemper, H. *Angew. Chem., Int. Ed.* **1987**, *26*, 1167−1169.
(20) Schwesinger, R.; Willaredt, J.; Schlemper, H.; Keller, M.; Schmitt, D.; Fritz, H. *Chem. Ber.* **1994**, *127*, 2435−2454.
(21) Lee, Y.-J.; Lee, J.; Kim, M.-J.; Jeong, B.-S.; Lee, J.-H.; Kim, T.-S.; Lee, J.; Ku, J.-M.; Jew, S.-S.; Park, H.-G. *Org. Lett.* **2005**, *7*, 3207−3209.
(22) Bensa, D.; Constantieux, T.; Rodriguez, J. *Synthesis* **2004**, *6*, 923−927.
(23) Lee, J.; Lee, Y.-I.; Kang, M. J.; Lee, Y.-J.; Jeong, B.-S.; Lee, J.-H.; Kim, M.-J.; Choi, J.-Y.; Ku, J.-M.; Park, H.-G.; Jew, S.-S. *J. Org. Chem.* **2005**, *70*, 4158−4161.
(24) Mitchell, J. M.; Shaw, J. T. *Angew. Chem., Int. Ed.* **2006**, *45*, 1722−1726.
(25) Wack, H.; Taggi, A. E.; Hafez, A. M.; William, J.; Drury, I.; Lectka, T. *J. Am. Chem. Soc.* **2001**, *123*, 1531−1532.
(26) Taggi, A. E.; Hafez, A. M.; Wack, H.; Young, B.; Ferraris, D.; Lectka, T. *J. Am. Chem. Soc.* **2002**, *124*, 6626−6635.
(27) Schuchardt, U.; Sercheli, R.; Vargas, R. M. *J. Braz. Chem. Soc.* **1998**, *9*, 199−210.
(28) Kricheldorf, H. R.; Boettcher, C.; Tonnes, K.-U. *Polymer* **1992**, *33*, 2817−2824.
(29) Kasperczyk, J. E. *Macromolecules* **1995**, *28*, 3937−3939.
(30) Zhong, Z.; Dijkstra, P. J.; Feijen, J. *J. Am. Chem. Soc.* **2003**, *125*, 11291−11298.
(31) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316−1326.
(32) Zell, M. T.; Padden, B. E.; Paterick, A. J.; Thakur, K. A. M.; Kean, R. T.; Hillmyer, M. A.; Munson, E. J. *Macromolecules* **2002**, *35*, 7700−7707.
(33) Bosman, A. W.; Vestberg, R.; Heumann, A.; Frechet, J. M. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 715−728.
(34) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3688.
(35) Thang, S. H.; Chong, Y. K.; Mayadunne, R. T. A.; Moad, G.; Rizzardo, E. *Tetrahedron Lett.* **1999**, *40*, 2435−2438.
(36) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562.
(37) Movassaghi, M.; Schmidt, M. A. *Org. Lett.* **2005**, *7*, 2453−2456.
(38) Kaljurand, I.; Kutt, A.; Soovali, L.; Rodima, T.; Maemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2005**, *70*, 1019−1028.

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