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Diphenyl Phosphate as an Efficient Cationic Organocatalyst for Controlled/Living Ring-Opening Polymerization of δ-Valerolactone and ε-Caprolactone

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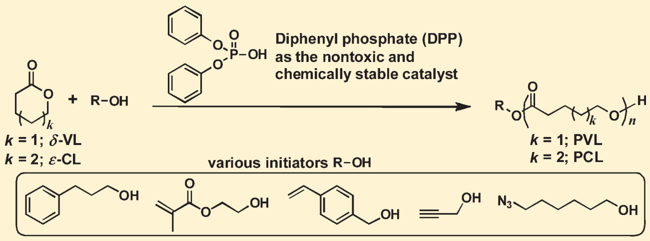
Supporting Information



ABSTRACT: The ring-opening polymerization of δ-valerolactone (δ-VL) and ε-caprolactone (ε-CL) using 3-phenyl-1-propanol (PPA) as the initiator and diphenyl phosphate (DPP) as the catalyst in toluene at room temperature with the [δ-VL or ε-CL]$_0$/[PPA]$_0$/[DPP] ratio of 50/1/1 homogeneously proceeded to afford poly(δ-valerolactone) (PVL) and poly(ε-caprolactone) (PCL) with narrow polydispersity indices. The molecular weights determined from a ^{1}H NMR analysis (PVL, $M_{n,NMR}$ = 5170 g mol^{-1} and PCL, $M_{n,NMR}$ = 5920 g mol^{-1}) showed good agreement with those estimated from the initial ratio of [δ-VL or ε-CL]$_0$/[PPA]$_0$ and monomer conversions (PVL, $M_{n,theo}$ = 4890 g mol^{-1} and PCL, $M_{n,theo}$ = 5680 g mol^{-1}). The ^{1}H NMR, SEC, and MALDI-TOF MS measurements of the obtained PVL and PCL clearly indicated the presence of the initiator residue at the chain end, confirming that the DPP-catalyzed ROP of lactones proceeded through an activated monomer mechanism. The kinetic and chain extension experiments confirmed the controlled/living nature for the DPP-catalyzed ROP of lactones. In addition, the block copolymerization of PVL and PCL successfully proceeded to afford PVL-*b*-PCL regardless of the monomer addition sequence. The DPP-catalyzed ROP of δ-VL and ε-CL using functional initiators, such as 2-hydroxyethyl methacrylate, 4-vinylbenzyl alcohol, propargyl alcohol, and 6-azido-1-hexanol, produced the corresponding end-functionalized PVLs and PCLs with narrow molecular weight distributions.

INTRODUCTION

Polymer synthesis using metal-free catalysts, so-called organocatalysts, has been rapidly developed to improve and expand the synthetic methods of polymeric materials because the organocatalyzed polymerization produces metal-free polymers, which is an important property for utilizing them as biocompatible and electric materials.[1,2] In particular, precisely controlled polymerization methods, such as living polymerization systems using organocatalysts, are required for synthesizing complex macromolecular architectures with well-defined structures.[3,4] For example, we, along with Waymouth and Hedrick and Gnanou and Taton,[5,6] reported the organocatalyzed group transfer polymerization (GTP) of (meth)acrylates and acrylamides, in which a loaded amount of organocatalysts, such as *N*-heterocyclic carbene (NHC) and trifluoromethanesulfonimide (HNTf$_2$), was significantly low compared to those for the GTPs using conventional Lewis acids and nucleophilic catalysts.[7,8] In addition, there have been many efforts to utilize various types of organocatalysts for the ring-opening polymerization (ROP) of various cyclic monomers. In particular, Waymouth and Hedrick determined that the ROP of cyclic esters and carbonates using organocatalysts, such as NHC,[9−12] 4-(dimethylamino)pyridine,[13] thiourea/amine,[14,15] alcohol derivatives,[16] guanidine,[17−19] phosphazene,[20,21] and phosphine,[22] was one of the best methods for producing metal-free polymers. These organocatalysts are bases or nucleophiles, and they generally activate initiators/chain end and/or monomers, producing a controlled/living nature.

On the other hand, the acid-catalyzed ROP has only been rarely reported, in which carboxylic acids,[3,23,24] trifluoromethanesulfonic acid (TfOH),[25,26] methanesulfonic acid,[25] and HCl·Et$_2$O complex,[3,27−29] were utilized as effective acid catalysts for the ROP of cyclic esters leading to well-defined polyesters. In addition, we recently reported that the ROP of δ-valerolactone (δ-VL) with 3-phenyl-1-propanol (PPA) as the initiator occurred using HNTf$_2$, one of the strong Brønsted acids, as the acid-type organocatalyst to afford the well-defined poly(δ-valerolactone) (PVL).[30] Although a loaded amount of HNTf$_2$ toward δ-VL was very low in comparison with other acid catalysts due to the extremely strong acidity of HNTf$_2$, this property caused undesirable reactions, such as transesterification, resulting in broadening of the molecular weight distributions of the obtained PVLs. Thus, it is interesting to elucidate the scope and limit of applicable acid catalysts in connection with suitable cyclic monomers for the ROP.

Of great interest is studying the catalytic activity of weak acids for the ROP of cyclic monomers compared to those using strong

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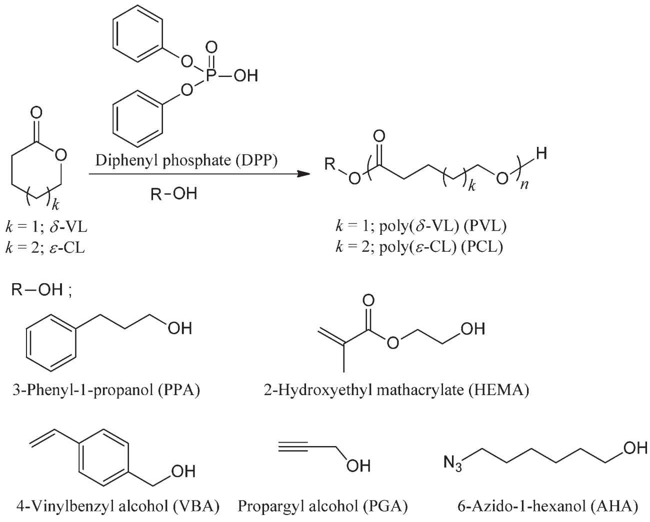
Scheme 1. Ring-Opening Polymerization of δ-Valerolactone (δ-VL) and ε-Caprolactone (ε-CL) Using Diphenyl Phosphate (DPP) as the Organocatalyst and Alcohol (ROH) as the Intitiator



Brønsted acids, such as TfOH and $HNTf_2$. We now focused on diphenyl phosphate (DPP) as the weak acid organocatalyst because DPP is commercially available, has a low toxicity, and is chemically stable.[31] In this study, we report that DPP was used as the organocatalyst for the ROPs of δ-valerolactone (δ-VL) and ε-caprolactone (ε-CL) using PPA as the initiator (Scheme 1). This article describes (1) the characterization and optimization of the DPP-catalyzed ROPs of δ-VL and ε-CL, (2) the mechanism of the DPP-catalyzed ROP of cyclic esters using ^1H NMR, SEC, and MALDI-TOF MS analyses of the obtained polyesters, and (3) the syntheses of diblock copolymers consisting of PVL and PCL and end-functionalized PVLs and PCLs using functional initiators, such as 2-hydroxyethyl methacrylate (HEMA), 4-vinylbenzyl alcohol (VBA), propargyl alcohol (PGA), and 6-azido-1-hexanol (AHA), as shown in Scheme 1.

EXPERIMENTAL SECTION

Materials. Toluene (>99.5%; water content, <0.001%) was purchased from Kanto Chemical Co., Inc., and distilled over sodium benzophenone ketyl under an argon atmosphere. δ-Valerolactone (δ-VL; 99%, Kanto Chemical Co., Inc.) and ε-caprolactone (ε-CL; 99%, Tokyo Kasei Kogyo Co., Ltd. (TCI)) were distilled over CaH_2 under reduced pressure. Diphenylphosphate (DPP, TCI) was used as received. 3-Phenyl-1-propanol (PPA, TCI) was distilled over CaH_2 under an argon atmosphere. A weak base anion exchange resin, Amberlyst A21 (Organo Co., Ltd.), was used as received. 2-Hydroxyethyl methacrylate (HEMA, TCI) was distilled under reduced pressure. 4-Vinylbenzyl alcohol (VBA)[32] and 6-azido-1-hexanol (AHA)[33] were synthesized using previously reported techniques. Propargyl alcohol (PGA, TCI) was distilled over CaH_2.

Instruments. The number-average molecular weight ($M_{n,NMR}$) was determined from the ^1H NMR spectra recorded using a JEOL JNM-A400II instrument. The polymerization was carried out in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) in a dry argon atmosphere (H_2O, $O_2 < 1$ ppm). The moisture and oxygen contents in the glovebox were monitored by an MB-MO-SE 1 and an MB-OX-SE 1, respectively. The size exclusion chromatography (SEC) was performed at 40 °C in $CHCl_3$ (0.8 mL min^{-1}) using a Jasco GPC-900 system equipped with a set of two Shodex K-805 L columns (linear, 8 mm ×300 mm). The polydispersity (M_w/M_n) of the polymers was calculated on the basis of a polystyrene calibration. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) of the obtained polymers was performed using an Applied Biosystems Voyager-DE STR-H equipped with a 337 nm nitrogen laser (3 ns pulse width). Two hundred shots were accumulated for the spectra at a 20 kV acceleration voltage in the reflector mode and calibrated using insulin (TAKARA BIO, Inc.) as the internal standard. Samples for the MALDI-TOF MS were prepared by mixing the polymer (1.0 mg mL^{-1}) and a matrix (2,5-dihydroxybenzoic acid, 15 mg mL^{-1}, 10 μL) in THF. For the measurement, a sample plate, which was coated by a solution (1.0 μL) of NaI as the cationic agent in acetone (1.0 mmol L^{-1}), was used.[34]

Polymerization of δ-Valerolactone. A typical procedure for the polymerization is as follows: δ-VL (0.270 mL, 3.00 mmol) was added to a stock solution of PPA (60.0 μL, 60.0 μmol) in toluene at 27 °C in the glove box. A toluene stock solution of DPP (60.0 μL, 60.0 μmol) was then added to the solution to initiate the polymerization under an argon atmosphere. After 1 h, the polymerization was quenched by the addition of Amberlyst A21. Before the addition of the Amberlyst A21, we obtained a portion of the polymerization mixtures and then added a small amount of triethylamine to the mixtures for determining the monomer conversion that was directly determined from the ^1H NMR measurements of the polymerization mixtures. The polymer was isolated by reprecipitation from CH_2Cl_2 in cold methanol/hexane. Yield, 49.8%; $M_{n,NMR}$, 5170 g mol^{-1}; M_w/M_n, 1.09. ^1H NMR ($CDCl_3$) δ (ppm), 1.66 (m, 2H × n, $(-CH_2\mathit{CH_2}CH_2O-)_n$), 1.69 (m, 2H × n, $(-COCH_2\mathit{CH_2}CH_2-)_n$), 1.93 (q, 2H, J = 6.2, $ArCH_2\mathit{CH_2}CH_2-$), 2.34 (t, 2H × n, J = 6.5 Hz, $(-OCOC\mathit{H_2}CH_2-)_n$), 2.68 (t, 2H, J = 7.8 Hz, $Ar\mathit{CH_2}CH_2-$), 3.61 (t, 2H, J = 6.8 Hz, $-CH_2\mathit{CH_2}OH$), 4.08 (t, 2H × n, J = 5.9, $(-CH_2\mathit{CH_2}O-)_n$), 4.12 (m, 2H, $ArCH_2CH_2\mathit{CH_2}O-$) 7.15−7.34 (m, 5H, aromatic).

A similar condition for δ-VL was used for the polymerization of ε-CL. Yield, 75.8%; $M_{n,NMR}$, 5920 g mol^{-1}; M_w/M_n, 1.07. ^1H NMR ($CDCl_3$) δ (ppm), 1.38 (m, 2H × n, $(-CH_2CH_2\mathit{CH_2}CH_2CH_2-)_n$), 1.57 (m, 2H × n, $(-CH_2\mathit{CH_2}CH_2O-)_n$), 1.65 (m, 2H × n, $(-COCH_2\mathit{CH_2}CH_2-)_n$), 1.93 (q, 2H, J = 6.3, $ArCH_2\mathit{CH_2}CH_2-$), 2.31 (t, 2H × n, J = 7.3 Hz, $(-OCOC\mathit{H_2}CH_2-)_n$), 2.63 (t, 2H, J = 7.3 Hz, $Ar\mathit{CH_2}CH_2-$), 3.65 (t, 2H, J = 6.6 Hz, $-CH_2\mathit{CH_2}OH$) 4.06 (t, 2H × n, J = 6.9, $(-CH_2\mathit{CH_2}O-)_n$), 4.12 (m, 2H, $ArCH_2CH_2\mathit{CH_2}O-$) 7.15−7.34 (m, 5H, aromatic).

RESULTS AND DISCUSSION

Ring-Opening Polymerization of δ-Valerolactone and ε-Caprolactone Using 3-Phenyl-1-propanol and Diphenyl Phosphate. In order to use diphenyl phosphate (DPP) as the acid catalyst for the ring-opening polymerizations (ROPs) of δ-valerolactone (δ-VL) and ε-caprolactone (ε-CL), we first carried out the polymerizations of δ-VL and ε-CL using 3-phenyl-1-propanol (PPA) as the initiator in toluene at room temperature at the $[\delta\text{-VL or }\varepsilon\text{-CL}]_0/[PPA]_0/[DPP]$ ratio of 50/1/1 (Table 1, runs 1 and 5, respectively). Both polymerizations homogeneously proceeded and were quenched with immobilized base, and the obtained polymers were purified by reprecipitation using CH_2Cl_2 as the good solvent and cold methanol/hexane as the poor solvent. The conversion of δ-VL was 95.0% for the polymerization time of 1 h and that of ε-CL was 97.1% for 8 h, which were directly determined by the ^1H NMR spectra of aliquots of the polymerization mixtures in $CDCl_3$. The consumption rate of δ-VL was faster than that of ε-CL, which agreed with other systems for the polymerizations of δ-VL and ε-CL.

Table 1. Ring-Opening Polymerization of δ-Valerolactone (δ-VL) and ε-Caprolactone (ε-CL) Using 3-Phenyl-1-propanol (PPA) and Diphenyl Phosphate (DPP) in Toluene[a]

run	monomer (M)	$[M]_0/[PPA]_0$	time (h)	conv (%)[b]	$M_{n,theo}$[c] (g mol^{-1})	$M_{n,NMR}$[b] (g mol^{-1})	M_w/M_n[d]
1	δ-VL	50	1	95.0	4 890	5 170	1.09
2	δ-VL	100	2.5	94.8	9 630	10 000	1.07
3	δ-VL	150	4	94.6	14 300	14 800	1.07
4	δ-VL	300	6	90.7	27 400	27 500	1.08
5	ε-CL	50	8	97.1	5 680	5 920	1.07
6	ε-CL	100	24	95.1	11 000	11 500	1.07
7	ε-CL	150	29	80.4	13 900	15 200	1.06
8	ε-CL	300	43	61.6	21 200	21 600	1.07

[a] $[M]_0$, 1.0 mol L^{-1}; temperature, rt. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from $([M]_0/[PPA]_0) \times$ conv $\times$ (MW of δ-VL or ε-CL) + (MW of PPA). [d] Determined by SEC in $CHCl_3$ using PSt standards.

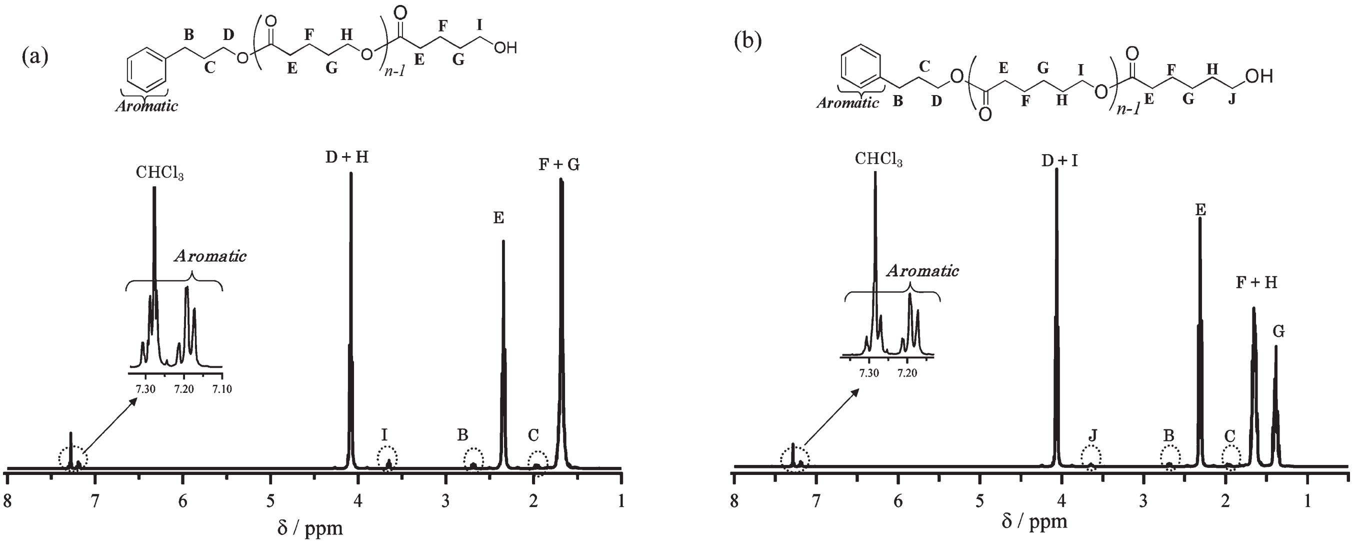


Figure 1. (a) ^{1}H NMR spectra of the obtained PVL (Table 1, run 1) and (b) ^{1}H NMR spectra of the obtained PCL (Table 1, run 5) in $CDCl_3$.

The chemical structures of the obtained polymers were assigned to poly(δ-valerolactone) (PVL) and poly(ε-caprolactone) (PCL) by the ^{1}H NMR measurement (Figure 1a, 1b). The characteristic peaks due to the initiator of PPA were observed as the peaks due to the phenyl protons, the benzyl protons, and the methylene protons adjacent to the ester linkage that appeared in the range from 7.15 to 7.34, 2.68, and 1.93 ppm, respectively, and the peak due to the methylene protons adjacent to the ω-chain end of the hydroxyl group was clearly observed at 3.61 ppm. In addition, the peaks for PCL appeared in the ranges of 7.15−7.34, 2.63, 1.93, and 3.65 ppm, respectively. These results implied that both polymerizations were initiated from PPA. More importantly, the number-average molecular weight ($M_{n,NMR}$) of the obtained polymer estimated from the ^{1}H NMR measurement fairly agreed with that ($M_{n,theo}$) calculated from the initial ratio of $[\delta\text{-VL or }\varepsilon\text{-CL}]_0/[PPA]_0$ and monomer conversions; the $M_{n,NMR}$ and $M_{n,theo}$ values for PVL were 5170 and 4890 g mol^{-1}, respectively, and those for PCL were 5920 and 5680 g mol^{-1}, respectively. These results indicated that the obtained polyesters should possess a PPA residue as the initiating end group.

Further evidence for the PPA residue confirming with the polyesters was obtained from the SEC measurements. Figure 2 shows the monomodal SEC traces of the obtained PVL and PCL. The molecular weight distributions (M_w/M_ns) estimated by the SEC measurement were relatively low, i.e., 1.09 for PVL and 1.07 for PCL (Figure 2, a and b, respectively). In addition, the SEC traces of the obtained PVL and PCL monitored by an RI detector showed almost the same shapes and retention times as those by an UV detector, indicating that the PPA moiety was definitely connected to the PVL and PCL chains.

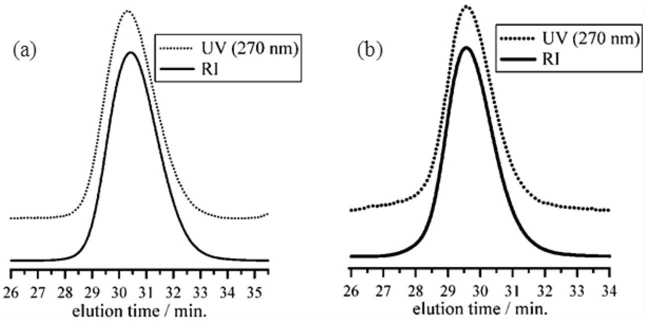
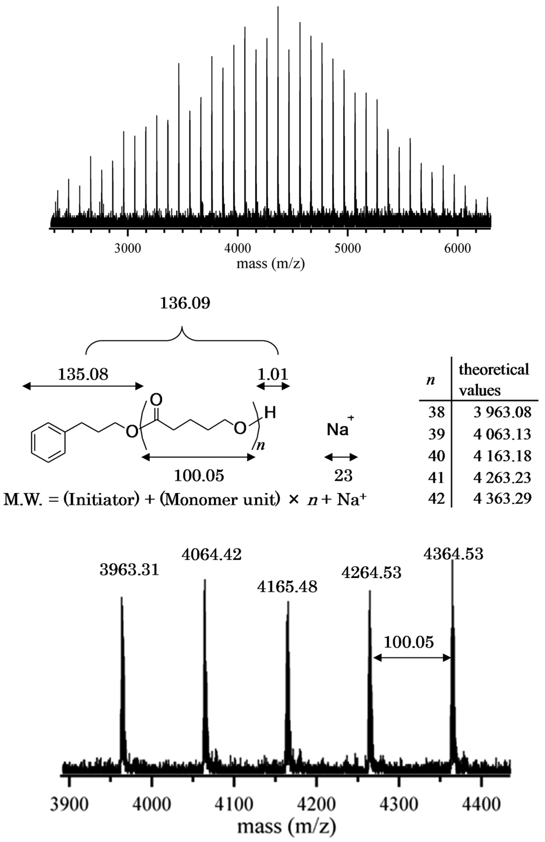
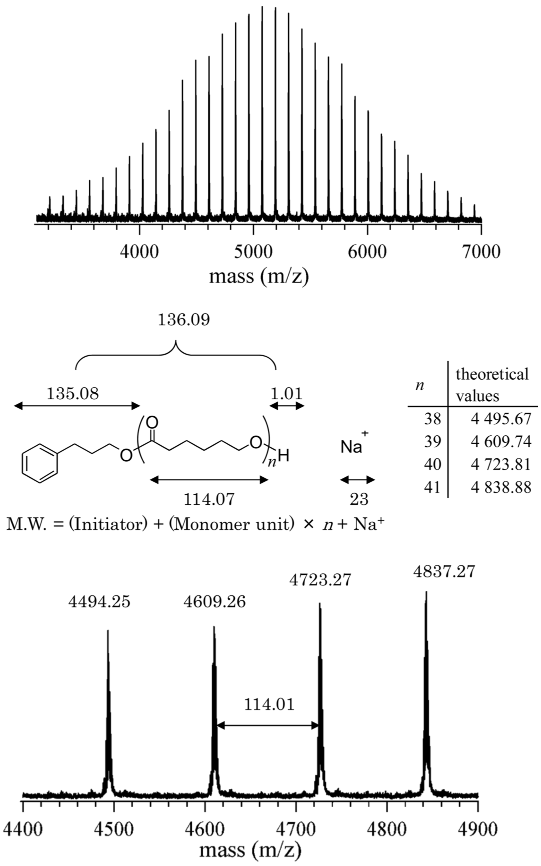


Figure 2. (a) SEC traces of the obtained PVL (Table 1, run 1) detected by RI and UV (270 nm) detectors and (b) SEC traces of the obtained PCL (Table 1, run 5) detected by RI and UV (270 nm) detectors (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.4 mL min^{-1}).



n	theoretical values
38	3 963.08
39	4 063.13
40	4 163.18
41	4 263.23
42	4 363.29

Figure 3. MALDI-TOF MS spectrum in reflector mode of the obtained PVL ($[\delta\text{-VL}]_0/[\text{PPA}]_0/[\text{DPP}] = 50/1/1$, conversion = 95.0%, $M_{n,\text{NMR}}$ = 5 170 g mol^{-1}, $M_w/M_n = 1.09$).



n	theoretical values
38	4 495.67
39	4 609.74
40	4 723.81
41	4 838.88

Figure 4. MALDI-TOF MS spectrum in reflector mode of the obtained PCL ($[\varepsilon\text{-CL}]_0/[\text{PPA}]_0/[\text{DPP}] = 50/1/1$, conversion = 97.4%, $M_{n,\text{NMR}}$ = 5 840 g mol^{-1}, $M_w/M_n = 1.09$).

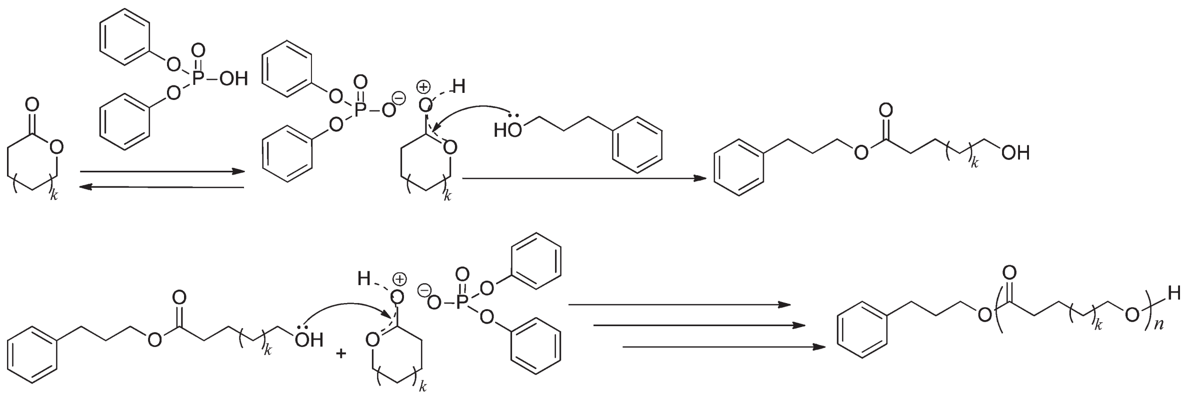
Additionally, a MALDI-TOF MS measurement provided direct evidence that the ROP of δ-VL and ε-CL initiated by PPA proceeded through an activated monomer mechanism. Figures 3 and 4 show the MALDI-TOF MS spectra of the obtained PVL and PCL, respectively. For example, one series of peaks perfectly agreed with the molecular weight of PVL possessing the PPA residue and the hydroxyl chain end (Figure 3). In addition, we confirmed that PCL showed results similar to the SEC and MALDI-TOF MS spectra (Figure 4). These results mean that the DPP-catalyzed ROPs of δ-VL and ε-CL proceeded in a living manner without any side reactions, such as backbiting and transesterification reactions, and PPA was obviously the initiator.

All the results based on the ^{1}H NMR, SEC, and MALDI-TOF MS measurements lead to the conclusion that PVL and PCL possessed the 3-phenylpropoxy group as the α-chain end and the hydroxyl group as the ω-chain end, i.e., PPA acted as the initiating agent for the DPP-catalyzed ROPs of δ-VL and ε-CL. Previously, Penczek et al. reported that the Brønsted acid-catalyzed ROP of cyclic esters proceeded via the so-called activated monomer mechanism leading to well-defined polyesters.[35] Thus, we assumed an activated monomer mechanism for the DPP-catalyzed ROP of δ-VL and ε-CL using the PPA initiator, as shown in Scheme 2, meaning that the DPP-catalyzed ROP of δ-VL and ε-CL proceeded in a controlled/living nature.

Controlled/Living Nature of DPP-Catalyzed ROP of δ-VL and ε-CL. The kinetic and postpolymerization experiments were carried out to confirm the controlled/living nature for the DPP-catalyzed ROPs of δ-VL and ε-CL. For the kinetic plots, as shown in Figures 5a and 6a, a distinct first-order relationship between the reaction time and monomer conversion was observed, meaning that the monomer consumption rate was constant during the polymerization. In addition, the molecular weight of the obtained PVL and PCL linearly increased with the reaction time, and the monomer conversion was as high as ≈95%, as shown in Figures 5b and 6b, respectively. More importantly, the $M_{n,\text{NMR}}$ values of the obtained PVLs and PCLs fairly agreed with those calculated by the initial ratio of $[\delta\text{-VL or }\varepsilon\text{-CL}]_0/[\text{PPA}]_0$ and the monomer conversion. From the SEC results, the polydispersity indices (M_w/M_n) of the obtained PVLs and PCLs showed low values ranging from 1.07 to 1.12 and from 1.07 to 1.17, respectively.

The chain extension experiment also supported the controlled/living nature of the DPP-catalyzed ROPs of δ-VL and ε-CL. Figure 7 shows SEC traces for the chain extension experiment. A PVL with $M_{n,\text{NMR}}$ = 5120 g mol^{-1} and $M_w/M_n = 1.10$ was first obtained from the polymerization with $[\delta\text{-VL}]_0/[\text{PPA}]_0/[\text{DPP}]_0 = 50/1/1$ and the monomer conversion of 97.5%. A further polymerization was then carried out by the subsequent addition of 50 equiv of δ-VL to afford a PVL with $M_{n,\text{NMR}}$ = 10 100 g mol^{-1} and $M_w/M_n = 1.10$, indicating that the chain end group of the PVL truly possessed a living nature (Figure 7a). Furthermore, the postpolymerization of ε-CL was confirmed as the first polymerization with $M_{n,\text{NMR}}$ = 5550 g mol^{-1} and $M_w/M_n = 1.07$ and then the second one with $M_{n,\text{NMR}}$ = 11 000 g mol^{-1} and M_w/M_n = 1.09 (Figure 7b). Thus, the DPP-catalyzed ROPs of δ-VL and ε-CL

Scheme 2. An Activated Monomer Mechanism for the DPP-Catalyzed ROP of δ-VL and ε-CL Using PPA



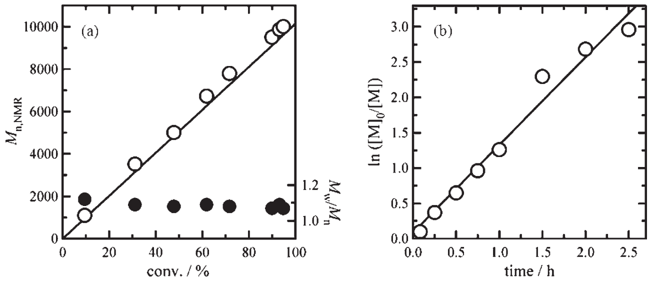


Figure 5. (a) Kinetic plots for the poslymerization of δ-VL and (b) dependence of molecular weight (M_n) and polydispersity (M_w/M_n) on the monomer conversion (conv). Solid line shows the $M_{n,theo}$ values calculated from the equation ($[\delta\text{-VL}]_0/[\text{PPA}]_0$) × conv × (MW of δ-VL) + (MW of PPA).

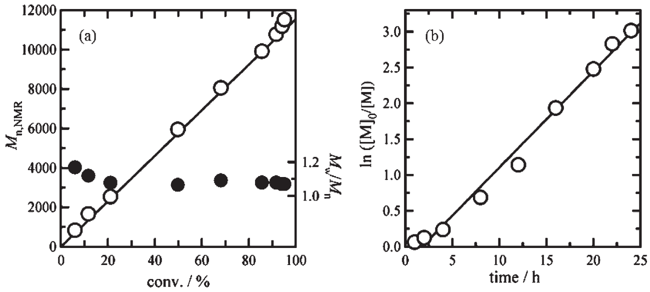


Figure 6. (a) Kinetic plots for the polymerization of ε-CL and (b) dependence of molecular weight (M_n) and polydispersity (M_w/M_n) on the monomer conversion (conv). Solid line shows the $M_{n,theo}$ values calculated from the equation ($[\varepsilon\text{-CL}]_0/[\text{PPA}]_0$) × conv × (MW of ε-CL) + (MW of PPA).

were revealed to possess a living nature and produce a precisely controlled PVL at ambient temperature.

To confirm that the polymerization system proceeded in a controlled/living fashion, we carried out the ROPs of δ-VL and ε-CL with varying [δ-VL or ε-CL]$_0$/[PPA]$_0$ ratios from 100 to 300 (Table 1, runs 2−4 and 6−8, respectively). The molecular weights of the resultant PVLs linearly increased with the increasing initial ratio of $[\delta\text{-VL}]_0/[\text{PPA}]_0$, whose values fairly agreed with the molecular weights predicted from the initial ratios of $[\delta\text{-VL}]_0/[\text{PPA}]_0$ and the monomer conversions. Their polydispersities were narrow, as shown in Figure 8, and their indices

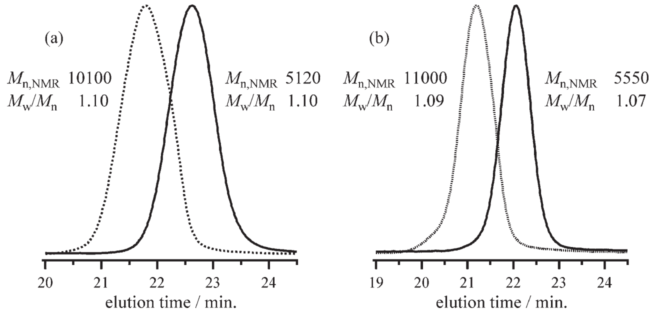


Figure 7. (a) SEC traces of first PVL sequence (solid line) and postpolymerization (dashed line) and (b) SEC traces of first PCL sequence (solid line) and postpolymerization (dashed line) (eluent, $CHCl_3$; flow rate, 0.8 mL min^{-1}).

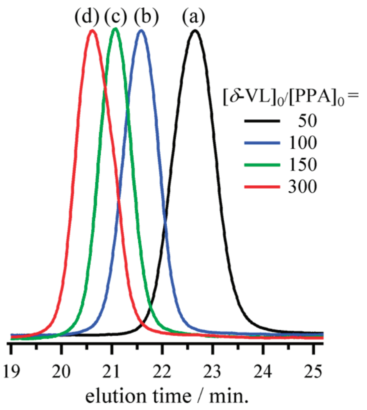


Figure 8. SEC traces of the obtained PVLs with various monomer-to-initiator ratios ($[\delta\text{-VL}]_0/[\text{PPA}]_0$ = (a) 50, (b) 100, (c) 150, and (d) 300) (eluent, $CHCl_3$; flow rate, 0.8 mL min^{-1}).

(M_w/M_n) were as low as 1.07−1.09 even though relatively high molecular weights; e.g., the M_w/M_n value was 1.08 for the PVL with a $M_{n,NMR}$ of 27 500 g mol^{-1} (Table 1, run 4). In addition, the $M_{n,NMR}$ value of 27 500 g mol^{-1} was higher than that prepared from the ROP of δ-VL using $HNTf_2$, such as the $M_{n,NMR}$ of 12 700 g mol^{-1} was obtained as a high molecular weight with a relatively narrow molecular weight of M_w/M_n = 1.10 from the polymerization with the $[\delta\text{-VL}]_0/[\text{PPA}]_0/[\text{HNTf}_2]_0$ of 130/

1/0.1 for 14 h. This fact suggested that DPP is a suitable acid organocatalyst rather than $HNTf_2$ for the controlled/living ROP of δ-VL.

For PCL, the molecular weight distributions were low with M_w/M_n values of 1.08−1.11, as shown in Figure 9. However, the characteristics for the ROP of ε-CL apparently differed from those of δ-VL, which was caused by the difference in the polymerization rate between δ-VL and ε-CL. In particular, the monomer conversion was required to be low for the synthesis of PCLs with relatively high molecular weights because the excess polymerization time induced the intra- and intermolecular esterification process leading to broad polydispersed PCLs. Thus, we obtained a PCL of 1.07 and 21 600 g mol^{-1} for the monomer conversion of 61.6%.

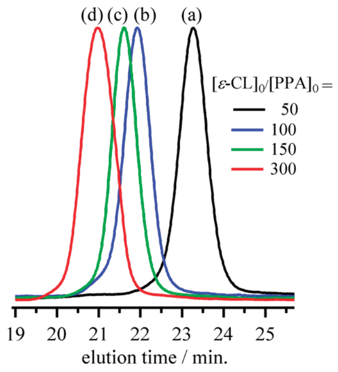


Figure 9. SEC traces of the obtained PCLs with various monomer-to-initiator ratios ($[ε\text{-CL}]_0/[PPA]_0$ = (a) 50, (b) 100, (c) 150, and (d) 300) (eluent, $CHCl_3$; flow rate, 0.8 mL min^{-1}).

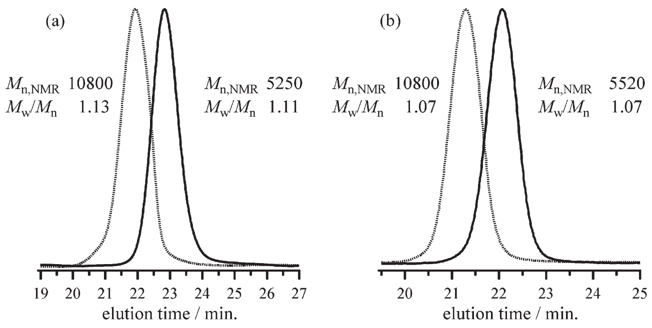


Figure 10. (a) SEC traces of first PVL sequence (solid line) and PVL-*b*-PCL (dashed line) and (b) SEC traces of first PCL sequence (solid line) and PCL-*b*-PVL (dashed line) (eluent, $CHCl_3$; flow rate, 0.8 mL min^{-1}).

Block Copolymerization of δ-VL and ε-CL. The postpolymerization property indicated that both the chain ends of PVL and PCL maintained the proper structures possessing a further polymerization ability. The polymerization characteristic can be used to synthesize block copolymers consisting of PVL and PCL, which are interesting biodegradable polymeric materials with two different mechanistic properties. First, we carried out the polymerization of δ-VL at $[δ\text{-VL}]_0/[PPA]_0/[DPP]$ = 50/1/1, and then the same mole of ε-CL was added to the reaction mixture. A monomodal SEC trace of the first δ-VL polymerization shifted to a higher molecular weight region while keeping the monodispersity after the second ε-CL polymerization, as shown in Figure 10a; i.e., the molecular weight increased from 5250 to 10 800 g mol^{-1}, and the polydispersity slightly varied from 1.11 to 1.13. The block copolymer consisting of PVL and PCL, PVL-*b*-PCL, was confirmed by the ^1H NMR measurement (see Supporting Information). In addition, we first polymerized ε-CL and then δ-VL, and a similar result was obtained, as shown in Figure 10b; monomodal SEC traces were observed for the first PCL (M_n = 5520 g mol^{-1}, M_w/M_n = 1.07) and the final PCL-*b*-PVL (M_n = 10 800 g mol^{-1}, M_w/M_n = 1.07). Applying the cotrolled/living nature to the block copolymerization of δ-VL and ε-CL, the well-defined PVL-*b*-PCL was synthesized regardless of the monomer addition sequence.

Synthesis of End-Functionalized PVLs and PCLs with Various Groups. To provide an intrinsic advantage of the DPP-catalyzed ROPs of δ-VL and ε-CL, we finally focused on the synthesis of the end-functionalized PVLs and PCLs using functional initiators (FIs), such as 2-hydroxyethyl methacrylate (HEMA), 4-vinylbenzyl alcohol (VBA), propargyl alcohol (PGA), and 6-azido-1-hexanol (AHA), as shown in Scheme 1. HEMA and VBA are FIs with the methacrylate and 4-vinylbenzyl groups, respectively, leading to the end-functionalized polyesters as macromonomers,[36,37] and PGA and AHA are FIs with the acetylenic and azido groups, respectively, leading to the end-functionalized polyesters as click ready polymers.[38,39] Table 2 lists the synthetic results of the end-functionalized polyesters. All the DPP-catalyzed ROPs of δ-VL and ε-CL using HEMA, VBA, PGA, and AHA proceeded in a well-controlled manner to afford the corresponding PVLs and PCLs with predictable molecular weights and narrow polydispersity indices. The $M_{n,NMR}$ values of the obtained PVLs and PCLs estimated by the ^1H NMR measurement agreed

Table 2. Synthesis of End-Functionalized Polyesters by the DPP-Catalyzed ROP of δ-VL and ε-CL Using Functional Initiators (FI) in Toluene[a]

run	monomer (M)	functional initiator (FI)	time (h)	conv (%)[b]	$M_{n,theo}$[c] (g mol^{-1})	$M_{n,NMR}$[b] (g mol^{-1})	M_w/M_n[d]
15	δ-VL	HEMA	1	87.8	4530	4550	1.12
16	δ-VL	VBA	1	94.3	4860	5030	1.11
17	δ-VL	PGA	1	94.6	4790	4840	1.13
18	δ-VL	AHA[f]	1	95.0	4900	4980	1.11
11	ε-CL	HEMA	5	89.7	5250	5260	1.08
12	ε-CL	VBA	5	84.9	4980	5220	1.08
13	ε-CL	PGA	5	84.9	4900	4980	1.11
14	ε-CL	AHA[e]	5	91.7	5380	5470	1.08

[a] $[M]_0$, 1.0 mol L^{-1}; $[M]_0/[FI]_0/[DPP]_0$, 50/1/1; temperature, rt. [b] Determined by ^1H NMR in $CDCl_3$. [c] Calculated from $([M]_0/[FI]_0)$ × conv × (MW of δ-VL or ε-CL) + (MW of FI). [d] Determined by SEC in $CHCl_3$ using PSt standards. [e] Using 0.43 mol L^{-1} stock solution in CH_2Cl_2. [f] Using 0.44 mol L^{-1} stock solution in CH_2Cl_2.

with the $M_{n,theo}$ values calculated by the [δ-VL or ε-CL]$_0$/[FI]$_0$ and monomer conversions; e.g., for the polymerization using HEMA, the $M_{n,NMR}$ values of the PVL and PCL were 4550 and 5260 g mol^{-1}, respectively, which agreed with the $M_{n,theo}$ values of 4530 and 5250 g mol^{-1}, respectively. In addition, the introduction of these functional groups at the α-end of the obtained PVLs and PCLs was confirmed by the ^{1}H NMR analysis (see Supporting Information). Thus, we revealed that DPP was an efficient organocatalyst for the ROP of δ-VL and ε-CL to afford well-defined polyester-based materials.

■ CONCLUSIONS

In this study, we achieved the production of well-controlled poly(δ-valerolactone)s (PVLs) and poly(ε-caprolactone)s (PCLs) by the ring-opening polymerization (ROP) of δ-valerolactone (δ-VL) and ε-caprolactone (ε-CL) using diphenyl phosphate (DPP) as the organocatalyst and 3-phenyl-1-propanol (PPA) as the initiator. All the polymerizations proceeded in a living fashion, and the molecular weights of the polymers were well controlled with narrow polydispersities. PVL-*b*-PCL was synthesized by the block copolymerization of δ-VL and ε-CL, regardless of the monomer addition sequence. In addition, initiators with functional groups, such as 2-hydroxyethyl methacrylate, 4-vinylbenzyl alcohol, propargyl alcohol, and 6-azido-1-hexanol, were used for the DPP-catalyzed controlled/living ROP system, affording end-functionalized polyesters as macromonomers and click-ready materials. In conclusion, we demonstrated a new catalytic activity of DPP and various end-functionized polyesters were produced using the DPP-catalyzed ROP system.

■ ASSOCIATED CONTENT

S Supporting Information. Results of the end-functionalized PVLs and PCLs. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. *Chem. Rev.* **2007**, *107* (12), 5813–5840.

(2) Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2010**, *43* (5), 2093–2107.

(3) Sanda, F.; Sanada, H.; Shibasaki, Y.; Endo, T. *Macromolecules* **2002**, *35* (3), 680–683.

(4) Kakwere, H.; Perrier, S. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47* (23), 6396–6408.

(5) Scholten, M. D.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2008**, *41* (20), 7399–7404.

(6) Raynaud, J.; Gnanou, Y.; Taton, D. *Macromolecules* **2009**, *42* (16), 5996–6005.

(7) Kakuchi, R.; Chiba, K.; Fuchise, K.; Sakai, R.; Satoh, T.; Kakuchi, T. *Macromolecules* **2009**, *42* (22), 8747–8750.

(8) Fuchise, K.; Sakai, R.; Satoh, T.; Sato, S.; Narumi, A.; Kawaguchi, S.; Kakuchi, T. *Macromolecules* **2010**, *43* (13), 5589–5594.

(9) Connor, E. F.; Nyce, G. W.; Myers, M.; Mock, A.; Hedrick, J. L. *J. Am. Chem. Soc.* **2002**, *124* (69), 914–915.

(10) Nyce, G. W.; Glauser, T.; Connor, E. F.; Mock, A.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2003**, *125* (10), 3046–3056.

(11) Dove, A. P.; Pratt, R. C.; Lohmeijer, B. G. G.; Culkin, D. A.; Hagberg, E. C.; Nyce, G. W.; Waymouth, R. M.; Hedrick, J. L. *Polymer* **2006**, *47* (11), 4018–4025.

(12) Kamber, N. E.; Jeong, W.; Gonzalez, S.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2009**, *42* (5), 1634–1639.

(13) Nederberg, F.; Connor, E. F.; Moller, M.; Glauser, T.; Hedrick, J. L. *Angew. Chem., Int. Ed.* **2001**, *40* (14), 2712–2715.

(14) Dove, A. P.; Pratt, R. C.; Lohmeijer, B. G. G.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2005**, *127* (40), 13798–13799.

(15) Pratt, R. C.; Lohmeijer, B. G. G.; Long, D. A.; Lundberg, P. N. P.; Dove, A. P.; Li, H. B.; Wade, C. G.; Waymouth, R. M.; Hedrick, J. L. *Macromolecules* **2006**, *39* (23), 7863–7871.

(16) Coulembier, O.; Sanders, D. R.; Nelson, A.; Hollenbeck, A. N.; Horn, H. W.; Rice, J. E.; Fujiwara, M.; Dubois, P.; Hedrick, J. L. *Angew. Chem., Int. Ed.* **2009**, *48* (28), 5170–5173.

(17) 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* (25), 8574–8583.

(18) Pratt, R. C.; Lohmeijer, B. G. G.; Long, D. A.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2006**, *128* (14), 4556–4557.

(19) Zhang, L.; Nederberg, F.; Messman, J. M.; Pratt, R. C.; Hedrick, J. L.; Wade, C. G. *J. Am. Chem. Soc.* **2007**, *129* (42), 12610–12611.

(20) Zhang, L.; Pratt, R. C.; Nederberg, F.; Horn, H. W.; Rice, J. E.; Waymouth, R. M.; Wade, C. G.; Hedrick, J. L. *Macromolecules* **2010**, *43* (3), 1660–1664.

(21) Zhang, L.; Nederberg, F.; Pratt, R. C.; Waymouth, R. M.; Hedrick, J. L.; Wade, C. G. *Macromolecules* **2007**, *40* (12), 4154–4158.

(22) Myers, M.; Connor, E. F.; Glauser, T.; Mock, A.; Nyce, G.; Hedrick, J. L. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40* (7), 844–851.

(23) Persson, P. V.; Schroder, J.; Wickholm, K.; Hedenstrom, E.; Iversen, T. *Macromolecules* **2004**, 37 (16), 5889–5893.

(24) Oledzka, E.; Narine, S. S. *J. Appl. Polym. Sci.* **2011**, *119* (4), 1873–1882.

(25) Gazeau-Bureau, S.; Delcroix, D.; Martin-Vaca, B.; Bonrissou, D.; Navarro, C.; Magnet, S. *Macromolecules* **2008**, *41* (11), 3782–3784.

(26) Bourissou, D.; Martin-Vaca, B.; Dumitrescu, A.; Graullier, M.; Lacombe, F. *Macromolecules* **2005**, *38* (24), 9993–9998.

(27) Shibasaki, Y.; Sanada, H.; Yokoi, M.; Sanda, F.; Endo, T. *Macromolecules* **2000**, *33* (12), 4316–4320.

(28) Lou, X. D.; Detrembleur, C.; Jerome, R. *Macromolecules* **2002**, *35* (4), 1190–1195.

(29) Kim, M. S.; Seo, K. S.; Khang, G.; Lee, H. B. *Macromol. Rapid Commun.* **2005**, *26* (8), 643–648.

(30) Kakuchi, R.; Tsuji, Y.; Chiba, K.; Fuchise, K.; Sakai, R.; Satoh, T.; Kakuchi, T. *Macromolecules* **2010**, *43* (17), 7090–7094.

(31) Krasovec, F.; Jan, J. *Croat. Chem. Acta* **1963**, *35* (3), 183–193.

(32) Abramo, J. G.; Chapin, E. C. *J. Org. Chem.* **1961**, *26* (8), 2671–2673.

(33) Speers, A. E.; Adam, G. C.; Cravatt, B. F. *J. Am. Chem. Soc.* **2003**, *125* (16), 4686–4687.

(34) Kristofer, J. T.; Heise, A.; deGeus, M.; Villarroya, S.; Zhou, J.; Wyatt, M. F.; Howdle, S. M. *Macromolecules* **2006**, *39* (23), 7967–7972.

(35) Penczek, S. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38* (11), 1919–1933.

(36) Ydens, I.; Degee, P.; Dubois, P.; Libiszowski, J.; Duda, A.; Penczek, S. *Macromol. Chem. Phys.* **2003**, *204* (1), 171–179.

(37) Xu, X. Q.; Jia, Z. F.; Sun, R. M.; Huang, J. L. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44* (15), 4396–4408.

(38) Misaka, H.; Kakuchi, R.; Zhang, C. H.; Sakai, R.; Satoh, T.; Kakuchi, T. *Macromolecules* **2009**, *42* (14), 5091–5096.

(39) Hoskins, J. N.; Grayson, S. M. *Macromolecules* **2009**, *42* (17), 6406–6413.