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Organophosphate-Catalyzed Bulk Ring-Opening Polymerization as an Environmentally Benign Route Leading to Block Copolyesters, End-Functionalized Polyesters, and Polyester-Based Polyurethane

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Abstract. The ring-opening polymerizations (ROPs) of ε-caprolactone (ε-CL), δ-varelolactone, 1,5-dioxepan-2-one, trimethylene carbonate, and L-lactide were performed in the bulk using an organophosphate, such as diphenyl phosphate, bis(4-nitrophenyl)phosphate, and di(2,6-xylyl)phosphate, as the catalyst. The ROPs proceeded in a well-controlled manner even in the bulk condition to afford well-defined aliphatic polyesters, polyester-ether, and polycarbonate with relatively low dispersities. Notably, the amount of the loaded catalyst was successfully reduced when compared to the conventional organophosphate-catalyzed ROP in solution. A kinetic study revealed the controlled/living nature of the present bulk ROP system, which allowed us to produce the block copolymers composed of polyesters, polyester-ether, and polycarbonate in one-pot. Syntheses of the end-functionalized poly(ε-caprolactone)s (PCLs) and poly(trimethylene carbonate) were successfully demonstrated using alcohol initiators possessing highly reactive functional groups. Furthermore, the α,ω-dihydroxy telechelic PCL-diol as well as the three- and four-armed star-shaped PCL-polyols were also easily obtained by using the polyols as an initiator. Finally, the one-pot synthesis of polyurethane via the ROP of ε-CL and subsequent urethane forming reaction was demonstrated by taking advantage of the dual catalytic abilities of the organophosphate for both the ROP and polyurethane synthesis.

Introduction

Aliphatic polyesters have been widely utilized as textile and packaging materials as well as prepolymers for polyurethane forms and elastomeric fibers. In addition, there is a growing demand of aliphatic polyesters for medical, pharmaceutical, and environmental applications because of their good biodegradability and biocompatibility. However, Sn-, Al-, and Zn-based catalysts (or initiators) are still employed for the ring-opening polymerization (ROP) of cyclic esters to produce a series of aliphatic polyesters,[1-6] thus limiting their clinical uses due to the serious concerns about residual metal contamination. In order to avoid metal contamination without any special purification steps, the organocatalytic approach has emerged as a powerful metal-free polymerization process in recent years.[7]

Considerable effort has been directed toward the evaluation of various types of both organic acids/bases for the ROP of cyclic esters,[7-37] cyclic carbonates,[38-43] epoxides,[44-47] lactams,[48] cyclic (carbo)siloxanes,[49] cyclic phosphates,[50-54] etc. Regarding the ROP of cyclic esters, organic Brønsted acids, *e.g.*, methane sulfonic acid (MSA) and triflimide, were found to be suited for the polymerization of lactones,[8-19] whereas organic bases, *e.g.*, 1,8-diazadicyclo[5.4.0]undec-7-ene (DBU) and 4-dimethylaminopyridine (DMAP), were effective for the ROP of the lactide (LA).[7,20-24,26] In addition, the bifunctional catalytic system possessing two activation sites for the monomer and propagating chain end also turned out to be effective for the ROP of ε-caprolactone (ε-CL) and LA.[27-37] For example, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a bifunctional catalytic system promotes the ROP of the ε-CL, whereas DBU is ineffective,[20] and the MSA/DMAP bifunctional

catalytic system promotes the ROP of the LA, whereas MSA alone does not work.[31]

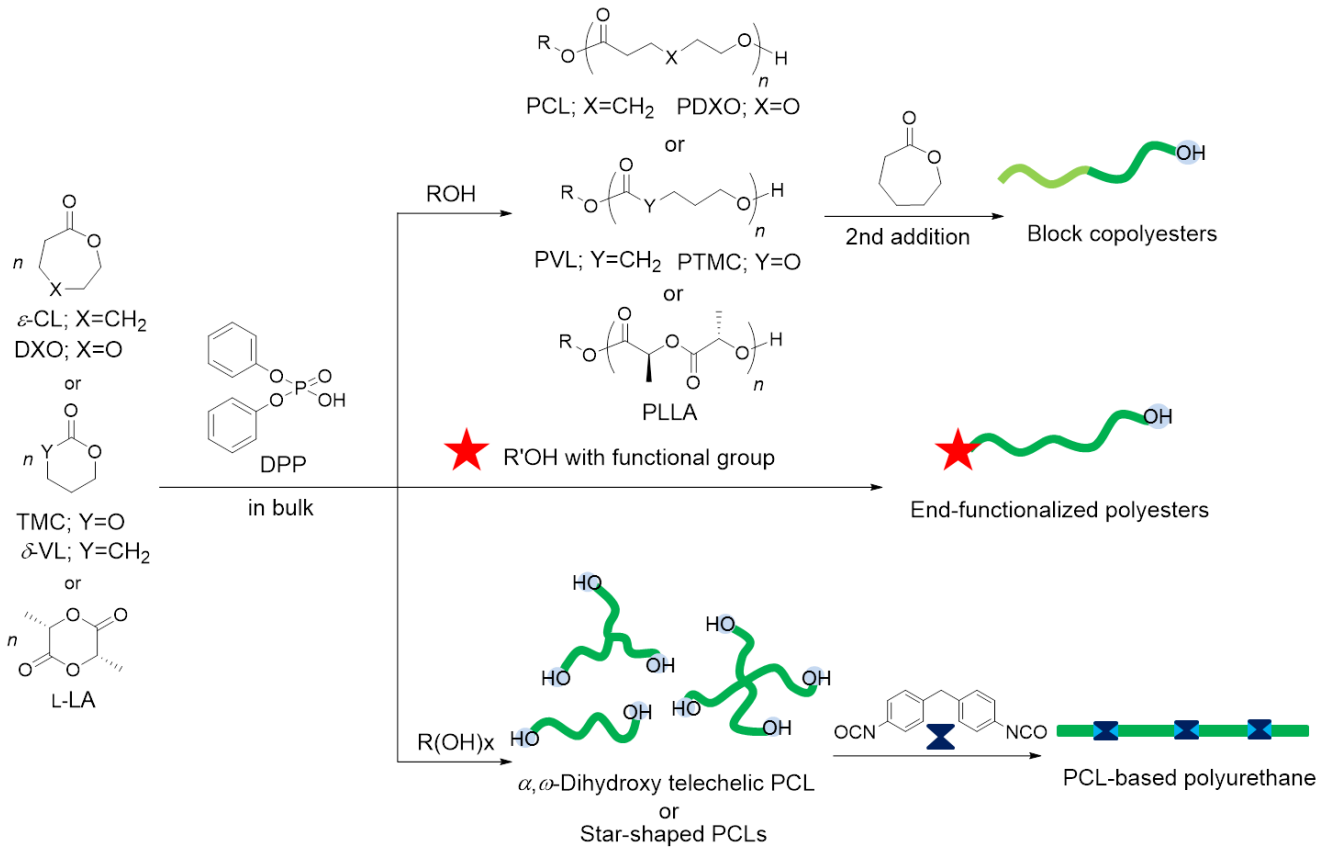
Despite such numerous efforts, there are still many problems to be overcome for the industrial scale production of aliphatic polyesters using an organocatalytic system. In general, a strong acidity is required to catalyze the ROP of cyclic esters, *e.g.*, the pK_a value of -2.6 for MSA and -14 for triflic acid (TfOH),[55] which is often accompanied by undesirable reactions, such as inter- and intra-transesterifications, resulting in less control over the molar mass and dispersity ($Đ_M$).[9,15] Furthermore, Bourrissou *et al*. reported that the high acidity of a catalyst caused deactivation of the propagation, resulting in interrupting the production of high molar mass polymers.[9] In addition, (super) strong acids/bases seriously damage the reaction vessel as well as the human body, and some of them are unstable with H_2O and/or air. These properties make it difficult to operate the polymerization process on an industrial scale.

Recently, we and others reported the organophosphates, which are one of the weak Brønsted acids including diphenyl phosphate (DPP; pK_a = 3.7) and bis(4-nitrophenyl)phosphate (BNPP; pK_a = 1.7),[16] as a new paradigm for an organocatalyst for the ROP of lactones and cyclic carbonates to produce the corresponding well-defined polyesters and polycarbonates.[15,16,56-58] The organophosphates have many significant advantages over the above-mentioned strong organic acids. The most significant point is that the organophosphates simultaneously activate the monomer and propagating chain end by the phosphoric acid moiety and phosphoryl oxygen, respectively, which enables it to effectively catalyze the ROPs under mild reaction conditions in spite of their low acidity.[15] In addition to the low acidity, the low toxicity, low corrosivity, and sufficient chemical stability of the organophosphates are highly

attractive for application in an industrial scale process.[59] However, some defects still remained in the organophosphate-catalyzed ROP, *e.g.*, the amount of loaded catalyst and the use of a solvent. In our previous procedure, an equimolar amount of the catalyst is required with respect to the initiator, and the monomer concentration is typically 1.0 mol L^{-1}, which lead to a higher economic cost and environmental pollution. To make the organophosphate-catalyzed ROP be more versatile, facile, and environmentally benign, of particular interest is establishing a solvent-free ROP process with a reduced catalyst loading. Although there are some reports about the bulk ROP of cyclic esters using organocatalysts, the advantages of bulk conditions have not been investigated in detail.[12-14,25,26,37,60-73] We now describe the organophosphate-catalyzed bulk ROP of various cyclic esters, such as ε-CL, δ-valerolactone (δ-VL), L-lactide (L-LA), 1,5-dioxepan-2-one (DXO), trimethylene carbonate (TMC), as an environmentally benign way to produce the aliphatic polyesters, polyester-ether, and polycarbonate (Scheme 1). In this study, the catalyst loading and reaction time could significantly be reduced along with keeping both the sufficient polymerization ability and controlled/living nature. Unexpectedly, we found that the bulk polymerization condition allowed the full potential of the catalytic ability of the organophosphates. The broad utility of the organophosphate-catalyzed bulk ROP system was verified through the synthesis of the block copolyesters as well as the functionalized polyesters including α,ω-dihydroxy telechelic PCL-diol and the three- and four-armed star-shaped PCL-polyols. Notably, the synthesis of the star-shaped PCL-polyols, which are the industrially important prepolymers for polyurethanes, was accomplished by applying the bulk conditions, whereas it was difficult by the conventional procedure in solution. For further application in industrial

processes without using metal catalysts, we demonstrated the one-pot synthesis of polyurethanes via the ROP of ε-CL and subsequent urethane formation reaction, in which both reactions were catalyzed solely by the organophosphate.

Scheme 1. Organophosphate-catalyzed bulk ROP leading to block copolyesters, end-functionalized polyesters, and PCL-based polyurethane



All the processes were performed in one-pot synthesis in the bulk

Experimental Section

Materials. ε-Caprolactone (ε-CL; >99%, Tokyo Kasei Kogyo Co., Ltd. (TCI)), δ-valerolactone (δ-VL; >99%, Sigma Aldrich), 3-phenyl-1-propanol (PPA, TCI), and 1,3-propanediol were distilled over CaH_2 under reduced pressure. Di(2,6-xylyl)phosphate (DXP), 6-azido-1-hexanol (AHA), and *N*-(2-hydroxyethyl)maleimide (HEMI) were synthesized according to previous reports.[74-76] 1,5-Dioxepan-2-one (DXO; >98%, TCI), and trimethylene carbonate (TMC; >98%, TCI) were dried by azeotropic distillation. L-Lactide (L-LA; >98%, TCI) was purified by recrystallization from dry toluene (twice). Diphenylphosphate (DPP; >99%, TCI), bis(4-nitrophenyl)phosphate) (BNPP; >99%, TCI), pentaerythritol (>98%, TCI), 4,4',-diphenylmethane diisocyanate (>97%, TCI), trimethylolpropane (>98%, TCI), and Amberlyst® A21 (Organo Co., Ltd.) were used as received.

Instruments. The polymerization was carried out in an MBRAUN stainless steel glove box 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 glove box were monitored by an MB-MO-SE 1 and MB-OX-SE 1, respectively. The number-average molar mass ($M_{n,NMR}$) was determined from the ^1H NMR spectra recorded using a JEOL JNM-A400II instrument. The size exclusion chromatography (SEC) was performed at 40 °C in $CHCl_3$ (1.0 mL min^{-1}) using a Shodex GPC-101 system equipped with a Shodex K-G guard column and a set of two Shodex K-805L columns (linear, 8 mm × 300 mm; bead size, 5 μm; exclusion limit, 4×10^6). The dispersity ($Đ_M$) 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 the obtained spectra were calibrated using polystyrene (average M_n = 3,600, Waters Associates) as the standard. Samples for the MALDI-TOF MS were prepared by mixing the polymer (4.0 mg mL^{-1}, 0.5 μL) and a matrix (2,5-dihydroxybenzoic acid, 60 mg mL^{-1}, 0.5 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. The Fourier transform infrared spectroscopy (FT-IR) analysis was carried out using a Perkin-Elmer Frontier MIR spectrometer equipped with a Single Reflection Diamond Universal Attenuated Total Reflection (ATR) accessory. The turnover frequency (TOF) for the propagation reaction was evaluated using the following formula.

$$\text{TOF}\ (\text{h}^{-1}) = \frac{[\text{M}]_0 \times \text{conv.}}{[\text{DPP}]_0 \times \text{polymerization time (h)}}$$

Bulk ring-opening polymerization of *ε*-caprolactone catalyzed by diphenyl phosphate. A typical procedure for the polymerization is as follows (Procedure A): *ε*-CL (1.120 mL, 10.0 mmol), PPA (27.2 μL, 200 μmol), and DPP (2.50 mg, 10.0 μmol) were placed in a reaction vessel, which was sealed under an argon atmosphere. The reaction mixture was stirred at 80 °C in an oil bath. After 250 min, we obtained a portion of the reaction mixture for determining the monomer conversion from the ^{1}H NMR measurements, and the polymerization was quenched by adding Amberlyst® A21. Before the addition of the Amberlyst® A21, we obtained a portion of the reaction mixture and then added a small amount of triethylamine for determining the monomer conversion from the ^{1}H NMR measurements.

The reaction mixture was purified by reprecipitation from a CH_2Cl_2 solution into cold methanol/*n*-hexane (v/v = 9/1) to give PCL (713 mg) as a white solid. Yield, 66.6%. $M_{n,NMR}$ = 5,500; $M_{n,SEC}$ = 11,100, $Đ_M$ = 1.08. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.36 (m, 2H × *n*, (-$CH_2CH_2CH_2CH_2CH_2$-)$_n$), 1.61 (m, 2H × *n*, (-$CH_2CH_2CH_2O$-)$_n$), 1.63 (m, 2H × *n*, (-$COCH_2CH_2CH_2$-)$_n$), 1.94 (q, 2H, *J* = 6.3 Hz, Ar$CH_2CH_2CH_2$-), 2.29 (t, 2H × *n*, *J* = 7.6 Hz, (-$OCOCH_2CH_2$-)$_n$), 2.67 (t, 2H, *J* = 8.0 Hz, ArCH_2CH_2-), 3.63 (t, 2H, *J* = 6.4 Hz, -CH_2CH_2OH) 4.04 (t, 2H ×(*n-1*), *J* = 6.6 Hz, (-CH_2CH_2O-)$_{n-1}$), 4.08 (m, 2H, Ar$CH_2CH_2CH_2O$-), 7.15-7.30 (m, 5H, aromatic).

Bulk ring-opening polymerization of *δ*-varelolactone catalyzed by diphenyl phosphate. Procedure A was used for the ROP of *δ*-VL (0.905 mL, 10.0 mmol) in the presence of PPA (27.2 μL, 200 μmol) and DPP (2.50 mg, 10.0 μmol) for 40 min to give PVL (719 mg) as a white solid. Yield, 79.5%. $M_{n,NMR}$ = 5,000; $M_{n,SEC}$ = 9,400, $Đ_M$ = 1.08. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.66 (m, 2H × *n*, (-$CH_2CH_2CH_2O$-)$_n$), 1.69 (m, 2H × *n*, (-$COCH_2CH_2CH_2$-)$_n$), 1.93 (quin, 2H, *J* = 7.2 Hz, Ar$CH_2CH_2CH_2$-), 2.32 (m, 2H × *n*, (-$OCOCH_2CH_2$-)$_n$), 2.66 (t, 2H, *J* = 7.8 Hz, ArCH_2CH_2-), 3.63 (t, 2H, *J* = 6.4 Hz, -CH_2CH_2OH), 4.08 (t, 2H × (*n-1*), *J* = 6.0 Hz, (-CH_2CH_2O-)$_{n-1}$), 4.10 (m, 2H, Ar$CH_2CH_2CH_2O$-), 7.15-7.34 (m, 5H, aromatic).

Bulk ring-opening polymerization of trimethylene carbonate catalyzed by diphenyl phosphate. Procedure A was used for the ROP of TMC (510 mg, 5.00 mmol) in the presence of PPA (13.6 μL, 100 μmol) and DPP (1.2 mg, 0.50 μmol) for 17 h to give PTMC (389 mg) as a colorless waxy solid. Yield, 83.0%. $M_{n,NMR}$ = 4,700; $M_{n,SEC}$ = 6,800, $Đ_M$ = 1.07. ^{1}H NMR ($CDCl_3$, 400MHz): δ (ppm) 1.92

(m, 2H, -C*H*$_2$CH$_2$OH), 1.97-2.11 (m, 2H, ArCH$_2$C*H*$_2$-; 2H × (*n-1*), (-OCH$_2$C*H*$_2$-)$_{n-1}$), 2.70 (t, 2H, *J* = 7.8 Hz, ArC*H*$_2$-), 3.74 (q, 2H, *J* = 9.0 Hz, -C*H*$_2$OH), 4.13-4.32 (m, 2H, ArCH$_2$CH$_2$C*H*$_2$-, m, 4H × *n-1*, (-OC*H*$_2$CH$_2$C*H*$_2$O-)$_{n-1}$; 2H, -C*H*$_2$CH$_2$CH$_2$OH), 7.16-7.29 (m, 5H, aromatic).

Bulk ring-opening polymerization of 1,5-dioxepane-2-one catalyzed by diphenyl phosphate. Procedure A was used for the ROP of DXO (580 mg, 5.00 mmol) in the presence of PPA (13.6 μL, 100 μmol) and DPP (1.2 mg, 0.50 μmol) for 450 min to give PDXO (470 mg) as a colorless waxy solid. Yield, 91.6%. $M_{n,NMR}$ = 5,300; $M_{n,SEC}$ = 4,400, $Đ_M$ = 1.13. ^{1}H NMR (CDCl$_3$, 400MHz): δ (ppm) 1.97 (m, 2H, ArCH$_2$C*H*$_2$-), 2.63 (t, 2H × *n-1*, *J* = 6.6 Hz, (-COC*H*$_2$-)$_{n-1}$), 2.76 (m, 2H, ArC*H*$_2$-), 3.67 (t, 2H × *n-1*, *J* = 5.0 Hz, (-C*H*$_2$CH$_2$OCO-)$_{n-1}$), 3.76 (t, 2H × *n-1*, *J* = 6.4 Hz, (-COCH$_2$C*H*$_2$-)$_{n-1}$), 4.09 (t, 2H, *J* = 6.6 Hz, ArCH$_2$CH$_2$C*H*$_2$-), 4.21 (t, 2H × *n-1*, *J* = 4.8 Hz, (-C*H*$_2$OCO-)$_{n-1}$), 7.15-7.29 (m, 5H, aromatic).

One-Pot Synthesis of PCL-based Polyurethane via Organophosphate-Catalyzed Bulk ROP. ε-CL (2.240 mL, 20.0 mmol), 1,3-propanediol (57.6 μL, 800 μmol) and DPP (5.00 mg, 40.0 μmol) were placed in a reaction vessel, which was sealed under an argon atmosphere. The reaction mixture was stirred at 80 °C in an oil bath. After 120 min, we obtained a portion of the reaction mixture for SEC measurement and ^{1}H NMR measurement, then MDI (200 mg, 800 μmol) was added to the reaction mixture. The polymerization was quenched by adding Amberlyst® A21. The reaction mixture was purified by reprecipitation from CH_2Cl_2 solution into cold methanol to give the PCL-based polyurethane (1.73 g) as a white solid. Yield, 69.8%. $M_{n,SEC}$ = 32,800, $Đ_M$ = 2.03. ^{1}H NMR (CDCl$_3$,

400 MHz): δ (ppm) 1.38 (m, 2H × n, (-$CH_2CH_2CH_2CH_2CH_2$-)$_n$), 1.61-1.72 (m, 2H × n, (-$CH_2CH_2CH_2O$-)$_n$; 2H × n, (-$COCH_2CH_2CH_2$-)$_n$), 1.97 (m, 2H, -$OCH_2CH_2CH_2O$-), 2.31 (t, 2H × n, J = 8.2 Hz, (-$OCOCH_2CH_2$-)$_n$), 3.88 (s, 2H × X, -$ArCH_2Ar$-), 4.06 (t, 2H × n, J = 6.6 Hz, (-CH_2CH_2O-)$_n$), 4.14 (t, 4H, J = 8.4 Hz, -$CH_2CH_2CH_2$-), 6.74 (s, 2H × X, N*H*), 7.08-7.31 (m, 8H × X, aromatic).

Results and Discussion

Ring-Opening Polymerization of Cyclic Esters Catalyzed by Organophosphates in the Bulk. We previously found that DPP effectively catalyzed the ROP of ε-CL in toluene (1.0 mol L^{-1}) with an alcohol initiator at room temperature to give the well-defined PCL with the predictable molar mass and narrow $Đ_M$, in which an equimolar amount of DPP with respect to the alcohol initiator was required.[15] To clarify the advantage of the use of the bulk condition for the DPP-catalyzed ROP over the previous solution polymerization conditions, we first attempted the polymerization of ε-CL in the bulk at the $[\varepsilon\text{-CL}]_0/[\text{initiator}]_0/[\text{DPP}]_0$ ratio of 50/1/0.05 at 80 °C, where 3-phenyl-1-propanol (PPA) was used as the initiator (run 1 in Table 1). The polymerization homogeneously proceeded while the viscosity of the reaction mixture increased with the reaction time. The monomer conversion for this system reached 92.4% within 250 min to give the PCL as a white powder, indicating the high catalytic performance of DPP under the bulk polymerization conditions. The size exclusion chromatography (SEC) trace of the obtained PCL was monodispersed with the $Đ_M$ value of 1.08 (Figure 1). Note that there is no difference between the SEC traces of the PCL obtained before and after the reprecipitation,

indicating that the polymerization proceeded without the production of low molar mass byproducts, such as cyclic oligomers. The ^{1}H NMR spectrum of the obtained PCL exhibited minor signals due to the 3-phenyl-1-propoxy group in addition to the signals due to the PCL main chain (Figure S1). The number-average molar mass ($M_{n,NMR}$) was determined to be 5,500 from the ^{1}H NMR measurement, which was in good agreement with the theoretical value ($M_{n,th.}$ = 5,400) calculated based on the initial monomer-to-initiator ratio and the monomer conversion. These results implied the well-controlled nature of the bulk polymerization system. Furthermore, the matrix-assisted laser desorption/ionization time-of-flight mass spectral (MALDI-TOF MS) analysis provided detailed information about the chemical structure of the obtained PCL (Figure S2). The MALDI-TOF MS spectrum displayed only one series of peaks corresponding to the PCL possessing a PPA residue at the α-chain end, which again confirmed the absence of the low molar mass byproducts. These data demonstrated that the DPP-catalyzed ROP in the bulk offers a high degree of control over the molar mass and dispersity as well as the polymer structure, which is comparable to that observed for the conventional DPP-catalyzed ROP in solution. Thus, the present bulk polymerization procedure has the greater advantage of being able to produce the well-defined PCLs without any solvents at a lower catalyst loading.

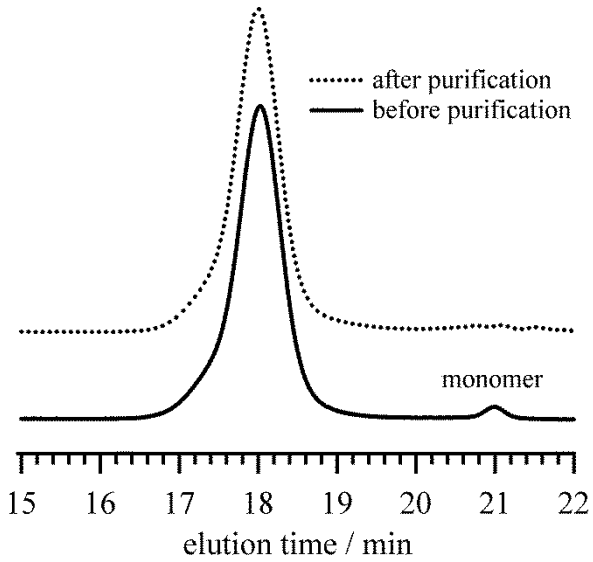


Figure 1. SEC traces of the PCL obtained before (solid line) and after reprecipitation (dotted line) from run 1 in Table 1 (eluent, $CHCl_3$; flow rate, 1.0 mL min^{-1}).

To explore the full potential of the organophosphate as the catalyst, we examined BNPP and di(2,6-xylyl)phosphate (DXP), which are analogues of DPP having electron-withdrawing and electron-donating substituents, respectively, as the catalyst for the bulk ROP of ε-CL (runs 2 and 3 in Table 1). Each organophosphate catalyzed the ROP of ε-CL at the $[\varepsilon\text{-CL}]_0/[\text{PPA}]_0/[\text{BNPP or DXP}]_0$ ratio of 50/1/0.05 at 80 °C to produce well-defined PCLs with predicted molar mass values and narrow $Đ_M$ values. The quality of the PCLs obtained with the different organophosphates is virtually the same. However, the kinetics of the ROP was significantly varied depending on the substituent of the organophosphates. The turnover frequency (TOF) values were calculated to be 222, 306, and 155 for the ROPs at the $[\varepsilon\text{-CL}]_0/[\text{PPA}]_0/[\text{organophosphate}]_0$ ratio of 50/1/0.05 using DPP, BNPP, and DXP, respectively. These results revealed that the electron withdrawing substituents on the organophosphate have a positive effect to increase the polymerization kinetics. Thus, the appropriate choice of the

substituents on the organophosphates allows the precise tuning of the polymerization conditions, such as the reaction time and temperature as well as the catalyst loading.

We next investigated the effect of the catalyst loading on the polymerization behavior. The DPP-catalyzed bulk ROP of ε-CL with varying $[PPA]_0/[DPP]_0$ ratios from 1/1.00 to 1/0.01 were conducted (runs 1, 4 – 7 in Table 1) at 80 °C. In case of the bulk ROP at the $[\varepsilon\text{-CL}]_0/[PPA]_0/[DPP]_0$ ratio of 50/1/1, the monomer conversion reached 86.3% within 12 min. This is in sharp contrast to the ROP in toluene at the $[\varepsilon\text{-CL}]_0/[PPA]_0/[DPP]_0$ ratio of 50/1/1 (run 8 in Table 1), which required 300 min to reach an 83.6% monomer conversion. These results clearly demonstrated the advantage of the DPP-catalyzed bulk ROP over the solution polymerization conditions. Surprisingly, the DPP-catalyzed bulk ROP proceeded in a well-controlled manner with sufficient TOF values even at the $[PPA]_0/[DPP]_0$ ratio of 1/0.01, leading to the well-defined PCLs. In contrast, the DPP-catalyzed ROP of ε-CL in solution did not proceed even at the $[PPA]_0/[DPP]_0$ of 1/0.1 (run 9 in Table 1), meaning that the amount of loaded catalyst was successfully reduced to 1/100 of the DPP-catalyzed ROP of cyclic esters, due to bulk conditions. Therefore, the bulk condition allowed the full potentials of the catalytic ability of the organophosphate, resulting in remarkably higher TOF values and a lower catalyst loading than that required for the conventional solution polymerization while keeping the well-controlled manner of the polymerization.

Table 1. Ring-opening polymerization of ε-CL catalyzed by organophosphates in the bulk [a]

run	cat.	$[M]_0/[PPA]_0/[cat.]_0$	time	conv. (%) [b]	$M_{n,th.}$ [c]	$M_{n,NMR}$ [b]	$M_{n,SEC}$ [d]	$Đ_M$ [d]	TOF (h^{-1})
1	DPP	50/1/0.05	250 min	92.4	5,400	5,500	11,100	1.08	222
2	BNPP	50/1/0.05	180 min	91.8	5,400	5,400	11,000	1.09	306
3	DXP	50/1/0.05	360 min	93.1	5,500	5,500	11,900	1.11	155
4	DPP	50/1/1.00	12 min	86.2	5,100	5,200	9,900	1.27	215
5	DPP	50/1/0.10	120 min	84.5	5,000	5,100	9,100	1.14	211
6	DPP	50/1/0.03	420 min	78.4	4,600	4,800	9,700	1.07	186
7	DPP	50/1/0.01	1560 min	84.7	5,000	5,200	11,300	1.09	163
8 [e]	DPP	50/1/1.00	300 min	83.6	4,900	5,100	10,000	1.08	8
9 [e]	DPP	50/1/0.10	300 min	4.8	400	800	800	1.16	4

[a] Polymerization conditions: atmosphere, Ar; temperature, 80 °C. [b] Determined by ^{1}H NMR spectrum of the obtained polymer in $CDCl_3$. [c] Calculated from $[\varepsilon\text{-CL}]_0/[PPA]_0 \times$ conv. × (M.W. of ε-CL) + (M.W. of PPA). [d] Determined by SEC measurement of the obtained polymer in $CHCl_3$ using polystyrene standards. [e] Polymerization was conducted in toluene with $[M]_0 = 1.0$ mol L^{-1} at room temperature.

In order to demonstrate the tolerance of the organophosphate to moisture and oxygen, the DPP-catalyzed bulk ROP of the unpurified ε-CL was conducted in air in the presence of H_2O as an initiator at the $[\varepsilon\text{-CL}]_0/[H_2O]_0/[DPP]_0$ ratio of 50/1/0.05. The polymerization well proceeded and the monomer conversion reached 93.4% within 270 min giving the corresponding PCL with the $M_{n,SEC}$ and $Đ_M$ values of 9,500 and 1.19, respectively (Figure S3). The MALDI-TOF MS analysis revealed

that the obtained PCL had a carboxylic acid α-end group, indicating that H_2O was incorporated as an initiator (Figure S4). These results confirmed the sufficient tolerance of organophosphates toward moisture and oxygen during the bulk polymerization, which is in clear contrast to the metal-based catalyst system. Such features of the organophosphates coupled with the easy handling of the bulk polymerization are highly favorable for the industrial scale production of aliphatic polyesters.

DPP-Catalyzed Bulk ROP of Cyclic Esters, Cyclic Ester-ether, and Cyclic Carbonate. The above results encouraged us to further investigate the scope of the DPP-catalyzed bulk ROP procedure. To this end, we performed the DPP-catalyzed ROP of δ-VL, DXO, TMC, and L-lactide (L-LA) to produce the corresponding polymers, *i.e.*, poly(δ-valerolactone) (PVL), poly(1,5-dioxepan-2-one) (PDXO), poly(trimethylenecarbonate) (PTMC), and poly(L-lactide) (PLLA), respectively. The bulk ROP of δ-VL, an analog of ε-CL having a six-membered ring, was first attempted at the $[\delta\text{-VL}]_0/[\text{PPA}]_0/[\text{DPP}]_0$ ratio of 25/1/0.05 at 80 °C. The monomer conversion reached 94.9% within 15 min to give a narrowly dispersed PVL with the $M_{n,NMR}$ value of 2,400 that was in good agreement with the $M_{n,th}$ value (2,500), as listed in Table 2. The PVLs with the desirable molar mass values were produced by varying the $[\delta\text{-VL}]_0/[\text{PPA}]_0$ ratios (runs 12 – 14 in Table 2). The optimized bulk ROP procedure was applied to DXO with the varying $[\text{DXO}]_0/[\text{PPA}]_0$ of 25 – 100, which gave the PDXOs with the $M_{n,NMR}$ and $Đ_M$ values of 2,900 – 10,900 and 1.13 – 1.23, respectively (runs 15 – 17 in Table 2). The bulk ROP of TMC at the $[\text{TMC}]_0/[\text{PPA}]_0/[\text{DPP}]_0$ ratios of 25/1/0.05, 50/1/0.05, and 100/1/0.05 also smoothly proceeded at 80 °C to give the corresponding PTMCs with the $M_{n,NMR}$s and $Đ_M$s of

2,500 – 7,900 and 1.07 – 1.09, respectively (runs 18 – 20 in Table 2). The ^{1}H NMR spectra of all the obtained polymers showed signals corresponding to a 3-phenyl-1-propoxy group at the α-chain end, suggesting that PPA was incorporated as the initiator in all cases (Figures S5, S7, and S9). In addition, the MALDI-TOF MS spectral analysis provided further evidence that the DPP-catalyzed bulk ROPs led to well-defined polymers without any undesirable reactions (Figures S6, S8, and 2). It is noteworthy that there was no evidence of a decarboxylation reaction during the bulk ROP of TMC. In the MALDI-TOF MS spectrum of the obtained PTMC (run 19 in Table 2), only one series of peaks was observed, which corresponded to the expected chemical structure of the PTMC (Figure 2). For example, the measured molar mass value of 4343.65 matched well with the theoretical one ($[M+Na]^+$ = 4343.38) for the 41-mer of the PTMC possessing a 3-phenyl-1-propoxy group at the α-chain end. This is in contrast to the ROP system for TMC catalyzed by super Bronsted acids such as TfOH, which usually suffers from decarboxylation resulting in partial incorporation of ether bonds in the PTMC backbone.[40] Therefore, we achieved the highly efficient solvent-free production of various aliphatic polyesters, polyester-ether, and polycarbonate using organophosphates with a remarkably small catalyst loading. Indeed, the DPP-catalyzed bulk ROPs of ε-CL, δ-VL, DXO, and TMC could be operated with 0.05 – 0.20 mol% catalyst loadings, which correspond to 1/20 of catalyst loading required for a conventional solution polymerization procedure.

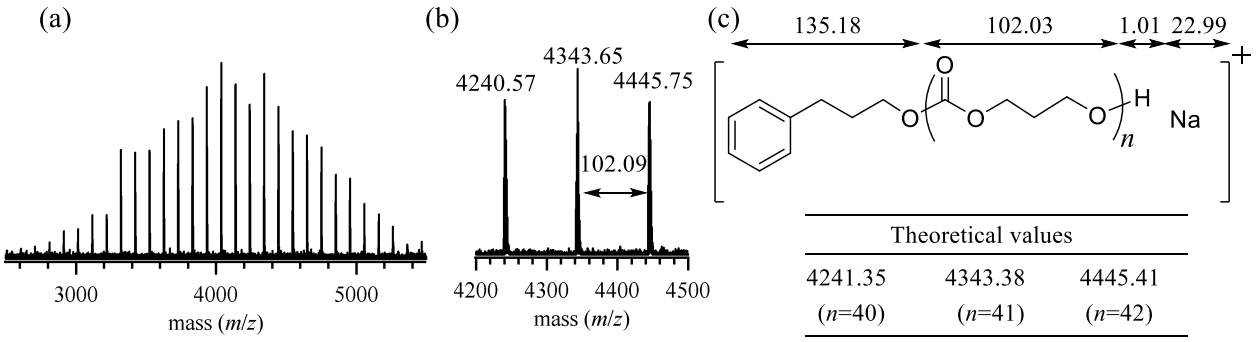


Figure 2. (a) MALDI-TOF MS spectrum of PTMC (run 19 in Table 2), (b) expanded spectrum (ranging from 4,200 to 4,500), and (c) theoretical molar mass values.

We previously reported that the DPP-catalyzed ROP of L-LA hardly proceeded under the conventional solution polymerization conditions.[36] Thus, a challenge still exists in the synthesis of polylactides using the DPP catalyst. Therefore, we attempted the DPP-catalyzed ROP of L-LA at the $[\text{L-LA}]_0/[\text{PPA}]_0/[\text{DPP}]_0$ ratio of 50/1/0.50 using the bulk conditions. Considering the higher melting and crystallization temperatures of the resulting PLLA, the bulk polymerization was conducted at 130 °C (run 21 in Table 1). Surprisingly, the monomer conversion reached 85.7% within 24 h, giving a PLLA with the $M_{\text{n,NMR}}$ and $Đ_{\text{M}}$ values of 6,800 and 1.23, respectively (Figures S11 and S12). In addition, the homonuclear decoupled ^{1}H NMR spectrum of the resulting PLLA displayed a singlet signal due to the methine group derived from an exclusive *iii* tetrad stereosequence, suggesting that stereoinversion of the monomer did not occur during the polymerization (Figure S13). This result is in contrast to the organobase-catalyzed ROP of L-LA or D-LA, which often suffer from stereoinversion leading to the PLLAs with an imperfect isotacticity.[24] Although the MALDI-TOF MS spectrum detected evidence of side reactions, such as intramolecular and intermolecular transesterifications, the

above-described results clearly demonstrated the broad monomer scope of the present polymerization procedure (Figure S14).

Table 2. Bulk ring-opening polymerization of cyclic esters, cyclic ester-ether, and cyclic carbonate catalyzed by DPP [a]

run	monomer (M)	$[M]_0/[PPA]_0/[DPP]_0$	Time	conv. (%) [b]	$M_{n,th.}$ [c]	$M_{n,NMR}$ [b]	$M_{n,SEC}$ [d]	$Đ_M$ [d]
10	ε-CL	25/1/0.05	100 min	94.2	2,800	2,700	5,900	1.16
1	ε-CL	50/1/0.05	250 min	92.4	5,400	5,500	11,100	1.08
11	ε-CL	100/1/0.05	17 h	77.0	8,900	9,200	17.100	1.12
12	δ-VL	25/1/0.05	15 min	94.9	2,500	2,400	5,800	1.08
13	δ-VL	50/1/0.05	40 min	90.4	4,700	5,000	9,400	1.08
14	δ-VL	100/1/0.05	180 min	80.6	8,200	8,600	17,900	1.07
15	DXO	25/1/0.05	200 min	96.8	3,000	2,900	2,900	1.14
16	DXO	50/1/0.05	450 min	88.3	5,300	5,300	4,400	1.13
17	DXO	100/1/0.05	24 h	90.1	10,600	10.900	7,200	1.23
18	TMC	25/1/0.05	570 min	93.0	2,500	2,500	4,100	1.09
19	TMC	50/1/0.05	17 h	91.8	4,800	4,700	6,800	1.07
20	TMC	100/1/0.05	54 h	75.0	7,800	7,900	9,000	1.08
21 [e]	L-LA	50/1/0.50	22 h	85.7	6,300	6,800	9,700	1.23

[a] Polymerization conditions: atmosphere, Ar; temperature, 80 °C. [b] Determined by ^{1}H NMR spectrum of the obtained polymer in $CDCl_3$. [c] Calculated from $[M]_0/[PPA]_0$ × conv. × (M.W. of M) + (M.W. of PPA). [d] Determined by SEC measurement of the obtained polymer in $CHCl_3$ using polystyrene standards. [e] The polymerization was conducted at 130 °C.

Controlled/Living Nature of DPP-Catalyzed ROP in the Bulk. To clarify the controlled/living nature of the present polymerization system, kinetic studies for the DPP-catalyzed bulk ROP of ε-CL and TMC were carried out at the [ε-CL or TMC]$_0$/[PPA]$_0$/[DPP]$_0$ ratio of 50/1/0.05 at 80 °C (Figures S15 and S16). In both cases, the kinetic plots showed a linear increase in the monomer conversion with the reaction time. In addition, the $M_{n,NMR}$s values of the resulting PCLs and PTMCs were in good agreement with the $M_{n,th.}$s values, and the $Đ_M$s were maintained in relativity low values ranging from 1.07 to 1.16 for the PCL and from 1.05 to 1.11 for the PTMC, respectively. These results obviously represent distinctive features of the typical controlled/living polymerization. To further confirm the living character of the growing chain end, we performed the block copolymerization by the sequential monomer addition in the bulk; the ε-CL or TMC are polymerized as the first monomer (M_1) at the [ε-CL or TMC]$_0$/[PPA]$_0$/[DPP]$_0$ ratio of 25/1/0.05 to reach almost complete conversion, and an equimolar amount of δ-VL with respect to the M_1 was then added to the reaction mixture to afford PCL-*b*-PVL and PTMC-*b*-PVL (Table S1). The monomodal SEC traces of the polymers obtained from the first polymerization clearly shifted to the higher molar mass region while maintaining low $Đ_M$s after the second polymerization, indicating that the second polymerization of δ-VL was efficiently initiated from the ω-chain end hydroxyl group of PCL or PTMC (Figures S17 and S19). In the ^{1}H NMR spectra, the signals due to the PCL or PTMC as well as the PVL backbones were observed along with the minor signals due to the PPA residue (Figures S18 and S20). These results obviously represent the success of the block copolymerization to afford the well-defined PCL-*b*-PVL and PTMC-*b*-PVL, which confirmed that the growing chain end had a living character even in the

bulk condition. In addition, PVL-*b*-PCL and PDXO-*b*-PCL were also obtained using the same procedure, which suggests the versatility of the present bulk ROP system for the production of various block copolymers regardless of the monomer addition sequence (Figures S21-S24).

Syntheses of Functional PCLs and PTMCs with Various Initiators. To further expand the synthetic utility of the present bulk polymerization procedure, we attempted to produce end-functionalized PCLs and PTMCs by combining functional alcohol initiators, such as 6-azido-1-hexanol (AHA), *N*-(2-hydroxyethyl)maleimide (HEMI), 1,3-propanediol, trimethylolpropane, and pentaerythritol, as shown in Scheme 2. AHA and HEMI possess highly reactive functional groups, *i.e.*, azido and maleimide groups, respectively, which can be used to create various macromolecular architectures through the copper-catalyzed azido-alkyne cycloaddition and maleimide-thiol coupling reactions, respectively. The bulk polymerizations of ε-CL at the $[\varepsilon\text{-CL}]_0/[\text{initiator}]_0/[\text{DPP}]_0$ ratio of 50/1/0.05 using AHA and HEMI as the initiator proceeded in a well-controlled manner to afford the azido- and maleimide-functionalized PCLs (N_3-PCL and MI-PCL, respectively) and with relativity low $Đ_M$s ($Đ_M$ = 1.11 for N_3-PCL, 1.15 for MI-PCL), as listed in Table 3. In a similar manner, the azido- and maleimide-functionalized PTMCs (N_3-PTMC and MI-PTMC) were obtained with $Đ_M$ values less than 1.13. These results confirmed that a wide range of end-functionalized polyesters can be produced by the present bulk polymerization procedure even at a higher reaction temperature.

To elevate the DPP-catalyzed bulk ROP system to be more versatile, the syntheses of the α,ω-dihydroxy telechelic PCL-diol as well as three- and four-armed star-shaped PCL-polyols, which

are industrially important raw materials for the polyurethane synthesis, were conducted using polyols, such as 1,3-propanediol, trimethylolpropane, and pentaerythritol, as an initiator to afford PCL-diol, PCL-triol, and PCL-tetraol, respectively. It is notable that the DPP-catalyzed ROPs of ε-CL using trimethylolpropane and pentaerythritol were unsuccessful in solution because such polyol initiators are usually insoluble in organic solvents. In contrast, the reacting mixtures of the bulk polymerization using trimethylolpropane and pentaerythritol became homogeneous with the reaction time, though the polymerization heterogeneously initiated. The SEC traces of the obtained PCL-polyols exhibited a monodisperse elution peak with a low $Đ_M$s ($Đ_M$ = 1.13 for PCL-diol, 1.07 for PCL-triol, 1.04 for PCL-tetraol). The ^{1}H NMR spectra suggest that the polymerization proceeded from all the initiating sites of the initiator (Figures S29-S31). The integration ratios of the signal due to methylene protons adjacent to the ω-end hydroxyl group of PCL and the signal due to the methyl protons of the trimethylolpropane residue or methylene protons of the pentaerythritol residue were calculated and found to be reasonable values of 2:1 for the PCL-triol and 1:1 for the PCL tetraol. The $M_{n,NMR}$s of the obtained PCLs were in good agreement with the $M_{n,th.}$s, and the molar mass values of the PCL-tetraols were controlled up to 16,100 along with low $Đ_M$s in the range of 1.04-1.08 (Figure S32).

Scheme 2. Syntheses of functionalized PCLs and PTMCs using functional initiators

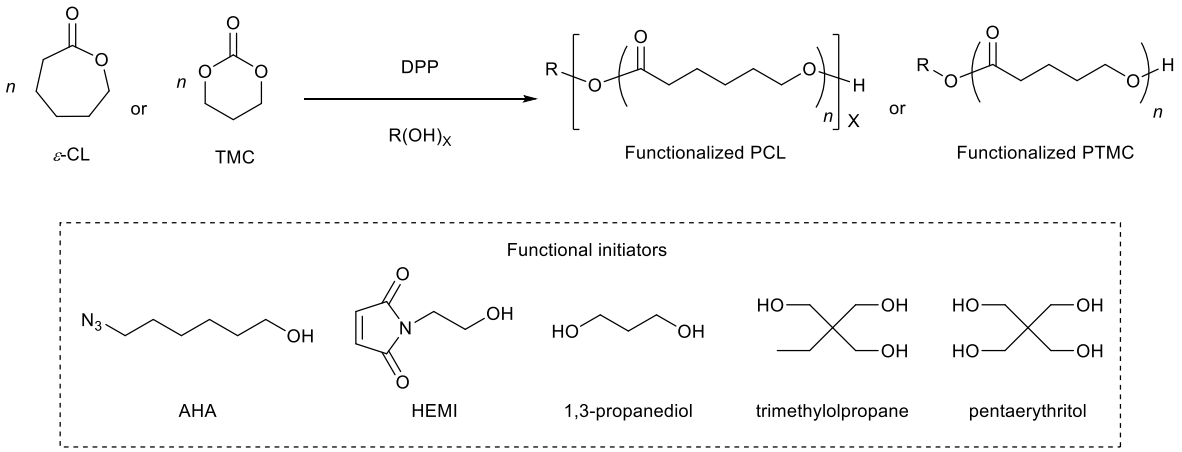


Table 3. Bulk ring-opening polymerization of ε-CL or TMC catalyzed by DPP with various initiators [a]

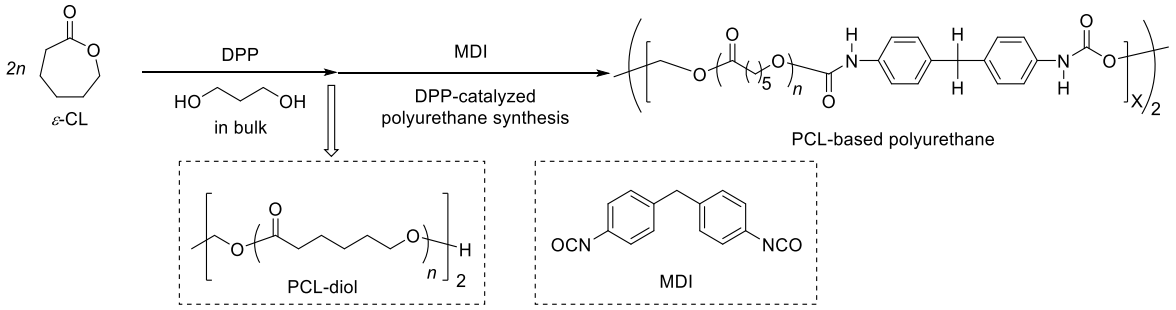
run	M	initiator	time	conv. (%) [b]	$M_{n,th.}$ [c]	$M_{n,NMR}$ [b]	$M_{n,SEC}$ [d]	$Đ_M$ [d]
22	ε-CL	AHA	420 min	90.3	5,300	5,500	12,700	1.11
23	ε-CL	HEMI	450 min	90.8	5,300	5,500	13,400	1.15
24	TMC	AHA	19 h	85.6	4,500	4,500	5,600	1.09
25	TMC	HEMI	19 h	91.0	4,800	4,700	6,400	1.13
26	ε-CL	1,3-propanediol	180 min	88.8	5,100	5,100	11,400	1.13
27	ε-CL	trimethylolpropane	150 min	86.0	5,000	5,200	11,500	1.07
28	ε-CL	pentaerythritol	120 min	95.5	5,600	5,600	11,900	1.04
29 [e]	ε-CL	pentaerythritol	430 min	85.3	9,600	10,600	16,900	1.07
30 [f]	ε-CL	pentaerythritol	21 h	64.1	14,800	16,100	28,000	1.08

[a] Polymerization conditions: atmosphere, Ar; temperature, 80 ˚C; $[M]_0/[initiator]_0/[DPP]_0$, 50/1/0.05. [b] Determined by ^1H NMR spectrum of the obtained polymer in $CDCl_3$. [c] Calculated from $[M]_0/[initiator]_0$ × conv. × (M.W. of M) + (M.W. of initiator). [d] Determined by SEC measurement of the obtained polymer in $CHCl_3$ using polystyrene standards. [e] Polymerization was conducted with $[M]_0/[initiator]_0/[DPP]_0$ = 100/1/0.05. [f] Polymerization was conducted with $[M]_0/[initiator]_0/[DPP]_0$ = 200/1/0.05.

One-Pot Synthesis of PCL-based Polyurethane via Organophosphate-Catalyzed Bulk ROP. Polyurethanes are industrially produced using organometallic catalysts represented by organotin compounds, which are difficult to remove from the product, therefore, an alternative metal-free route is required to achieve environmentally benign and safe production. Recently, Hedrick *et al.* reported that organic acids effectively promoted the polyurethane formation reaction.[77] Inspired by the report, the one-pot synthesis of polyurethane via the organophosphate-catalyzed bulk ROP was demonstrated

as shown in Scheme 3. ε-CL was first polymerized at the $[\varepsilon\text{-CL}]_0/[\text{1,3-propanediol}]_0/[\text{DPP}]_0$ ratio of 25/1/0.05 to afford the PCL-diol, and an equimolar amount of 4,4'-diphenylmethane diisocyanate (MDI) with respect to 1,3-propanediol was then added to the reaction mixture while keeping the temperature at 80 ˚C. After the addition of MDI, the viscosity of the reacting mixture drastically increased, which implied the production of a higher molar mass product. The SEC measurement revealed that the PCL-diol was completely consumed to afford the PCL-based polyurethane within 16 h (Figure 3). The ^{1}H NMR measurement provide further evidence of the polyurethane formation. The characteristic signals due to the urethane bond in addition to the signals due to the PCL and MDI residue were observed, while the triplet signal due to the methylene protons adjacent to the ω-end hydroxyl group of PCL had disappeared (Figure 4). In addition, the FT-IR spectrum of the PCL-based polyurethane showed the characteristic absorptions at 1,532 cm^{-1} and 3,346 cm^{-1} due to the NH deformation and stretching vibrations, respectively (Figure S33). Although the polyurethane formation in the absence of DPP was observed, there was some remaining unreacted PCL-diol even after 16 h (Figure S34). The result suggested that DPP plays important roles to promote not only the ROP of ε-CL, but also the polyurethane formation reaction. Therefore, the present bulk polymerization procedure coupled with DPP has the potential for the polyurethane synthesis without using any organometallic catalysts in all the processes.

Scheme 3. One-pot synthesis of PCL-based polyurethane using organophosphate-catalyzed bulk ROP system



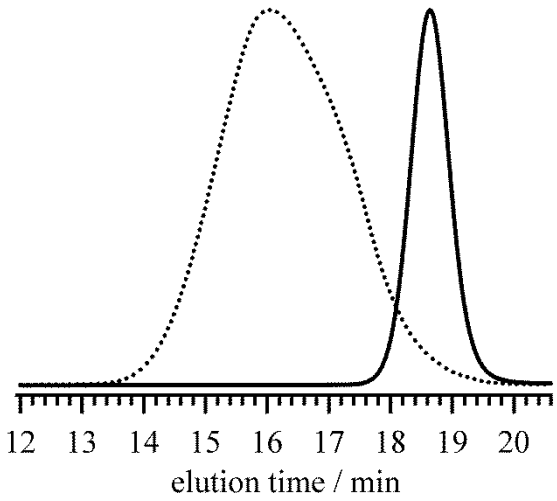


Figure 3. SEC traces of the PCL-diol obtained from the 1st polymerization with the $[\varepsilon\text{-CL}]_0/[\text{1,3-propanediol}]_0/[\text{DPP}]_0$ ratio of 25/1/0.05 ($M_{n,SEC}$ = 5,400, $Đ_M$ = 1.09; solid line) and the obtained PCL-based polyurethane ($M_{n,SEC}$ = 32,800, $Đ_M$ = 2.03; dotted line) (eluent, $CHCl_3$; flow rate, 1.0 mL min^{-1}).

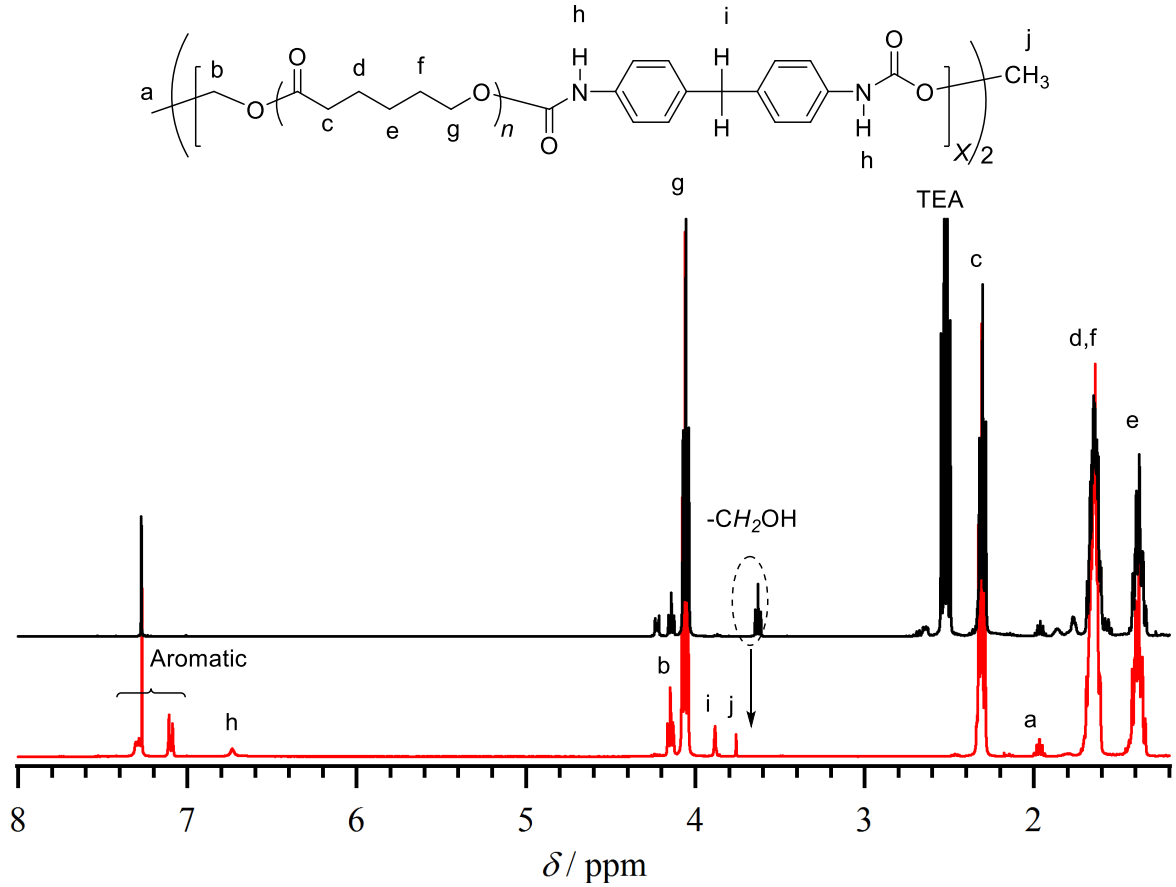


Figure 4. ^{1}H NMR spectra of the PCL-based polyurethane (red line) and corresponding PCL-diol obtained before adding MDI (conv. = 95.0%; black line) in $CDCl_3$.

Conclusions

In this study, the environmentally benign way to produce well-defined polyesters, polycarbonate, and polyester-ether was established by using organophosphate as a catalyst under bulk conditions. The significant advantages of the present polymerization procedure were fully demonstrated regarding a shorter reaction time, remarkably lower catalyst loading, and wider scope of applicable monomers. The kinetic and block copolymerization studies revealed the controlled/living nature of the present polymerization system even under the bulk conditions, which enables the production of well-defined end-functionalized, α,ω-dihydroxy telechelic, and star-shaped polyesters. These demonstrations confirmed that the bulk conditions overcome the difficulties of the organophosphate-catalyzed ROP, such as the amount of loaded catalyst and the use of solvent. Furthermore, the high catalytic abilities of the organophosphate for both the ROP and urethane formation reaction enabled the production of a PCL-based polyurethane in one-pot through a metal-free route. Considering the low acidity, low toxicity, and high chemically stability of the organophosphates, the organophosphate-catalyzed bulk ROP is an attractive candidate for the environmentally benign production of various polymers for both industrial and biomedical purposes.

Acknowledgements

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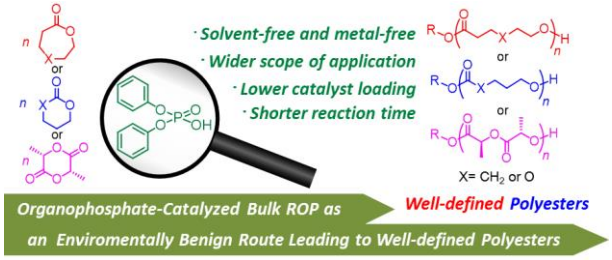
Table of Contents Use Only

Organophosphate-Catalyzed Bulk Ring-Opening Polymerization as an Environmentally Benign Route Leading to Block Copolyesters, End-Functionalized Polyesters, and Polyester-Based Polyurethane

Tatsuya Saito, Yusuke Aizawa, Kenji Tajima, Takuya Isono, Toshifumi Satoh



To expand the potential of organophosphate catalyst, ring-opening polymerization of cyclic esters, cyclic ester-ether, and cyclic carbonate was demonstrated under the bulk conditions.