Polymer Journal

REGULAR ARTICLE

Microwave-assisted Ring-Opening Polymerization of ε-Caprolactone in Presence of Hydrogen Phosphonates

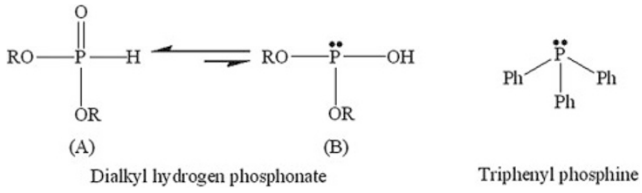
*By Ye TAN, Shaojun CAI, Liqiong LIAO, Qingrong WANG, and Lijian LIU**

Microwave-assisted ring-opening polymerization (MROP) of ε-caprolactone (ε-CL) in the presence of hydrogen phosphonate was investigated. Poly(ε-caprolactone) with molecular weight of 8100 g/mol was synthesized in 100 min at 510 W microwave irradiation in the presence of 2.9% of diisopropyl hydrogen phosphonate. It was found that the MROP of ε-CL was first initiated by the trace water in the reaction mixture; a subsequent transesterification reaction occurred between the oligo(ε-caprolactone) and diisopropyl hydrogen phosphonate at the early stage of the MROP, and the resulting oligo(ε-caprolactone)-substituted hydrogen phosphonate could act as the catalyst during the MROP after diisopropyl hydrogen phosphonate was consumed out.

KEY WORDS: Microwave / Ring-Opening Polymerization / Poly(ε-caprolactone) / Phosphonate / Transesterification /

Poly(ε-caprolactone) (PCL) is one of the most important biodegradable polyesters for biomedical purposes.[1–4] The ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) is a well-developed method for preparation of high molar mass PCL. The most widely used catalysts/initiators for the ROP of lactones are tin salts and aluminum alkoxides; however, there is concern on the potential toxicity of residue metallic compounds in biomedical applications.[5–7] Since the biomedical application of the polymers demands extremely high purity and the absence of any toxic compounds, the development and use of biocompatible low-toxic or non-toxic catalysts/initiators, one of which is the metal-free organo-catalyst, may have significant benefits.[8–10]

The most studied organo-catalytic compounds for the ROP of cyclic esters are some well-known transesterification agents such as 4-(dimethylamino) pyridine,[11] nucleophilic tertiary phosphines,[12] N-heterocyclic carbenes,[13] bifunctional amino-thioureas,[14] and 1,5,7-triazabicyclo-[4.4.0]dec-5-ene.[15] Among these organocatalyst, the nucleophilic tertiary phosphines are quite interesting for their catalytic mechanism. Hedrick studied tertiary phosphine catalyzed ROP of lactide (L- or D, L-), the lactide monomer was found to be activated by the forming a complex with the electron-rich phosphine (*i.e.*, triphenyl phosphine), and then polymerized to generate narrowly distributed polylactides with predictable molecular weights.[12] This polymerization was similar to that with biocatalysts, which was postulated to have a monomer-activated mechanism.[16,17] Since dialkyl hydrogen phosphonate may be converted into to a phosphine-like tautomer that has a lone pair and could have nucleophilic characteristics (Scheme 1, structure B), dialkyl hydrogen phosphonate might possess similar nucleophilic characteristics in organic synthesis as that of tertiary phosphine.[18] Also, it has been reported that dimethyl hydrogen phosphonate can undergo transesterification with poly(ethylene glycol) to produce poly(oxyethylene) hydrogen phosphonate under microwave irradiation.[19]



Scheme 1. Structures of dialkyl hydrogen phosphonate and triphenyl phosphine.

Microwave heating is an environmentally benign method for chemical synthesis due to its high efficiency and homogeneous heating.[20,21] Polymerization reactions also can be significantly improved by microwave irradiation, and the microwave-assisted syntheses of biodegradable polymers have proved to be successful.[22–29] Our group has previously reported the microwave-assisted ROP (MROP) of cyclic esters such as ε-caprlactone[30,31] and lactides,[32] and the corresponding polyesters have been successfully synthesized using this method.

In present work, we investigated the ROP of ε-CL under microwave irradiation in the presence of dialkyl hydrogen phosphonate (DHP), expecting the DHP compounds would act as non-metallic initiators/catalysts for the polymerization. Unexpectedly, instead of acting as the initiator for the ROP of ε-CL, it was found that the DHP participated the formation of oligo(ε-caprolactone)-substituted hydrogen phosphonate during the initial stage of the reaction; this oligo(ε-caprolactone)-substituted hydrogen phosphonate may actually act as a macromolecular catalyst for the ROP of ε-CL. The mechanism of the polymerization in the presence of DHP also was briefly discussed.

EXPERIMENTAL

Materials

ε-Caprolactone (99.9%, Solvay Caprolactone) was dried over CaH_2 for 72 h and distilled under reduced pressure. PPh_3

Department of Polymer Science, College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072, P. R. China
*To whom correspondence should be addressed (Tel/Fax: +86-27-6875-6825, E-mail: liulj@whu.edu.cn).

was an analytical grade reagent and azeotropically distilled with toluene three times before use. Benzyl alcohol was refluxed over CaH_2 for 8 h and then distilled. Toluene was dried by refluxing over sodium and distilled before use. PCL diol ($M_n = 4000$, CAPA 2402, Solvay Caprlactone) was dried under vacuum before use. Diethyl hydrogen phosphonate (DEHP), diisopropyl hydrogen phosphonate (DIPHP) and dibutyl hydrogen phosphonate (DBHP) were synthesized according to the literature,[33] the proton nuclear magnetic resonance (^{1}H NMR) and ^{31}P nuclear magnetic resonance (^{31}P NMR) spectra of the product were identical to the authentic sample previously reported.

Measurements

^{1}H and ^{31}P NMR spectra were recorded on a Mercury VX-300 (300 MHz) apparatus using $CDCl_3$ as solvent with TMS as the internal standard for ^{1}H NMR and 85% phosphoric acid for ^{31}P NMR.

The weight-average molar mass (M_w) and polydispersity (PDI) of the samples was determined by gel permeation chromatography (GPC) on a Waters HPLC system equipped with a Model 2690D separation module, a Model 2410 refractive index detector and Shodex K802.5 & K805 columns in series. $CHCl_3$ was used as the eluent (1.0 mL/min) at 35 °C. Polystyrene standard (PS) was used for the calibration of the molecular weight. The universal calibration of the molar mass also was performed accoding to the following equation: $M_{PCL} = 0.45\ M_{PS}$.[34–36]

Matrix-assisted laser deionization time-of-flight mass spectrometry (MALDI-TOF MS) was recorded on a Shimadzu AXIMA-CFR Plus mass spectrometer equipped with a time-of-flight (TOF) analyzer, and using a nitrogen laser source (337 nm, 3 ns pulse width). A positive polarity and 1.8-kV acceleration voltage in the reflection mode were employed. 2, 5-Dihydroxybenzoic acid (DHB) was used as matrices. Samples were prepared by mixing approximately 5 μL of matrix solution (25 mg/mL in THF) before drying on the sample slide. The analyte solution (1 mg/mL) was mixed in a 1:1 v/v ratio with the matrix solution.

Microwave-Assisted Ring-Opening Polymerzation of ε-Caprolactone in the Presence of Dialkyl Hydrogen Phsphonate

MROP of ε-CL was carried out in a domestic multimode microwave oven (Whirlpool-VIP273F) with a frequency of 2.45 GHz and maximum power output of 850 W. Briefly, a mixture of ε-CL (1.000 g, 8.77 mmol) and DHP (0.175 mmol) in a vacuum-sealed ampoule (50 Pa) was irradiated at a predetermined microwave power for a period of time (50–250 min). The temperatures of the reactions were measured by inserting a thermocouple into the ampoule as previously reported.[37] After the irradiation, the ampoule was quenched in an ice-water bath; the crude product was dissolved in 10 mL of dichloromethane, one drop of the solution was dried for monomer conversion measurement using ^{1}H NMR and the remaining solution was precipitated in 200 mL cold petroleum ether. The precipitate was then collected by filtration and dried in vacuum at ambient temperature.

The monomer conversion in the ROP of ε-CL was calculated from the relative integral of peaks in the ^{1}H NMR spectra of reaction mixtures; briefly, the integrals from the ω-methylene protons in the monomer ($I_{4.2}$) and the repeating units of the resulting PCL ($I_{4.0}$) was compared and the conversion was calculated as $100 \times I_{4.0}/(I_{4.0} + I_{4.2})$.[38]

Ring-Opening Polymerzation of ε-Caprolactone in the Presence of Dialkyl Hydrogen Phsphonate under Conventional Heating Method

The thermal ROP was carried out in a salt bath for predetermined period of time. The temperature of the salt bath was carefully adjusted to keep the temperature of the reaction system the same as that of the MROP. The other procedures were identical to those of the microwave method.

Microwave-Assisted Transesterification of Poly(ε-Caprolactone) with Dialkyl Hydrogen Phsphonate

The procedure for the transesterification of PCL diol ($M_w = 4000$) with DHP was same as that of the ROP of ε-CL.

RESULTS AND DISCUSSION

Microwave-Assisted Ring-Opening Polymerization in the Presence of DHP

The MROP of ε-CL was carried out in the presence of DEHP, DIPHP, and DBHP, respectively. The chemical structure of the resulting products was confirmed by the ^{1}H NMR. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.40 (-CH_2-CH_2CH_2-, 2H), 1.66 (-$CH_2CH_2CH_2$-, 4H), 2.30 (-$COCH_2$-, 2H), 4.04 (-OCH_2-, 2H). The ^{1}H NMR data were in accordance to the literature.[3] The M_w of resulting polymer ranged from 600 to 8100 g/mol (Figure 1), with the PDI ranging from 1.16–1.68.

Microwave-Assisted Ring-Opening Polymerization in the Presence of PPh_3

Triphenyl phosphine catalyzed MROP of ε-CL was conducted for comparison purpose in combination with benzyl alcohol as an initiator. The structure of the resultant product

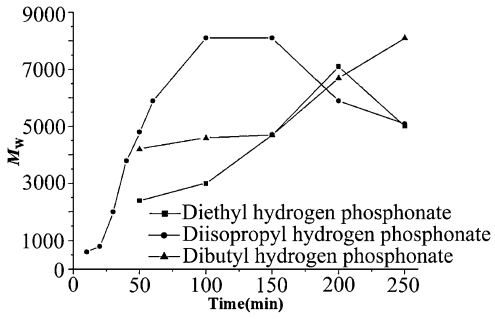


Figure 1. M_w of resulting polymer by the ROP in the presence of DEHP, DIPHP and DBHP. (ε-CL/DHP = 50, 510 W)

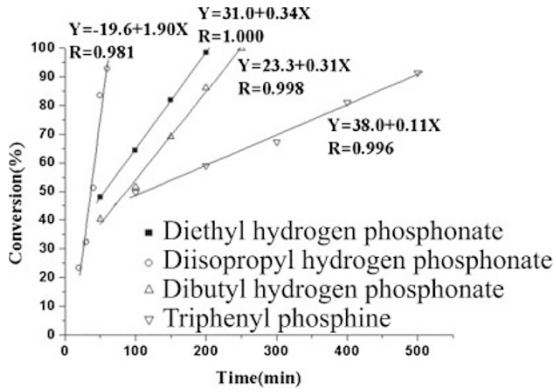


Figure 2. Conversion-time curves of the MROP in the presence of dialkyl hydrogen phosphonates and triphenyl phosphine. (ε-CL/catalyst = 50, 510 W)

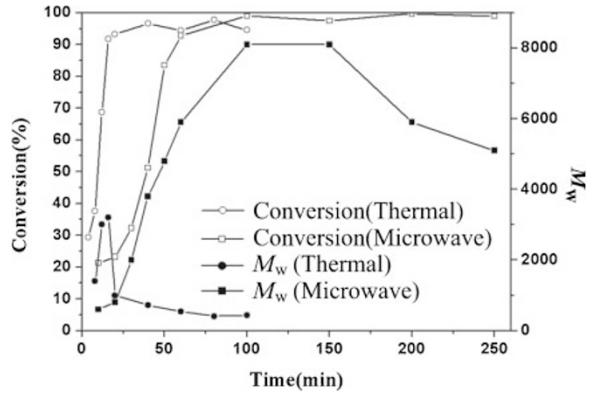


Figure 3. Conversion-time curves and M_w-time curves of the ROP. (ε-CL/DIPHP = 50, 275 °C, 510 W)

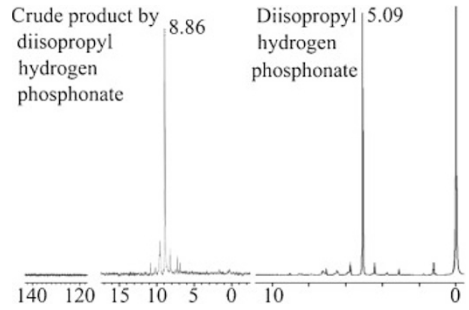


Figure 4. ^{31}P NMR spectra of pure DIPHP and the reaction mixtures. (ε-CL/DIPHP = 50, 510 W, 250 min)

was confirmed using ^{1}H NMR. The maximum M_w the product was 6,100 g/mol with a PDI of 1.4.

Figure 2 shows the conversion-time curves of the MROP in the presence of DHPs and PPh_3/benzyl alcohol. High monomer conversions could be achieved in much shorter time using the same concentration of DHPs as the catalysts, indicating DHPs were more effective catalysts for the MROP. It is interesting that all the conversion-time curves of the MROP in the presence of DHPs and PPh_3 revealed zero order kinetics. The DHPs were more effective than triphenyl phosphine in catalyzing the ROP of ε-CL as the kinetics constant (0.31–1.90) was higher than that of the latter (0.11).

Ring-Opening Polymerization by Conventional Heating in the Presence of DIPHP

The ROPs were also conducted under conventional heating at 305 °C to ensure a temperature of 275 °C inside the reaction mixture, which was the same as that of the reaction mixtures under 510 W microwave irradiation. The results of the conversion and M_w as a function of the ROP reaction time are showed in Figure 3.

It was noted that the conversion of the monomer was much faster under conventional thermal polymerization compared with the MROP (Figure 3). However, as shown in Figure 3, the M_ws of the PCL produced by MROP were higher than those by conventional heating method. A maximum M_w of PCL was found to be 8100 g/mol after 100 min microwave irradiation, while it was only 3200 g/mol for 16 min conventional thermal polymerization. The degradation of polymer in thermal polymerization occurred earlier than in microwave polymerization (Figure 3). As illustrated in Figure 3, the decrease in M_w occurred after 20 min conventional thermal heating while the monomer conversion was increasing, indicating the degradation of the polymer and the ring opening of the monomer (*i.e.*, the polymerization) took place simultaneously. For the reaction under microwave irradiation, no obvious degradation was observed until the monomer conversion reached its equilibrium at 150 min. It revealed the monomer and polymer exhibited higher stability under microwave than conventional heating method at the same temperature.

Mechanism Aspects of the Microwave-Assisted Ring-Opening Polymerization in the Presence of DIPHP

It was noted that the dialkyl hydrogen phosphonates were more effective than the triphenyl phosphine in catalyzing the MROP of ε-CL; it is of interest to investigate the mechanism of the MROPs of ε-CL in the presence of DHPs. The mechanism of the MROP of ε-CL was studied utilizing NMR and MALDI TOF, DIHP was chosen since it was the most effective in catalyzing the MROP of ε-CL.

The ^{31}P NMR spectra of the pure DIPHP and the reaction mixtures of ε-CL/DIPHP (510 W, 250 min) are shown in Figure 4. Peaks of trialkyl phosphite would appear in the spectrum if the polymerization had been presumably initiated by the hydroxyl dialkyl phosphite, which is the tautomer of the DHP (Scheme 1), and forms a trialkyl phosphite. However, no peak at 130 ppm was observed for the trialkyl phosphite as expected, indicating that the MROP of ε-CL was not initiated by the hydroxyl group in the tautomer of DIPHP. In stead, a peak at 8.86 ppm appeared in the ^{31}P NMR spectra of the reaction mixtures, which was different from that of DIPHP (at 5.09 ppm), depicting the DIPHP underwent some reaction other than acted as the initiator during the ROP process.

Figure 5 shows the ^{1}H NMR spectra of the reaction mixture of ε-CL and DIPHP after 1 and 30 min of microwave irradiation. The peaks at 1.32 and 4.70 ppm, which belong to the methyl proton (-CH_3) and methenyl proton (-C*H*-) in the

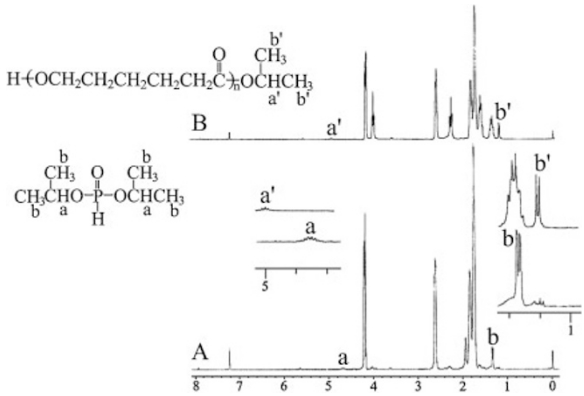


Figure 5. ^{1}H NMR spectra of the reaction mixtures: A, 1 min; B, 30 min. (ε-CL/DIPHP = 50, 510 W)

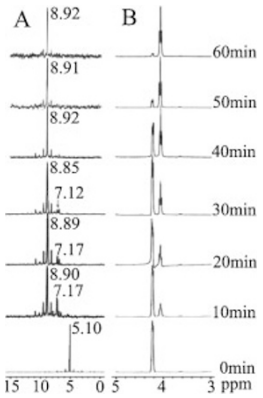
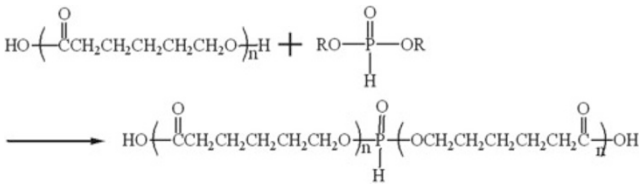


Figure 6. NMR traces of the reaction mixtures at different irradiation time: A. ^{31}P NMR, B. ^{1}H NMR. (ε-CL/DIPHP = 50, 510 W)

DIPHP (peak a and b, Figure 5A), shifted to 1.22 and 5.0 ppm after 30 min microwave irradiation (peak a′ and b′, Figure 5B). It has been shown in the ^{1}H NMR spectrum of isopropyl alcohol the chemical shifts of the methyl proton (-CH_3) and methenyl proton (-C*H*-) were 1.29 and 3.99 ppm, respectively. The discrepancy of the chemical shifts from those of isopropyl alcohol indicated that no isopropyl alcohol was formed as the by product of transesterification reaction between the oligo(ε-caprolactone) (oligo-CL) and DIHP; the isopropyl group was rather incorporated in the PCL as the terminal group.

Figure 6 showed the ^{31}P NMR and ^{1}H NMR changes of the reaction mixtures of ε-CL and DIPHP with the irradiation time increased from 0 to 60 min. Two obvious changes in the ^{31}P chemical shift (5.10 ppm → 7.17 ppm → 8.90 ppm) were observed (Figure 6A), indicating the DIPHP experienced two reactions sequentially during the polymerisation. The ^{1}H NMR spectra of reaction process (Figure 6B) showed a continuous increase of the monomer conversion with reaction time. It was observed that the ^{31}P peak at 5.09 ppm disappeared after the reaction mixture was irradiated for 10 min at 510 W, suggesting a complete consumption of DIPHP in the transesterification. However, the monomer conversion was less than 25% at this point. After 10 min microwave irradiation, a peak around



Scheme 2. Hypothesized transesterification between DHP and oligo(ε-CL).

7.17 ppm appeared and disappeared after 30 min microwave irradiation, while the ε-CL monomer conversion continued increasing in this process.

It was reported that three peaks that belong to the monomer, end group and the repeating units were observed in the ^{31}P NMR during the synthesis of polyphosphonates from dimethyl hydrogen phosphonate (DMHP).[35,36,38] A peak at 11.00 ppm could be attributed to DMHP; peak at 9.80 ppm belongs to the P atom in the end group that bonded with -OCH_3 and -OCH_2 groups; 8.40 ppm is the chemical shift of P atom in the repeating unit. The ^{31}P chemical shift changed when the reaction proceeded. In this experiments, the change of ^{31}P chemical shift followed a sequence of 11.00 → 9.80 → 8.40, suggesting the methoxy groups were replaced by the *oligo*-phosphonates stepwise.

In our reaction, the peak at 8.90 ppm in the ^{31}P NMR spectra of ε-CL/DIPHP reaction mixture was close to the reported chemical shift of polyphosphonates.[39–41] The similarity of the chemical shift of the reaction product to that of the repeating units of these polyphosphonates strongly suggested that a transesterification between the oligo(ε-CL) and DIPHP occurred during the polymerization process as hypothesized in Scheme 2.

To elucidate this hypothesis, reaction was conducted between oligo(ε-CL) ($M_n = 4000$) and DIPHP at a weight ratio of 47.54, which is equivalent to a ε-CL/DIPHP molar ratio of 50. Figure 7 showed the ^{31}P NMR spectrum of the reaction mixture after being irradiated at 510 W for 200 min. It was evidenced that a reaction occurred between the DIPHP and PCL, and the product was the same as that presented in Figure 6. This result meant a transesterification occurred between DIPHP and oligo(ε-CL), so the products were same to that from the ε-CL/DIPHP reaction mixture. It was in agreement with the transesterification in the MROP of ε-CL.

In Figure 6a, the ^{31}P peak at 5.09 ppm disappeared after 10 min irradiation at 510 W, suggesting that DIPHP had been consumed up. In contrast, the monomer conversion was less than 25% after 10 min irradiation and the polymerization went on until 60 min.

MALDI-TOF MS also was utilized to analyze the ε-CL/DIPHP reaction mixture. As shown in the MALDI-TOF MS spectrum of the ε-CL/DIPHP reaction mixture (Figure 8), the peaks (A) represented the OH-terminated oligo(ε-CL), the masses of the sodiated quasi molecular ion peaks (M_A) can be defined according to eq 1:

$$M_A = 18 + 23 + 114 \times n = 41 + 114 \times n \qquad (1)$$

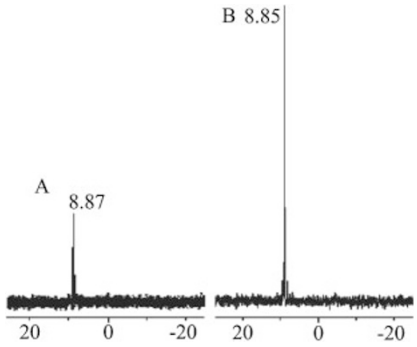


Figure 7. ^{31}P NMR spectrum of a mixture of oligo(ε-CL) (M_w = 4000) with DHPs [A) DIPHP, B) DBHP, PCL/DIPHP = 47.54 (wt/wt), 510 W, 200 min].

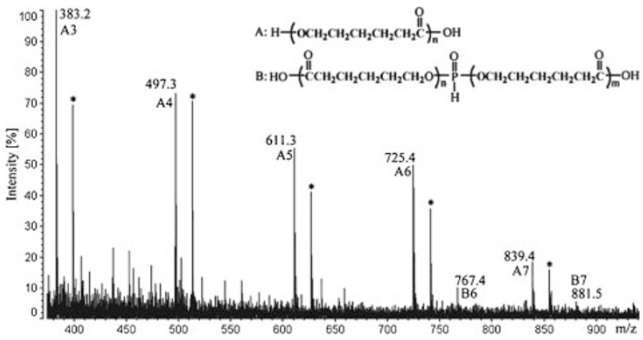


Figure 8. MALDI-TOF MS spectra of the reaction mixture.

Where n was number of the repeating unit; 18, 23, and 114 were the mass of the end group, sodium cation, and repeating unit, respectively. The mass of 18 Da corresponds to the mass of -H and the -OH end group shown in Figure 8 (Structure A). The result demonstrated that the MROP was initiated by trace of water. Asterisks denote the potassium-cationized peaks (ε-CL/DIPHP = 50, 510 W, 60 min).

The (Mass+H^+)/Charge 767.4 (Peak B6) and 881.5 (Peak B7) (M_B) can be attributed to the phosphorated oligo(ε-CL) with the degree of polymerization of 6 and 7, respectively (eq 2):

$$\begin{aligned} M_B &= 1 + (17 \times 2) + 48 + 114(m + n) \\ &= 83 + 114(n + m) \end{aligned} \tag{2}$$

Where n + m was number of the repeating unit of the oligomer, 17, 48, and 114 were the mass of the end group, hydrogen phosphonate, and the repeating unit of PCL, respectively. The results also showed that the MROP was initiated by trace of water in the reaction system, thus the molecular weight/chain length of the polymerization product could be controlled by varying the amount of water in the reaction; oligomers with higher molecular weight can be obtained through decreasing the water concentration.

CONCLUSIONS

Microwave-assisted ring-opening polymerization of ε-CL in the presence of dialkyl hydrogen phosphonate was investigated. The result showed that the ring-opening polymerization of ε-CL was first initiated by trace water in the reaction mixture, phosphorated oligo(ε-CL) was then formed during the polymerization process *via* a transesterification of oligo(ε-CL) with diisopropyl hydrogen phosphonate. The phosphorated oligo(ε-CL) can act as the catalyst for the ROP of ε-CL after the DIPHP was consumed out at the early stage of the polymerization.

Acknowledgment. The authors thank the National Natural Science Foundation of China (20574053 and 20274032) and the Hubei Province Natural Science Foundation (2003ABA195) for financial support of this investigation.

Received: March 28, 2009
Accepted: June 26, 2009
Published: August 12, 2009

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