Ring-opening Copolymerization of $\varepsilon$-Caprolactone and $\delta$-Valerolactone Catalyzed by a 2,6-Bis(aminophenol) Zinc Complex

Qian Hu$^a$, Su-Yun Jie$^a$, Pierre Braunstein$^b$, and Bo-Geng Li$^a$

$^a$ State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China
$^b$ Université de Strasbourg, CNRS, CHIMIE UMR 7177, Laboratoire de Chimie de Coordination, 4 rue Blaise Pascal, 67081 Strasbourg Cedex, France

Abstract In combination with methyllithium, a 2,6-bis(aminophenol) zinc complex 1 was used in the ring-opening polymerization of $\delta$-valerolactone in the absence or presence of benzyl alcohol and showed high efficiency, mainly producing cyclic and linear polyvalerolactones, respectively. On the basis of homopolymerization, the ring-opening copolymerization of $\varepsilon$-caprolactone and $\delta$-valerolactone was investigated. The P(CL-co-VL) random copolymers, PCL-b-PVL and PVL-b-PCL diblock copolymers, were prepared by varying the feeding strategy (premixing or sequential feeding). The copolymer composition was adjusted by varying the feeding ratio of two monomers. The structure and thermal properties of obtained polymers were characterized by GPC, $^1$H-NMR, $^{13}$C-NMR, MALDI-TOF mass spectroscopy, and DSC, respectively.

Keywords Zn complex; Copolymerization; Block copolymer; Random copolymer

INTRODUCTION

Aliphatic polyester is one of the most important biodegradable polyesters and has been widely used as a sustainable material in various fields.$^{[1,2]}$ The catalytic ring-opening polymerization (ROP) of cyclic esters can conveniently generate biodegradable and renewable polyester materials.$^{[3,4]}$ Metal complexes as more efficient catalysts play an important role in the development of ROP.$^{[5−9]}$ especially nontoxic metals (such as zinc) in view of biological compatibility and biomedical applications.$^{[10,11]}$ Zinc complexes bearing various organic ligands have been used as active catalysts in the ROP of cyclic esters to prepare aliphatic polyesters.$^{[12−15]}$

Polyvalerolactone (PVL) and polycaprolactone (PCL) as two types of important aliphatic polyesters have almost similar properties in chemistry and biological medicine.$^{[16−18]}$ PVL exhibits low thermal stability, low mechanical strength, and low gas permeability and solvent resistance, which greatly limits its application in different fields.$^{[19−21]}$ However, because of its good biocompatibility, biodegradability, and permeability, PVL can be used as a hydrophobic block in amphiphilic block copolymers for in vivo drug delivery systems of chemotherapy drugs.$^{[22−25]}$ On the other hand, the high crystallinity and hydrophobicity let PCL usually exhibit a slow rate of degradation (1–2 years), so it is limited to a long-term use.$^{[19]}$

Copolymerization provides an effective strategy for simply tailoring the properties of materials by adjusting the copolymer composition to synthesize polymers with different properties.$^{[26−29]}$ For example, by adding a second comonomer, such as L-lactide, $\delta$-valerolactone ($\delta$-VL), $\gamma$-butyrolactone ($\gamma$-BL), $\varepsilon$-valerolactone (g-VL), or $g$-caprolactone (g-CL) in the PCL chains randomly, the degradation rate was observed to become faster.$^{[30−33]}$ PCL can be also combined with other polymers, such as cellulose propionate, cellulose acetate butyrate, poly(lactic acid), and poly(lactic acid-co-glycolic acid), to improve the stress crack resistance, dyeability, and adhesion.$^{[33,34]}$ The copolymers of $\varepsilon$-CL and $\delta$-VL could be very useful biodegradable materials in the environmental applications because the rate of degradation should be uniform in a more amorphous morphology.$^{[35]}$

We recently reported the application of zinc complexes bearing 2,6-bis(aminophenol) ligands as highly active catalysts for the ROP of $\varepsilon$-CL.$^{[36]}$ In this study, a 2,6-bis(aminophenol)zinc complex 1 as a catalyst was first used in the ROP of $\delta$-VL. On the basis of homopolymerization, the ring-opening copolymerization of $\varepsilon$-CL and $\delta$-VL was further studied. The structure and thermal properties of homopolymers and copolymers were characterized and analyzed.

EXPERIMENTAL

General Considerations

All the manipulations of air- or moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Toluene and THF from J&K Scientific Ltd. were purified by passing through solvent purification systems (MB-SPS, MBRAUN). Benzyl alcohol (BuOH, from J&K Scientific Ltd.), $\varepsilon$-caprolactone ($\varepsilon$-CL, from Energy Chemical Ltd.),
Characterization

\[ \delta \text{-VL} \text{ and } \delta \text{-valerolactone (} \delta \text{-VL, from J&K Scientific Ltd.) were dried } \]

over 5Å molecular sieves and CaH₂, and further purified by vacuum distillation. Methylolithium (MeLi, 1.6 mol/L in diethyl ether) was purchased from J&K Scientific Ltd. All other chemicals were used directly without further purification unless otherwise stated. Zinc complex 1 (Chart 1) was prepared by our previous procedure.[36]

Typical Procedure for Ring-opening Polymerization

All the polymerization reactions were conducted by Schlenk techniques in a sealed Schlenk flask. In a typical polymerization experiment of \( \delta \text{-VL} \), a suspension of zinc complex 1 (0.02 mmol) in purified toluene was filled in a 50 mL Schlenk flask, and methylolithium solution ([MeLi]/[Zn] = 4) was added dropwise at \(-10 \, ^\circ\text{C}\). The mixture consisting of yellow solution and white precipitate was slowly warmed to room temperature and stirred for 2 h. After that, BnOH (if needed) and \( \delta \)-valerolactone were added to the above suspension in sequence and the polymerization time was measured from that point. After polymerization, the reaction was quenched with deionized water (0.5 mL) and the mixture was poured into \( n \)-hexane to precipitate the polymer. The white precipitate was collected by filtration under reduced pressure, redissolved in a few drops of \( CH_2Cl_2 \), and then added with \( n \)-hexane (3 mL) to precipitate the polymer; this process was repeated three times. The polymer was finally dried under vacuum.

The general procedure for random copolymerization was as follows. The monomers, certain amounts of \( \varepsilon \text{-CL} \) and \( \delta \text{-VL} \), were mixed in a sealed Schlenk flask and then added with BnOH (if needed) and \textit{in situ} produced catalyst solution (zinc complex 1/MeLi) sequentially at 30 \( ^\circ\text{C} \). After 20 min, the polymerization was quenched with deionized water (0.5 mL). The washing procedure same as above was used to isolate the random copolymers.

The general procedure for the preparation of block copolymers was as follows. After zinc complex reacted with MeLi for 2 h in a 25 mL Schlenk flask under N₂, a certain amount of BnOH (if needed) and \( \varepsilon \text{-CL} \) or \( \delta \text{-VL} \) were sequentially added to the above suspension at 30 \( ^\circ\text{C} \) and stirred for 10 min. Then, a certain amount of the second monomer (\( \delta \text{-VL} \) or \( \varepsilon \text{-CL} \)) was added and stirred for another 10 min. The polymerization was quenched with deionized water (0.5 mL). The washing procedure same as above was used to isolate the block copolymers.

Calculation of Randomness

The average sequence length (\( L \)) and the randomness degree (\( R \)) were calculated according to the following formulas,[19,26,37] in which \( L_C \) and \( L_V \) represent the sequence lengths of CL and VL chain segments, respectively.

\[
L_C = \frac{I_{CC}}{I_{VC}} + 1 \quad \text{and} \quad L_V = \frac{I_{VV}}{I_{VC}} + 1 \quad \text{and} \quad R = \frac{1}{L_C} + \frac{1}{L_V}
\]

\( I_{CC}, I_{VV}, I_{VC} \) and \( I_{LC} \) represent the integral areas of the signals at 64.18, 64.10, 63.87, and 63.79 ppm in the \( ^{13} \text{C} \)-NMR spectra of copolymers. The signals at 64.18 and 64.10 ppm were attributed to the methylene-C atom (\(-CH_2O\)) of CL unit in CL-VL and CL-CL sequences, respectively. Similarly, the signals at 63.87 and 63.79 ppm were assigned to the methylene-C atoms (\(-CH_2\)) of VL unit in VL-VL and VL-CL sequences. It is known that \( R \) value is equal to 1 or 2 for a completely random or alternating copolymer and \( R \) value is close to 0 for a block copolymer.

RESULTS AND DISCUSSION

Ring-opening Polymerization of \( \delta \text{-VL} \)

In combination with 4 equiv. of methylolithium, zinc complexes bearing 2,6-bis(aminophenol)phenol ligands showed very high activity in ROP of \( \varepsilon \text{-CL} \) both in the presence and in the absence of BnOH.[36] Herein, zinc complex 1/MeLi catalytic system was used in the ROP of \( \delta \text{-VL} \) and also proved to be highly active in the presence or absence of BnOH with a complete conversion of \( \delta \text{-VL} \) in 3–10 min (Table 1). It is clearly observed that the PVLs obtained in the presence of BnOH have lower molecular weight (\( M_n \)) and narrower molecular weight distribution (\( D \)) than those of PVLs obtained without BnOH.

The PVLs obtained in the presence (entry 1 in Table 1) or absence (entry 5 in Table 1) of BnOH were characterized by \( ^{1} \text{H} \)- and \( ^{13} \text{C} \)-NMR spectra (Figs. 1 and 2). In the \( ^{1} \text{H} \)-NMR spectra (Fig. 1), the typical signals of characteristic methylene protons in the VL units were observed for both samples, including 1.67 (CH₃), 2.33 (CH₂C=O), and 4.07 (OCH₂) ppm. In the spectra of PVLs obtained in the presence of BnOH, the characteristic signals of protons of methylene and phenyl ring in the terminal benzylic ester groups were located at 5.11 and 7.34 ppm, respectively. The triplet signals at 3.64 ppm were assigned to the protons in the chain ends (CH₂OH). Besides, similar signals showed up in the spectra of PVLs obtained in

https://doi.org/10.1007/s10118-020-2347-4
the absence of BnOH, because the ROP of δ-VL was quenched
by deionized water, which probably resulted in the formation
of some linear PVLs.

The signals of methylene-C atoms in the VL repeating units
of δ-VL catalyzed by zinc complex/MeLi in the presence
or the absence of BnOH

| Entry | Time (min) | [VL]/[Zn]/[BnOH] | Yield (%) | \(M_{n,obs}\) (kg/mol) | \(D\) |
|-------|------------|------------------|-----------|--------------------------|-------|
| 1     | 3          | 50/1/0.5         | 100       | 3.30                     | 1.28  |
| 2     | 3          | 200/1/1          | 100       | 10.3                     | 1.25  |
| 3     | 10         | 500/1/1          | 100       | 16.6                     | 1.27  |
| 4     | 3          | 800/1/1          | 100       | 19.5                     | 1.47  |
| 5     | 3          | 50/1/0           | 100       | 3.18                     | 2.01  |
| 6     | 3          | 200/1/0          | 100       | 13.1                     | 1.62  |
| 7     | 10         | 500/1/0          | 100       | 21.2                     | 1.34  |
| 8     | 10         | 800/1/0          | 100       | 25.0                     | 1.24  |

*Polymerization conditions: zinc complex: 0.02 mmol, [Zn] = 0.0058 mol/L, [MeLi]/[Zn] = 4/1, solvent: toluene, reaction temperature: 30 °C; b Determined by weight of isolated polymer; c Measured by GPC in THF, calibrated with polystyrene standards, and corrected using a correction factor of 0.57 [28].

Fig. 1 ¹H-NMR spectra of PVLs obtained by 1/MeLi in the absence (top, entry 5 in Table 1) or presence (bottom, entry 1 in Table 1) of BnOH.

Fig. 2 ¹³C-NMR spectra of PVLs obtained by 1/MeLi in the absence (top, entry 5 in Table 1) or presence (bottom, entry 1 in Table 1) of BnOH.

Fig. 3 MALDI-TOF mass spectra of PVLs obtained by 1/MeLi (entry 5 in Table 1).

Fig. 4 MALDI-TOF mass spectra of PVLs by 1/MeLi in the presence of BnOH (entry 1 in Table 1).

can be observed at 21.4 (CH₂), 28.0 (CH₂), 33.7 (CH₂C=O),
and 63.9 (OCH₂) ppm in the ¹³C-NMR spectra of the two
samples. The characteristic signals of carbonyl-C atoms were
located at 173.3 ppm (C = O) (Fig. 2). For the PVLs obtained
in the presence of BnOH, the signals of phenyl-C and methy-
lene-C atoms of terminal benzyl ester groups were found
around 128.3 and 66.2 ppm, respectively, and the resonance
of the C₂H₅OH group in the chain end appeared at 62.2 ppm.

The MALDI-TOF mass spectra of PVLs catalyzed by Zn com-
xplex 1 in the absence (entry 5 in Table 1) or presence (entry 1
in Table 1) of BnOH are shown in Figs. 3 and 4, respectively. As
shown in Fig. 3, there were two main series of signal peaks in
the mass spectrum of PVLs obtained from the catalytic sys-
tem without benzyl alcohol: the signals peaks at m/z 2125.9
(n = 21), 2239.9 (n = 22), 2326.1 (n = 23), etc. and m/z 2141.0
(n = 21), 2241.1 (n = 22), 2341.2 (n = 23), etc. corresponded to
the cyclic PVLs [(VL)n] clustered with Na⁺ (m/z: 100.12 × n +
22.99) and K⁺ (m/z: 100.12 × n + 39.10), respectively. The
difference between each set of adjacent signal peaks (100.1) was
exactly the molecular weight of the VL repeating unit. The MALDI-TOF mass spectrum of PVLs obtained from the catalytic
system with benzyl alcohol (Fig. 4) exhibited two main series
of signal peaks, which corresponded to the linear PVLs
[BnO(VL)OH] ended by BnO— and hydroxyl groups with Li⁺
aggregation (m/z: 108.14 + 100.12 × n + 6.94) and with Na⁺
aggregation (m/z: 108.14 + 100.12 × n + 22.99), respectively. Two series of weaker signal peaks could be also observed in the amplified mass spectrum, which were attributed to a small number of linear PVLs clustered with double-charged Li⁺ or Na⁺. m/z values of the signal peaks for linear PVLs with different ion aggregations obtained from MALDI-TOF mass spectra were consistent with the calculated theoretical values, and the signals between adjacent peaks of each group were also separated by VL repeating units. Other small peaks in the mass spectrum may be ascribed to some impurities from the matrix and the polymerization process.

In summary, the results of above structural analysis indicated that the mechanism of ring-opening polymerization of δ-VL catalyzed by zinc complex 1/MeLi system was the same as that of ε-CL. The addition of MeLi to the solution of zinc complex led to the in situ formation of zinc methyl species (LZn―CH₂). The coordination of monomer to the metal center (Zn), the insertion of monomer happened into Zn―L bond in the absence of BnOH and initiated the ROP. The sequential repeated coordination and insertion of monomers successively occurred and the final intramolecular transesterification led to the formation of cyclic polymers. The addition of BnOH resulted in the transformation of active species from Lriends from LZnO. In this case, the monomer inserted into Zn―OBn bond and the linear polymers were eventually produced after the termination.

**Ring-opening Copolymerization of ε-CL and δ-VL**

Because of the good performance in the ROP of ε-CL and δ-VL, zinc complex 1/MeLi system was further used in the copolymerization of ε-CL and δ-VL to prepare random and block copolymers by adopting different feeding modes. The random copolymers (P(CL-co-VL)) were obtained by premixing the two monomers (Table 2) and the block copolymers (PCL-b-PVL and PVL-b-PCL) were obtained by a sequential feeding mode (Table 3). The copolymer composition was adjusted by varying the feeding ratio of the two monomers.

Owing to the high activity, the total yields of 100% were achieved in most cases and the contents of VL/CL in the copolymers were close to the corresponding values in the feeding. The sequence lengths (Lc and Lₐ) and randomness (R) of random copolymers were calculated by ¹³C-NMR and are shown in Table 2. The CC, CV, VV, and VC sequences could be clearly observed around 64 ppm and the R values were close to 1, indicating that the copolymers obtained by premixing the two monomers were random. The average sequence length (Lₐ) of PCL chains increased with the increasing proportion of CL in feeding.

The NMR spectra of random copolymers (entry 6 in Table 2) are shown in Figs. 5 and 6. In the ¹H-NMR spectra, the multiple signals at 1.37 ppm were assigned to the methyl group (CH₃), c) in the CL units and the other three multiple signals around 1.65, 2.33, and 4.05 ppm corresponded to the combination of methylene groups attached to the C atoms (b), the carbonyl (a), and the O atom (d) in both CL and VL units, respectively. Therefore, the composition of two monomers in copolymers could be calculated through ¹H-NMR analysis.

**Table 2** Data of random copolymers P(CL-co-VL).a

| Entry | [CL]/[VL]/[BnOH] | VL in feed (%) | VL in copolymers b (%) | Yield c (%) | Mₙ,obs d (kg/mol) | D e | Lc f | Lₐ f | R e |
|-------|------------------|----------------|------------------------|-------------|------------------|-----|------|------|-----|
| 1     | 50/250/0         | 83.3           | 81.0                   | 100         | 29.0             | 1.62| 1.23 | 6.19 | 0.98|
| 2     | 100/200/0        | 66.7           | 67.1                   | 87          | 13.1             | 1.13| 1.49 | 3.60 | 0.95|
| 3     | 150/150/0        | 50.0           | 53.7                   | 100         | 22.1             | 1.38| 2.13 | 2.49 | 0.87|
| 4     | 200/100/0        | 33.3           | 27.5                   | 100         | 19.9             | 1.30| 3.09 | 1.61 | 0.95|
| 5     | 250/50/0         | 16.7           | 15.3                   | 100         | 32.7             | 1.61| 5.96 | 1.29 | 0.94|
| 6     | 100/200/1        | 66.7           | 62.8                   | 100         | 26.9             | 1.35| 1.73 | 2.94 | 0.92|

a Polymerization conditions: zinc complex: 0.02 mmol, [Zn] = 0.01 mol/L, [MeLi]/[Zn] = 4/1, solvent: toluene; reaction temperature: 30 °C, ε-CL and δ-VL were premixed; reaction time: 20 min, [BnOH]/[Zn] = 1/1; b Determined by ¹H-NMR spectroscopy; c Determined by the weight of isolated polymer; d Determined by the GPC in THF; e Calculated by ¹³C-NMR spectroscopy.

**Table 3** Data of block copolymers.

| Entry | Sample | [VL]/[CL]/[BnOH] | VL in feed (%) | VL in copolymers a (%) | Yield a (%) | Mₙ,obs b (kg/mol) | D e |
|-------|--------|------------------|----------------|------------------------|-------------|------------------|-----|
| 1 a   | PVL-b-PCL | 100/200/0        | 33.3           | 32.9                   | 100         | 25.7             | 2.33|
| 2 a   |        | 150/150/0        | 50.0           | 48.2                   | 100         | 22.5             | 1.52|
| 3 a   |        | 200/100/0        | 66.7           | 65.9                   | 100         | 36.4             | 1.58|
| 4 a   |        | 100/200/1        | 33.3           | 36.3                   | 100         | 21.8             | 1.29|
| 5 a   |        | 150/150/1        | 50.0           | 47.4                   | 100         | 19.2             | 1.32|
| 6 a   |        | 200/100/1        | 66.7           | 66.7                   | 100         | 20.1             | 1.35|
| 6 b   | PCL-b-PVL | 100/200/0        | 33.3           | 36.3                   | 100         | 29.9             | 1.62|
| 9 b   |        | 200/100/0        | 66.7           | 61.1                   | 100         | 25.5             | 1.36|
| 10 b  |        | 100/200/1        | 33.3           | 32.0                   | 100         | 18.2             | 1.48|
| 11 b  |        | 150/150/1        | 50.0           | 45.7                   | 100         | 15.9             | 1.41|
| 12 b  |        | 200/100/1        | 66.7           | 57.4                   | 100         | 16.2             | 1.40|

Polymerization conditions: zinc complex: 0.02 mmol, [Zn] = 0.01 mol/L, [MeLi]/[Zn] = 4/1, solvent: toluene; reaction temperature: 30 °C, [BnOH]/[Zn] = 1/1; a δ-VL was added for ROP first, and after 10 min, ε-CL was added and reacted for another 10 min; b ε-CL was added for ROP first, and after 10 min, δ-VL was added and reacted for another 10 min; c Determined by ¹H-NMR spectroscopy; d Determined by the weight of isolated polymer; e Determined by GPC in THF.

https://doi.org/10.1007/s10118-020-2347-4
The structure of binary sequence in the copolymers can be revealed by the resonance signals of carbonyl groups in the $^{13}$C-NMR spectra. The signals at 64.18 and 64.10 ppm were assigned to the methylene carbon ($-\text{CH}_2$O$-$) of CL units in the CL-VL and CL-CL sequences, respectively, while the signals at 63.87 and 63.79 ppm were assigned to the carbon atoms ($-\text{CH}_2$O$-$) of VL units in the VL-VL and VL-CL sequences, respectively. These signals were clearly observed in the $^{13}$C-NMR spectra of random copolymers (Fig. 6) and the other signals were attributed to the other methylene groups in the CL and VL units.

The $^{13}$C-NMR spectra of random copolymers and block copolymers with different compositions around 64 ppm are expanded in Figs. 7 and 8. The four binary sequence distributions corresponding to the CL-VL, CL-CL, VL-CL, and VL-VL sequences clearly appeared in the spectra of random copolymers. The almost same integral area of the four binary sequences of random copolymers from the 1/1 feeding ratio (CL/VL = 150/150) indicated that these sequences were uniformly distributed in the copolymers. The intensities of binary sequences of CL-CL and VL-VL homodyads in the $^{13}$C-NMR spectra of copolymers varied with the feeding ratio of two monomers. When the proportion of CL in the feeding and copolymers increased, the signal intensity of CL-CL sequences increased gradually; accordingly, the signal intensities of VL-VL sequences decreased gradually (Fig. 7). However, whether the feeding ratios of CL and VL were increased or decreased, the signal intensities of CL-VL and VL-CL sequences maintained almost uniform, indicating that these two sequences always occupied a certain proportion in the copolymers and the constitutional units were randomly distributed.

In the $^{13}$C-NMR spectra of block copolymers, the signals of two homodyads (CL-CL and VL-VL) were mainly observed and the signals of CL-VL and VL-CL heterodyads were very tiny (Fig. 8), indicating the absence of monomer alternation and thus the formation of diblock copolymers [39] in addition, the monomer feeding order and the presence or absence of benzyl alcohol almost had no effect on the sequence distribution. The intensities of the two signals around 64 ppm were consistent with the feeding ratio of two monomers, confirming the close relationship between the feeding ratio and the composition in the copolymers.

### Thermal Properties of Polymers

The thermal behaviors of random and block copolymers were investigated by DSC, and the results are shown in Figs. 9–12 and Tables 4 and 5. The melting points ($T_m$) of PVL and PCL homopolymers were around 55 °C and slightly varied with the different molecular weights whether they had a benzyl group as the chain end or not. Due to the different sequence distributions, the random and block copolymers with the same compositions had differ-

---

https://doi.org/10.1007/s10118-020-2347-4
ent melting points. Generally, when the structural units of copolymers changed from order to disorder, their melting points decreased. The random copolymers obtained by premixing the two monomers had a lower melting point than both homopolymers did. When the contents of CL and VL units in the copolymers were relatively close, there would be a stronger competition between them, leading to a more irregular distribution in the polymer chains and thus a lower melting point. As a result, the random copolymers obtained from the 150/150 feeding ratio of CL/VL had the lowest melting points (24.3 and 19.9 °C in the absence and presence of BnOH, respectively), observed as viscous solids at room temperature.

![Fig. 9](image1) DSC curves of homopolymers and random copolymers with different compositions in the absence of BnOH: cooling scans (left) and heating scans (right).

![Fig. 10](image2) DSC curves of homopolymers and random copolymers with different compositions in the presence of BnOH: cooling scans (left) and heating scans (right).

![Fig. 11](image3) DSC curves of PVL-b-PCL block copolymers with different compositions: cooling scans (left) and heating scans (right).

![Fig. 12](image4) DSC curves of PCL-b-PVL block copolymers with different compositions: cooling scans (left) and heating scans (right).

### Table 4 Thermal parameters of homopolymers and random copolymers.

| CL/VL/BnOH | ΔH_c (J/g) | ΔH_m (J/g) | T_c (°C) | T_m (°C) |
|------------|------------|------------|----------|----------|
| 0/50/0     | 72.9       | 73.8       | 32.0     | 55.1     |
| 50/250/0   | 53.8       | 54.4       | 12.1     | 40.9     |
| 100/200/0  | 54.8       | 56.3       | 6.12     | 31.4     |
| 150/150/0  | 57.4       | 57.0       | −3.67    | 24.3     |
| 200/100/0  | 62.8       | 63.8       | 3.47     | 29.1     |
| 250/300/0  | 54.7       | 52.1       | 13.8     | 41.5     |
| 300/0/0    | 72.7       | 75.4       | 31.4     | 55.2     |
| 0/50/0.5   | 77.7       | 80.8       | 32.0     | 53.2     |
| 0/500/1    | 75.5       | 74.6       | 33.0     | 57.4     |
| 0/800/1    | 72.6       | 76.2       | 33.0     | 57.8     |
| 100/200/1  | 49.7       | 51.3       | 0.04     | 27.5     |
| 150/150/1  | 61.8       | 57.9       | −7.88    | 19.9     |
| 500/0/1    | 63.4       | 72.1       | 30.1     | 55.6     |

### Table 5 Thermal parameters of block copolymers.

| Sample     | CL/VL/BnOH | ΔH_c (J/g) | ΔH_m (J/g) | T_c (°C) | T_m (°C) |
|------------|------------|------------|------------|----------|----------|
| PVL-b-PCL  | 100/200/0  | 61.9       | 62.5       | 24.7     | 55.0     |
|            | 150/150/0  | 62.9       | 64.2       | 21.8     | 49.2     |
|            | 200/100/0  | 65.2       | 65.9       | 23.8     | 55.9     |
|            | 100/200/1  | 69.5       | 74.3       | 28.6     | 55.2     |
|            | 150/150/1  | 62.1       | 67.7       | 20.2     | 48.7     |
|            | 200/100/1  | 65.4       | 66.1       | 21.8     | 51.9     |
| PCL-b-PVL  | 100/200/0  | 67.6       | 69.5       | 25.4     | 54.6     |
|            | 150/150/0  | 60.9       | 62.0       | 22.2     | 55.1     |
|            | 200/100/0  | 63.4       | 65.2       | 24.3     | 55.8     |
|            | 100/200/1  | 71.6       | 74.0       | 29.4     | 55.0     |
|            | 150/150/1  | 68.8       | 70.4       | 26.5     | 52.2, 54.8 |
|            | 200/100/1  | 60.8       | 66.8       | 27.3     | 52.5, 55.5 |

https://doi.org/10.1007/s10118-020-2347-4
formed and the sequence structures tended to be more regular, which would result in the gradual shift of melting points toward higher temperatures. For example, the random copolymers obtained from 50/250 or 250/50 feeding ratio of VL/CL exhibited higher melting points at ca. 41 °C.

Compared with the random copolymers, the sequence distribution of two monomers in the block copolymers was much more ordered. Therefore, the block copolymers had higher melting and crystallization temperatures than the random copolymers with similar copolymer composition did. DSC analysis revealed that the feeding sequence of the monomers had an influence on the thermal properties of block copolymers. When δ-VL was first added, the lowest melting points were obtained for the PVL-b-PCL block copolymers with the 1/1 feeding ratio of VL/CL both in the absence (49.2 °C) and presence (48.7 °C) of BnOH. However, the melting points of PCL-b-PVL block copolymers were similar and close to those of the homopolymers. The DSC curves of PCL-b-PVL block copolymers from the 150/150/1 and 200/100/1 feeding ratios of CL/ VL/BnOH showed two melting peaks at 52–55 °C. Besides, the crystallization temperatures of block copolymers were slightly affected by the copolymer composition.

CONCLUSIONS

In summary, in combination with methyllithium, 2,6-bis(aminophenol) zinc complex 1 showed excellent catalytic properties for the ring-opening polymerization of δ-valerolactone, producing cyclic and linear PVLS in the absence and presence of BnOH, respectively. On the basis of homopolymerization, the random and block copolymers of ε-CL and δ-VL with different copolymer compositions were synthesized by varying the feeding modes and adjusting the feeding ratio of the two monomers. The composition of copolymers determined by NMR characterization and calculations was close to the feeding ratio of two monomers. The crystallization behavior and mechanism studies.

ACKNOWLEDGMENTS

This work was financially supported by the National Key R&D Program of China (No. 2016YFC1100801) and the State Key Laboratory of Chemical Engineering (No. SKL-CH-E-18D01).

REFERENCES

1. Sangeetha, V. H.; Deka, H.; Varghese, T. O.; Nayak, S. K. State of the art and future perspectives of poly(lactic acid) based blends and composites. Polym. Compos. 2018, 39, 81–101.
2. Pany, H. R.; Kim, H. J.; Bhatt, L. R.; Joshi, M. K.; Kim, E. K.; Kim, J. I.; Abdal-hay, A.; Hui, K. S.; Kim, C. S. Chitin butyrate coated electrospun nylon-6 fibers for biomedical applications. Appl. Surf. Sci. 2013, 285, 538–544.
3. Cameron, D. J. A.; Shaver, M. P. Aliphatic polyester polymer stars: Synthesis, properties and applications in biomedicine and nanotechnology. Chem. Soc. Rev. 2011, 40, 1761–1776.
4. Shin, E. J.; Brown, H. A.; Gonzalez, S.; Jeong, W.; Hedrick, J. L.; Waymouth, R. M. Zwitterionic copolymerization: synthesis of cyclic gradient copolymers. Angew. Chem. Int. Ed. 2011, 50, 6388–6391.
5. Stirling, E.; Champouret, Y.; Visseaux, M. Catalytic metal-based systems for controlled statistical copolymerisation of lactide with a lactone. Polym. Chem. 2018, 9, 2517–2531.
6. Rad’Kova, N.; Rad’Kov, V.; Cherkasov, A.; Kovyfina, T.; Trifonov, A. Lanthanide bis(borohydride) complexes coordinated by tetradentate phenoxido ligand: synthesis, structure, and catalytic activity in ring-opening polymerization of rac-lactide and ε-caprolactone. Inorg. Chem. Acta 2019, 489, 132–139.
7. Cho, J.; Chun, M. K.; Nayab, S.; Jeong, J. H. Synthesis and structures of copper(II) complexes containing N,N-bidentate N-substituted phenylethanamine derivatives as pre-catalysts for heterotactic-enriched polylactide. Polyhedron 2019, 163, 54–62.
8. Caballero-Jiménez, D.; García-de-Jesús, O.; Lopez, N.; Reyes-Ortega, Y. Muñoz-Hernández, M. Tetranuclear complexes of group 12 and 13 supported on a polynucleating ligand and activity studies in the ROP of rac-lactide. Inorg. Chim. Acta 2019, 489, 120–125.
9. Dou, J.; Zhu, D.; Zhang, W.; Wang, R.; Wang, S.; Zhang, Q.; Zhang, X.; Sun, W. H. Highly efficient iron(II) catalysts toward ring opening polymerization of ε-caprolactone through in situ initiation. Inorg. Chim. Acta 2019, 488, 299–303.
10. Munzeiwa, W. A.; Nyamori, V. O.; Omendi, B. N,O-aminophenolate M(II) and Zn(II) Schiff base complexes: synthesis and application in ring-opening polymerization of ε-caprolactone and lactides. Inorg. Chim. Acta 2019, 487, 264–274.
11. Chen, X.; Wang, B.; Pan, L.; Li, Y. Homoleptic, bis-ligated magnesium complexes for ring-opening polymerization of lactide and lactones: synthesis, structure, polymerization behavior and mechanism studies. Appl. Organomet. Chem. 2019, 33, e4770.
12. Steiniger, P.; Schäfer, P. M.; Wölper, C.; Henkel, J.; Kiszakiewicz, A. N.; Pich, A.; Herres-Pawlis, S.; Schulz, S. Synthesis, structure, and catalytic activity of homo- and heteroleptic ketoamine zinc complexes in lactide polymerization. Eur. J. Inorg. Chem. 2018, 2018, 4014–4021.
13. Gonzalez, D. M.; Cisterna, J.; Brito, I.; Roisnel, T.; Harmon, J.; Manzur, C. Binuclear Schiff-base zinc(II) complexes: synthesis, crystal structures and reactivity toward ring opening polymerization of rac-lactide. Polyhedron 2019, 162, 91–99.
14. Yang, Z.; Hu, C.; Duan, R.; Sun, Z.; Zhang, H.; Pang, X.; Li, L. Salen-manganese complexes and their application in the ring-opening polymerization of lactide and ε-caprolactone. Asian J. Org. Chem. 2019, 8, 376–384.
15. Li, M.; Behzadi, S.; Chen, M.; Pang, W.; Wang, F.; Tan, C. Phenoxyimine ligands bearing nitrogen-containing second coordination spheres for zinc catalyzed stereoselective ring-opening polymerization of rac-lactide. Organometallics 2019, 38, 461–468.
16. Saeed, W.; Al-Doayni, A.; Alghamdi, A.; Alrahlah, A.; Aouak, T.; Chen, M. Thermal properties and non-isothermal crystallization kinetics of poly(ε-caprolactone) and poly(δ-valerolactone)/titanium dioxide nanocomposites. Crystals 2018, 8, 452.
17. D’auria, I.; Mazzeo, M.; Pappalardo, D.; Lamberti, M.; Pellecchia, C. Ring-opening polymerization of cycloolsters promoted by phosphido-diphosphine pincer group 3 complexes. J. Polym. Sci., Part A: Polym. Chem. 2011, 49, 403–413.
18. Khalil, M. I.; Al-Shamary, D. O. H.; Al-Deyab, S. S. Synthesis of poly(δ-valerolactone) by activated monomer polymerization, its characterization and potential medical application. Asian J. Biochem. Pharm. Res. 2015, 5, 137–147.
19. Woodruff, M. A.; Hutmacher, D. W. The return of a forgotten polymer—polycaprolactone in the 21st century. Prog. Polym. Sci. 2010, 35, 1217–1256.
20 Duale, K.; Ziga, M.; Chaber, P.; Di Fouque, D.; Membeouf, A.; Peptu, C.; Radecka, I.; Kowalczuk, M.; Adamus, G. Molecular level structure of biodegradable poly(δ-valerolactone) obtained in the presence of boric acid. *Molecules* **2018**, *23*, 2034.

21 Saeed, W. S.; Al-Odayni, A.; Ali Alghamdi, A.; Abdulaziz Al-Owais, A.; Semlali, A.; Aouak, T. Miscibility of poly(ethylene-co-vinylalcohol)/poly(δ-valerolactone) blend and tissue engineering scaffold fabrication using naphthalene as porogen. *Polym. Plast. Technol. Eng.* **2018**, *58*, 1–23.

22 Lee, H.; Zeng, F.; Dunne, M.; Allen, C. Methoxy poly(ethylene glycol)-block-poly(δ-valerolactone) copolymer micelles for formulation of hydrophobic drugs. *Biomacromolecules* **2005**, *6*, 3119–3128.

23 Nair, K. L.; Jagadeeshan, S.; Nair, S. A.; Kumar, G. S. V. Evaluation of triblock copolymeric micelles of δ-valerolactone and poly(ethylene glycol) as a competent vector for doxorubicin delivery against cancer. *J. Nanobiotechnol.* **2011**, *9*, 42.

24 Alonso, D. M.; Wettstein, S. G.; Dumesic, J. A. Gamma-valerolactonate: isodimorphism, mechanical properties and synthesis, structure and degradation behavior. *Macromolecules* **2015**, *48*, 173–182.

25 Zhang, L.; Dong, H.; Li, M.; Wang, L.; Liu, Y.; Wang, L.; Fu, S. Fabrication of polymeric acid-modified carbon black composites into improvement of levelness and mechanical properties of spun-dyeing polyacrylic acid composites membrane. *ACS Sustain. Chem. Eng.* **2016**, *7*, 688–696.

26 Xiao, Y.; Pan, J.; Wang, D.; Heise, A.; Lang, M. Chemo-enzymatic synthesis of poly(4-piperidine lactone-b-ω-pentadecalactone) block copolymers as biomaterials with antibacterial properties. *Biomacromolecules* **2018**, *19*, 2673–2681.

27 Wilson, J. A.; Hopkins, S. A.; Wright, P. M.; Dove, A. P. Synthesis of ω-pentadecalactone copolymers with independently tunable thermal and degradation behavior. *Macromolecules* **2015**, *48*, 3649–3655.

Hunley, M. T.; Beers, K. L. Nonlinear method for determining reactivity ratios of ring-opening copolymerizations. *Macromolecules* **2013**, *46*, 1393–1399.

30 Hong, M.; Tang, X.; Newell, B. S.; Chen, E. Y. X. "Nonstrained" γ-butyrolactone-based copolyesters: copolymerization characteristics and composition-dependent (thermal, eutectic, cocrystallization, and degradation) properties. *Macromolecules* **2017**, *50*, 8469–8479.

31 Fernández, J.; Etxeberria, A.; Sarasua, J. *In vitro* degradation studies and mechanical behavior of poly(ε-caprolactone-co-δ-valerolactone) and poly(ε-caprolactone-co-L-lactide) with random and semi-alternating chain microstructures. *Eur. Polym. J.* **2015**, *71*, 585–595.

32 Hunley, M. T.; Beers, K. L. Highly active tridentate amino-phenol zinc complexes for the catalytic ring-opening polymerization of ε-caprolactone and poly(ε-caprolactone-co-δ-valerolactone) as new degradable binder used for antifouling paint. *Eur. Polym. J.* **2007**, *43*, 4800–4813.

34 Chandra, R.; Rustgi, R. Biodegradable polymers. *Prog. Polym. Sci.* **1998**, *23*, 1273–1335.

35 Fay, F.; Renard, E.; Langlois, V.; Linossier, I.; Vallée-Rehel, K. Development of poly(ε-caprolactone-co-L-lactide) and poly(ε-caprolactone-co-δ-valerolactone) as new biodegradable polymers for tissue engineering and efficient approach to cyclic polyesters. *J. Polym. Sci.*, **2013**, *135*, 13306–13309.

39 Piedra-Arroni, E.; Ladavière, C.; Aouak, T. Poly(ethylene-glycol)-block-poly(ε-caprolactone) statistical copolymers. *J. Mech. Behav. Biomed. Mater.* **2012**, *9*, 100–112.