Preparation and polymerization mechanism of dihydroxy-capped PCL, poly(CL-b-PEG-b-CL) and poly(DTC-b-CL-b-DTC)

CHEN Wei, LING Jun & SHEN Zhiquan

Institute of Polymer Science, Zhejiang University, Hangzhou 310027, China
Correspondence should be addressed to Shen Zhiquan (email: zhiquan_shen@163.com)

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Abstract The ring opening polymerization of ε-caprolactone (CL) was initiated by glycol and yttrium tri(2,6-di-tert-butyl-4-methylphenolate)s (Y(OAr)₃), preparing dihydroxy-capped poly (ε-caprolactone) (PCL) with controllable molecular weight. ¹H NMR and SEC analyses indicate that two kinds of active species and corresponding PCL with different structures exist in the system. Increasing the ratio of glycol to Y(OAr)₃ benefits the formation of monofunctional active species. However, poly(ethylene glycol) (PEG)/Y(OAr)₃ system only contains sole bifunctional active species to synthesize copolymer of CL with PEG (poly(CL-b-PEG-b-CL)). Dihydroxy-capped PCL as macroinitiator can further initiate the polymerization of 2,2-dimethyltrimethylene carbonate (DTC). Thus, triblock copolymer of CL with DTC (poly(DTC-b-CL-b-DTC)) has been prepared.

Keywords: dihydroxy-capped PCL, DTC, macroinitiator.

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PCL possesses a wide range of medical applications, such as tissue engineering and controlled drug release, because of its good biodegradability and miscibility. In order to extend the use of PCL, researchers have been exploring its structural and chemical modifications through synthesizing new polymers with predetermined and controlled structure or functional groups. For example, the introduction of hydrophilic PEG segments into hydrophobic PCL backbone enhances hydrophilicity of parent PCL-based polymer[1-3]; the liquid cooligomers of CL with comonomer capped with photoactive groups, such as phenyl azide and coumarin, were rapidly converted to solid upon photoinitiation[4,5]; oligo PCL macromonomer with hydroxymethyl styrene as polymerizable end groups has been engaged into copolymerization with styrene[6]; the amine-terminated PCL has been used to synthesize triblock copolymer[7], etc.

In this work, dihydroxy-capped PCL with controlled molecular weight was prepared using glycol/Y(OAr)₃ initiating system, which was employed to initiate DTC polymerization as macroinitiator for preparing poly(DTC-b-CL-b-DTC) triblock copolymer. The structures of the polymers and the mechanism for polymerization are discussed in detail.

1 Experimental

CL (Acros) was distilled under reduced pressure after being dried with CaH₂, and then stored under argon atmosphere. DTC was synthesized according to the literature[8] and dried over P₂O₅ before use. Y(OAr)₃ was synthesized according to the known
method[9]. Ethylene glycol (EG), neopentyl glycol (NG), PEG and solvents were all purified with common methods.

All polymerizations were carried out with Schlenk techniques. The glycol and Y(OAr)₃ solutions (THF or toluene as solvent) were mixed in previously flamed and argon purged ampoules. The mixture was aged for 10 min at 40°C, then polymerization was started by the addition of monomer. The polymerization was terminated by HCl aqueous solution (ca. 6 mol/L) and the polymer was precipitated from hexane, dried under vacuum for 24 h and weighed for yield. The preparation procedure of triblock copolymer is similar. The conditions are 60°C, 5 h in THF, [DTC] = 0.4 mol/L, [PCL]/[Y(OAr)₃] = 2.0, and [DTC]/[Y(OAr)₃] = 50.

Size exclusion chromatography (SEC) was carried out to determine molecular weights and molecular weight distribution (MWD) on a Waters 208 apparatus equipped with columns of Styragel HT 3, HT 4, HT 5. THF was used as eluent at a flow rate of 1.5 mL/min at 25°C and the molecular weights were calibrated by polystyrene standards. ¹H NMR spectra were recorded in CDCl₃ with tetramethylsilane as inner standard on a Bruker Avance DMX 500 MHz spectrometer. Differential scanning calorimetric (DSC) curves were taken on a Universal V2.4F TA Instrument at a heating rate of 10°C/min. All samples were cooled to −100°C, maintained for 1 min, heated to 150°C for the first scan, cooled to −100°C again, maintained for 1 min, and then heated to 150°C for the second scan.

2 Results and discussion

CL has been successfully polymerized using Y(OAr)₃ and various glycols including EG and NG initiating systems, as shown in Table 1. The PCL was obtained in about 100% yield for 20 min polymerization. The amount of glycol added affects $M_n$ of the resultant PCL, which increases with the increasing molar ratio of CL to glycol. $M_n,SEC$ of PCL is about twice of $M_n,NMR$ in agreement with the reported data[10]. Meanwhile, $M_n,NMR$ coincides well with $M_n,cal$ calculated from the ratio of CL to glycol. Therefore $M_n$ of PCL can be controlled by adjusting the ratio of CL to glycol.

From end group analysis of PCL initiated by NG system by ¹H NMR (Fig. 1(a)), it is found that dihydroxy-capped PCL consists of two kinds of chain structure: one is NG-blocked PCL (I); the other is PCL with NG as end group (II). The signal H⁺ (3.63–3.66, triplet) is assigned to hydroxymethylene of end group ($-\text{CH}_2\text{OH}$) of PCL, and the signal Hf (3.88, singlet) to both the esterified hydroxymethylene of incorporated NG, which demonstrates that NG is blocked into the PCL backbone and chain structure I exists. Meanwhile, the appearance of two peaks with the same intensity at 3.30 stood for $-\text{C(CH}_3\text{)}_2\text{CH}_2\text{OH}$ and at 3.94 for $-\text{COOCH}_2\text{C(CH}_3\text{)}_2\text{CH}_2\text{OH}$ proves that PCL capped by hydroxymethylene at one end and glycol at the other extremity and the existence of chain structure of II. Similar chain structures (III and IV in Fig. 1(b)) for PCL initiated by EG system are also observed in ¹H NMR spectra.

The mechanism for glycol/Y(OAr)₃ initiated polymerization, which is more complex than alcohol/Y(OAr)₃[11] initiated polymerization, is presumed as shown in Scheme 1.

### Table 1: Polymerization of CL initiated by glycol and Y(OAr)₃

<table>
<thead>
<tr>
<th>Run</th>
<th>Glycol</th>
<th>[CL]</th>
<th>[glycol]</th>
<th>Conv. (%)</th>
<th>$M_{n,NMR}$ (10⁴)</th>
<th>$M_{n,cal}$ (10⁴)</th>
<th>$M_{n,SEC}$ (10⁴)</th>
<th>MWD</th>
</tr>
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<tr>
<td>1</td>
<td>EG</td>
<td>50.0</td>
<td>2.0</td>
<td>100</td>
<td>5.4</td>
<td>5.7</td>
<td>10.4</td>
<td>1.7</td>
</tr>
<tr>
<td>2</td>
<td>EG</td>
<td>25.6</td>
<td>3.9</td>
<td>99</td>
<td>2.2</td>
<td>2.9</td>
<td>4.6</td>
<td>1.8</td>
</tr>
<tr>
<td>3</td>
<td>EG</td>
<td>12.8</td>
<td>7.8</td>
<td>100</td>
<td>1.3</td>
<td>1.5</td>
<td>3.2</td>
<td>1.4</td>
</tr>
<tr>
<td>4</td>
<td>NG</td>
<td>33.3</td>
<td>3.0</td>
<td>90</td>
<td>3.4</td>
<td>3.4</td>
<td>6.4</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>NG</td>
<td>16.7</td>
<td>6.0</td>
<td>100</td>
<td>1.9</td>
<td>1.9</td>
<td>3.7</td>
<td>1.5</td>
</tr>
<tr>
<td>6</td>
<td>NG</td>
<td>12.8</td>
<td>7.8</td>
<td>100</td>
<td>1.4</td>
<td>1.5</td>
<td>3.1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

a) Conditions: 20 min, 40°C in THF, [CL] = 2.0 mol/L(run 1–3), [CL] = 1.2 mol/L(run 4–6); b) molar ratio; c) $M_{n,cal}$=[CL]×114×Conv.[glycol]; d) molecular weight distribution obtained from SEC.
In the first step, two kinds of active species are \textit{in-situ} formed, which directly lead to PCL with two kinds of chain structures. Y(OAr)$_3$ undergoes rapid and complete exchange reaction with a part of added glycol, leaving yttrium alkoxide as active species. For glycol there could be two kinds of active species: monofunctional active species and bifunctional active species, generated by partial and complete displacement of hydron by yttrium.

Increasing the ratio of glycol to Y(OAr)$_3$ is preferable to form monofunctional active species. As shown in Fig. 1(b), the proportion of chain structure IV from monofunctional active species increases from 0 to 0.5 with the increasing ratio of glycol to Y(OAr)$_3$. Accordingly, the SEC curves change from monomodal to bimodal (Fig. 2). These confirm the formation of two kinds of active species and the influence of glycol on $M_n$.

The second step is chain propagation and transfer, which begins with the addition of CL to the initiating system. PCL chain propagates by a coordination-insertion mechanism\cite{11}. Namely, the coordination of caprolactone carbonyl onto the polar yttrium alkoxide activates the selective acyl-oxygen cleavage of the CL ring followed by its insertion into the yttrium-oxygen bond. The signals of alkoxy attached to

![Diagram of chemical structures and NMR spectra](image-url)
Fig. 1. $^1$H NMR spectra of PCL initiated by glycol and Y(OAr)$_3$ system. (a) $^1$H NMR spectrum of PCL initiated by NG system, run 6 in Table 1. (b) Partial $^1$H NMR spectra for EG system initiated PCL obtained by various EG/Y(OAr)$_3$ ratios. (a'), (b'), (c'): run 1, 2, 3 in Table 1 respectively. The symbol $I_{IV/III}$ refers to the ratio of PCL IV to PCL III calculated from the integration intensities of signals a, b, c.

acyl are clearly observed in $^1$H NMR spectra: H$_f$ and H$_i$ (Fig. 1(a)), H$_i$ and H$_h$ (Fig. 1(b)). Then oxygen from ring opening CL coordinates with yttrium, which were deactivated to hydroxy group in the termination process. The methylene proton attached to hydroxy has been detected such as H$_a$ (Fig. 1(a)). On the contrary, if alkyl-oxygen bond cleavage of CL occurred, carboxyl end group and ether bond would appear. But, no signals for them were found.

During the chain propagation, excess glycol acts as effective chain transfer agent. The active hydrogen of glycol exchanges with the growing chain, which makes all kinds of initiator, growing chain and macromonomer in a propagation/dormancy equilibrium. Therefore, the equal activity and probability of grow-
Formation of active centers:

\[ \text{Y(OAr)}_3 + x \text{R(OH)}_2 \rightarrow \text{YOROY} \quad \text{V} + \text{YOROH} \quad \text{VI} \quad (x>1.5) \]

Chain propagation:

\[ \text{Y-O(CH}_2\text{)}_5\text{C} \quad \text{ORO} \quad \text{O} \quad \text{H} \quad \text{C}(\text{CH}_2\text{)}_5\text{O} \quad \text{Y} \quad \text{CL} \quad \text{Y-O(CH}_2\text{)}_5\text{C} \quad \text{ORO} \quad \text{O} \quad \text{H} \quad \text{C}(\text{CH}_2\text{)}_5\text{O} \quad \text{Y} \]

Chain transfer:

\[ \text{Y-O(CH}_2\text{)}_5\text{C} \quad \text{OROH} \quad \text{CL} \quad \text{Y-O(CH}_2\text{)}_5\text{C} \quad \text{OROH} \]

Chain transfer agents:

\[ \text{R(OH)}_2, \text{H-O(CH}_2\text{)}_5\text{C} \quad \text{OROH}, \text{H-O(CH}_2\text{)}_5\text{C} \quad \text{ORO} \quad \text{O} \quad \text{C}(\text{CH}_2\text{)}_5\text{O} \quad \text{H} \]

Scheme 1  Mechanism for the polymerization of CL initiated by glycol and Y(OAr).  

...ing chain produce the PCL with narrower distribution and controllable \( M_n \). ...tive species is substituted by hydrogen from HCl and dihydroxy-capped PCL is formed. This telechelic oligomer is versatile, affording function points for PCL functionality and modification.  

Besides EG and NG, PEG can also initiate the ring opening polymerization of CL in the presence of Y(OAr)\(_3\) and control the \( M_n \) of CL copolymer (Table 2). The copolymer of CL with PEG was obtained in high yield at 40\( ^\circ \)C for 10 min polymerization. Higher molecular weight copolymer was obtained by decreasing the amount of PEG added, i.e. increasing the ratio of CL to PEG. Additionally, SEC curves for PCL initiated by PEG system are monomodal (Fig. 3), indicating only one active species in the system, while SEC curves for PCL initiated by EG system are monomodal or bimodal.  

Fig. 4(a) shows \(^1\)H NMR spectrum of CL and PEG copolymer. The signal H\(^f\) (4.28\( ^\circ \) 4.31, triplet) is contributed by the direct link unit of [PEG] and [CL] ([OCH\(_2\)CH\(_2\)OCO\(\bigcap\) ). H\(^h\) (3.66\( ^\circ \) 3.77, multiplet) is assigned to the overlap of methylene proton of PEG and hydroxymethylene of PCL end group. Additionally no triplet signal for hydroxymethylene from PEG end group ([OCH\(_2\)CH\(_2\)OH, 3.59\( ^\circ \) 3.61) is observed. Only bifunctional active species is formed in PEG initiating system. Accordingly, copolymer of poly(CL\(-b\)-PEG\(-b\)-CL) is ABA block structure consistent with monomodal SEC curve.
Preparation & polymerization mechanism of dihydroxy-capped PCL, PEG & DTC

Fig. 2. SEC curves for EG system initiated PCL obtained by various EG/Y(OAr)₃ ratios. []: run 1, 2, 3 in Table 1, respectively.

Thermal behaviors of the sample are shown in Fig. 4(b). The copolymer gives a unimodal, sharp melting endotherm at 59°C in the first heating scan. In the second heating scan, double melting peaks (T_m = 54, 57°C) accounted for the presence of PCL crystals of different perfection or thickness, suggesting that the T_m of the copolymer is very similar to that of PCL.

Dihydroxy-capped PCL (run 3 in Table 1) was employed to initiate DTC polymerization in the presence of Y(OAr)₃ as macroinitiator. ¹H NMR spectrum of resultant copolymer displays peaks for characteristic protons in PDTC and PCL units (Fig. 5(a)). Thermal behaviors of triblock copolymer are shown in Fig. 5(b).

A crystal melting endotherm of PDTC (T_m=75°C) is observed in the first heating scan, while it disappears in the second heating scan. It is likely that the steric hindrance of PDTC chain makes difficult crystallization in the quench process. SEC curve of the copolymer is compared with that of macroinitiator (Fig. 6), which shows higher molecular weight and more symmetric modal curve than those of macroinitiator PCL.

In the light of all the above polymerization results, it is found that chain length of glycol is another important factor influencing the formation of active species. SEC curves display monomodal or bimodal MWD for PCL initiated by EG system but monomodal MWD for PCL-b-PEG-b-PCL. Most interestingly, dihydroxy-capped PCL with unsymmetrical MWD

Table 2 Polymerization of CL initiated by PEG and Y(OAr)₃

<table>
<thead>
<tr>
<th>Run</th>
<th>PEG</th>
<th>[CL] [PEG]</th>
<th>[PEG] [Y(OAr)]</th>
<th>Conv. (%)</th>
<th>Mₘ,SEC (10³)</th>
<th>MWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>PEG200</td>
<td>32.6</td>
<td>4.6</td>
<td>97</td>
<td>10.1</td>
<td>1.5</td>
</tr>
<tr>
<td>8</td>
<td>PEG200</td>
<td>46.9</td>
<td>3.2</td>
<td>100</td>
<td>10.6</td>
<td>1.5</td>
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<tr>
<td>9</td>
<td>PEG200</td>
<td>65.6</td>
<td>3.2</td>
<td>94</td>
<td>15.3</td>
<td>1.5</td>
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<tr>
<td>10</td>
<td>PEG200</td>
<td>93.8</td>
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<td>36.8</td>
<td>1.9</td>
</tr>
<tr>
<td>11</td>
<td>PEG400</td>
<td>46.9</td>
<td>3.2</td>
<td>95</td>
<td>11.7</td>
<td>1.6</td>
</tr>
<tr>
<td>12</td>
<td>PEG400</td>
<td>31.3</td>
<td>4.8</td>
<td>90</td>
<td>8.0</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Conditions: 10 min, 40°C in toluene, [CL] = 3.2 mol/L except run 9 [CL] = 4.0 mol/L, others are the same as in Table 1.
Fig. 4. Structure and thermal behavior of poly(CL-b-PEG-b-CL) triblock copolymer. (a) $^1$H NMR spectrum of poly(CL-b-PEG-b-CL), run 7 in Table 2. (b) DSC curves of poly(CL-b-PEG-b-CL), run 7 in Table 2.
Fig. 5. Structure and thermal behavior of poly(DTC-b-CL-b-DTC) triblock copolymer. (a) $^1$H NMR spectrum of poly(DTC-b-CL-b-DTC) triblock copolymer. (b) DSC curves of poly(DTC-b-CL-b-DTC) triblock copolymer.
initiated the DTC polymerization, producing the resultant copolymer with more symmetric and narrower MWD. Probably the short distance between two hydroxy in EG makes bifunctional active species unstable. However, the longer distance between two hydroxy alleviates the influence between two yttrium atoms of bifunctional active species, forming sole bifunctional active species during the polymerization and giving poly(CL-b-PEG-b-CL) and poly(DTC-b-CL-b-DTC) with narrower MWD.

3 Conclusion

This paper describes the CL polymerization initiated by glycol and Y(OAr)₃ in detail. The results indicate there are two kinds of active species in the polymerization and dihydroxy-capped PCL with controllable $M_n$ is prepared. As macronitiator, dihydroxy PCL can further initiate the polymerization of co-monomer for preparing triblock copolymer, which affords a novel experimental design approach to prepare dihydroxy-capped functional polymer and block copolymer.

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References