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# Facile Synthesis of Well-defined Linear-comb Highly Branched Poly( $\epsilon$ -caprolactone) using Hydroxylated Polybutadiene and Organocatalyst

Yingying Ren, Qing Gao, Cheng Zhou, Zhiyong Wei, Yu Zhang, and Yang Li\*

State Key Laboratory of Fine Chemicals, Department of Polymer Materials, School of Chemical Engineering,

Dalian University of Technology, Dalian 116024, China

**Abstract:** A series of linear-comb highly branched poly( $\epsilon$ -caprolactone) (LC-PCL) with well-defined structure, high molecular weight and narrow polydispersity was synthesized using hydroxylated polybutadiene as macroinitiator and 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD) as catalyst at room temperature. First, macroinitiator, functionalized hydroxylated polybutadiene was prepared by anionic polymerization of butadiene, epoxidation and ring-opening reaction. Then the hydroxyl groups in hydroxylated polybutadiene initiated the ring-opening polymerization of  $\epsilon$ -caprolactones in the presence of TBD. In an effort to optimize reaction system, the effects of different reaction factors on the ring-opening polymerization were investigated. The simplicity of the reaction conditions, the ready availability of the catalyst, and the exquisite control over the polymerization were also demonstrated. The arm number, side chain length, and molecular weight of branched LC-PCL were regulated by adjusting the number of hydroxyl groups on macroinitiator and monomer/hydroxyl group feed ratios. Physical properties (thermal property, crystal structure and spherulitic morphology) of the obtained polymers were analyzed by DSC, TGA, WAXD and POM. The results showed that the branched PCL crystallize in the ordinary crystal form similar to linear PCL, and the crystallization and melting behaviors are strongly dependent on the side PCL chain length.

**Keywords:** highly branched; linear-comb; poly( $\epsilon$ -caprolactone); hydroxylated polybutadiene

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\* Corresponding author.

*E-mail addresses:* liyang@dlut.edu.cn (Y. Li).

## Introduction

The study of highly branched polymers (such as hyperbranched, dendritic, star and comb) is one of the hottest areas of the polymer synthesis in recent years.[1,2,3,4,5,6] Highly branched polymers have attracted much attention because of their three-dimensional structure, special properties, potential applications and relatively simple synthesis to achieve high molecular weights in comparison with linear polymer.[2,7,8] The features of inner cavities and three-dimensional architecture endow highly branched polymers additional advantages for high value-added applications. For example, dendrigraft poly(L-lysine)s were reported as carriers for drug, gene, and antibody,[9-11] as well as dendrimers were used as magnetic resonance imaging contrast agents.[12] Besides, there are a large number of terminal function groups on the molecular surface and the desired properties of highly branched polymer can be achieved by modified the terminal groups.[7,8] Comb polymer is a special class of graft copolymer, in which side chains are anchored onto polymer backbone. As a result, those side chains are stretched away from the backbone to form a brush- or a worm-like cylindrical conformation, because of their crowding arrangement. Comb polymer can be prepared by three strategies, i.e. grafting-to, grafting-from, and grafting-through.[13] Furthermore, the amphiphilic comb polymer can be obtained by introducing hydrophilic side chains onto a hydrophobic backbone chain and it can self-assemble into nanoparticles. Our group recently successfully synthesized an amphiphilic polymer brush with PB and PEO side chains by combined “grafting-onto” and “grafting-from” strategies and studied the crystallization behavior.[14] Such amphiphilic comb polymers have potential biomedical applications in drug delivery and gene transfection field. For the sake of safety and biocompatibility, biodegradable polyesters are usually proposed as the biomedical materials. [15]

Poly( $\epsilon$ -caprolactone), an important aliphatic polyester, has been extensively used in biomedical areas, due to its excellent drug permeability, biocompatibility, and biodegradation.[16] Synthetic poly( $\epsilon$ -caprolactone) with controlled molecular weights, low polydispersity index, and high end group fidelity are deserved[17], and the ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone is an effective method to achieve these goals[18,19,20]. Generally, organic aluminum compounds,[21,22,23] tin octoate[24] or rare earth metal compounds[25] are widely used as a catalyst for the ROP of cyclic esters. Nevertheless, heavy metal contaminants from the catalyst residues in the polymer affect the performance of the final polymers as biomedical materials. Currently, great majority of the final polymers are linear homopolymers or copolymers with simple structure and low molecular weight.[23,26,27] In recent years, branched polyesters (e.g. comb-shaped, star-shaped etc.) were synthesized and studied using different methods[24,28,29,30] because they have ascendant rheological and mechanical properties than linear polymers of comparable molecular.[24] Yan and coworkers synthesized amphiphilic brush-dendritic-linear copolymers PPEGMEMA-*b*-D<sub>m</sub>-*b*-PCL by the combination techniques of click chemistry, ATRP and ROP.[13] Zhuo and coworkers synthesized dendrigraft poly( $\epsilon$ -caprolactone)s with high molecular weight and narrow polydispersity via a convenient generation-growth approach.[31] Whereas, both of these two polymerization systems contain metal Sn, which limits the final polymers for biomedical applications. On the other hand, branching architecture greatly influences the physical and chemical properties of the polymers. Such a

structure and property relationship will establish a bridge between syntheses and applications of highly branched polymers.[32] Anyhow, the control of branching architecture and metal-free are one of the most significant tasks in the study of highly branched polyesters.

In this work, we report a simple method to synthesize well-defined linear-comb highly branched poly( $\epsilon$ -caprolactone) (LC-PCL) with high molecular weight and low polydispersity index. First, the hydroxylated polybutadiene with designed molecular weight and narrow distribution was synthesized by anionic polymerization, epoxidation reaction, and hydroxylation reaction. Hydroxylated polybutadiene served as macroinitiator to initiate the ring-opening polymerization of  $\epsilon$ -caprolactone ( $\epsilon$ -CL) to obtain comb-shaped structural poly( $\epsilon$ -caprolactone). A metal-free organic compound of 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD) was selected as the catalyst of ROP of  $\epsilon$ -CL at room temperature. The arm number of PCL in the linear-comb branched polymers can be regulated by number of hydroxyl groups on the macroinitiator and the molecular weight of final polymers can be controlled by the ratio of monomer to hydroxyl groups. The microstructure, molecular weight and distribution of the obtained polymers were characterized by  $^1\text{H}$  NMR and GPC, and their physical properties were measured by DSC, TGA, WAXD and POM.

## Experimental Section

**Materials.** Butadiene (Yanshan Petrochem. Co., China, polymerization grade), *n*-BuLi (JK chemical, 2.5M solution in *n*-hexane), cyclohexane (Jinxi Chemical Plant, China, polymerization grade), 2-propanol were purified according to the technique our group described in previous publication.[33] Formic acid (HCOOH, 98 wt%), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30 wt%), trifluoromethanesulfonic acid (TfOH, 98%, Aladdin) and other reagents were available commercially and used as received unless otherwise noted.  $\epsilon$ -Caprolactone ( $\epsilon$ -CL, Aldrich, 99%) was dried over  $\text{CaH}_2$  and purified by vacuum distillation. 1,5,7-Triazabicyclo-[4.4.0]dec-5-ene (TBD, Aldrich, 98%) was used as received. Tetrahydrofuran (THF), toluene and other solvents were dried and purified in the conventional methods.

**Characterization.**  $^1\text{H}$  NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer at ambient temperature with  $\text{CDCl}_3$  as solvent. Gel Permeation Chromatography (GPC) was performed by Waters-2414 equipped with a Waters styragel HT4 and use PS as standards with molecular weights from  $1.2 \times 10^3$  to  $2.75 \times 10^6$  g/mol. THF was used as mobile phase at a rate of 1 mL/min and the column temperature of 30 °C. Thermal properties were measured with a differential scanning calorimeter (TA Q2000) on 5-10 mg samples as follows: the samples were heated from 25 to 100 °C at a heating rate of 10 °C/min under nitrogen atmosphere and kept for 2 min to eliminate the heat history; then they were cooled to -10 °C at a cooling rate of 10 °C/min; after keeping at -10 °C for 2 min, the samples were heated to 100 °C at a heating rate of 10 °C/min. Both the exothermic and endothermic curves were recorded. Thermogravimetric measurements were performed on a TA Q500 analyzer from ambient temperature to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Wide-angle X-ray diffraction (WAXD) patterns were characterized with X-ray diffractometer (XD-3A). The scanning angle ( $2\theta$ ) covered a range between 5 and 40° at a rate of 5°/min. The samples used for test were prepared at room temperature.

Spherulitic morphology was observed with a Leica-DM4500P polarizing optical microscope (POM) equipped with a hot stage (Link 600) and charge-coupled device (CCD) camera. Samples were first melted on a hot stage at 75 °C for 5 min, and then quickly cooled to 44 °C for observing the spherulitic morphology.

All the anionic syntheses and polymerization reactions were carried out under an inert atmosphere, and the glass assembly was dried with three cycles of a flaming/N<sub>2</sub>-puring/evacuating before polymerization initiated.

**Synthesis of hydroxylated polybutadiene.** Polybutadiene (PB) of defined molecular weight was synthesized by anionic polymerization of butadiene with *n*-BuLi in cyclohexane in a flask at 50 °C for 3h, quenched by the addition of excess 2-propanol, and dried under vacuum. Then the epoxidized polybutadiene (PB-O) with defined degree of epoxidation (E) was synthesized using H<sub>2</sub>O<sub>2</sub>/CHOOH and the hydroxylated polybutadiene (PB-OH) was prepared by acid-catalyzed hydrolysis according to literature procedures.[34] The crude product was purified by azeotropic drying and diluted with dry THF three times prior to use as initiator.

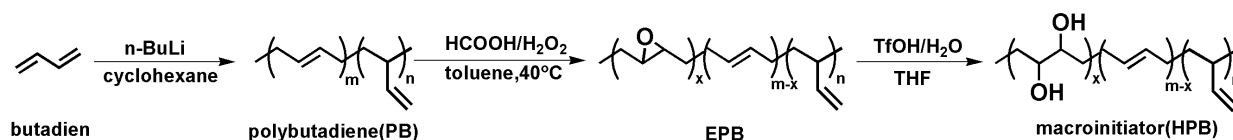
**Synthesis of Linear-comb highly branched poly( $\epsilon$ -caprolactone).**  $\epsilon$ -CL (7.70 g, 67.5 mmol) was added to a solution of TBD (47 mg, 0.34 mmol) and PB-OH (0.15 g, 1.35 mmol –OH) in toluene (35 ml). The solution was stirred for 10 h and quenched by addition of benzoic acid (0.33 g). The product was isolated by precipitation in cold methanol and then purified by dissolving in toluene and precipitating through slow addition of cold methanol. After filtration, the products were dried under vacuum for 24h and then were analyzed. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.41 (CH<sub>2</sub>CH<sup>\*</sup>=CH<sup>\*</sup>CH<sub>2</sub> PB backbone chain), 4.96 (CH<sub>2</sub><sup>\*</sup>=CH PB backbone chain), 4.06 (m, C(=O)OCH<sub>2</sub><sup>\*</sup> PCL side chain), 3.65 (t, 2H, CH<sub>2</sub><sup>\*</sup>OH), 2.31 (m, CH<sub>2</sub><sup>\*</sup>C(=O)O PCL side chain), 2.02 (t, CH<sub>2</sub><sup>\*</sup>CH<sub>2</sub><sup>\*</sup> PB main chain), 1.64 (t, CH<sub>2</sub><sup>\*</sup>CH<sub>2</sub>CH<sub>2</sub><sup>\*</sup> PCL side chain), 1.38 (t, CH<sub>2</sub>CH<sub>2</sub><sup>\*</sup>CH<sub>2</sub> PCL side chain).

## Results and Discussion

### Synthesis and characterization of macroinitiator

In order to synthesize well-defined linear-comb polylactones, it is imperative to control the structure of macroinitiator. The number of hydroxyl groups on the backbone chain (PB) determines arms of the final linear-comb polymers, and the proportion of monomer and hydroxyl group determines the molecular weight of single-arm. Therefore, highly branched linear-comb polylactones with designed number of arm and designed molecular weight of single-arm can be well-tailored. Accordingly, the first part of this research focused on the synthesis and characterization of macroinitiator. Because high molecular weight backbone precursor was not necessary in this work, linear PB was designed and synthesized with low molecular weight (<1.0 × 10<sup>4</sup> g/mol).

The synthesis route of hydroxylated polybutadiene is depicted in Scheme 1. Polybutadiene was polymerized by means of living anionic polymerization, which is one of the best methodologies for synthesis of polymers with predictable and well-defined structures. By controlling the amount of *n*-butyl lithium added, polybutadiene with designed molecular weight and narrow distribution was easily obtained. Subsequently, substrate with certain epoxidation degree was successfully obtained by controlling the amount of H<sub>2</sub>O<sub>2</sub> added.



Scheme 1. Synthesis of the macroinitiator hydroxylated polybutadiene.

Three macroinitiators with different epoxidations were prepared and used for the synthesis of linear-comb highly branched Poly( $\epsilon$ -caprolactone) with different branching levels. The microstructure, molecular weight and distribution of the obtained macroinitiators were characterized by  $^1\text{H}$  NMR and GPC. Figure 1 shows the  $^1\text{H}$  NMR spectra of polybutadiene, epoxidized, hydroxylated polybutadiene (HPB-1). The peaks (e and f) of the epoxy units at 2.9 and 2.7 ppm appear after epoxidation, which used to calculate the degree of epoxidation being 19.3 mol%. The disappearance of peaks at 2.9 and 2.7 ppm and the appearance of new peaks at 3.6 and 3.4 ppm suggest that the epoxy groups have been converted into hydroxyl groups completely.[34] The degrees of epoxidation of other two macroinitiators are 23.7 mol%, 27.4 mol% respectively. The GPC curves (Figure 2) show that all of the hydroxylated polybutadienes exhibit monomodal peaks and narrow distributions, and the data of molecular weight and distribution are summarized in Table 1.

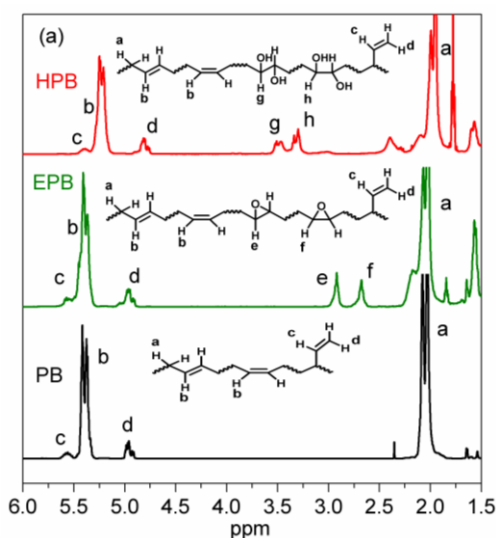


Figure 1.  $^1\text{H}$  NMR spectra of polybutadiene, epoxidized (E 19.3 mol%), hydroxylated polybutadiene (HPB-1).

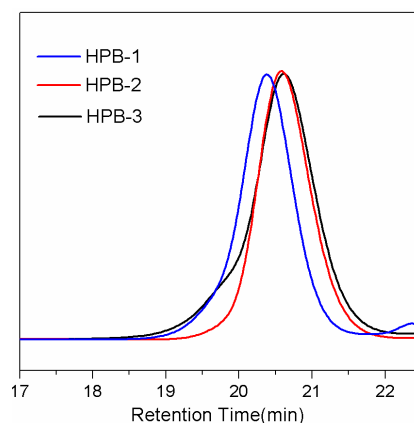


Figure 2. GPC curves of macroinitiators with different epoxidations.

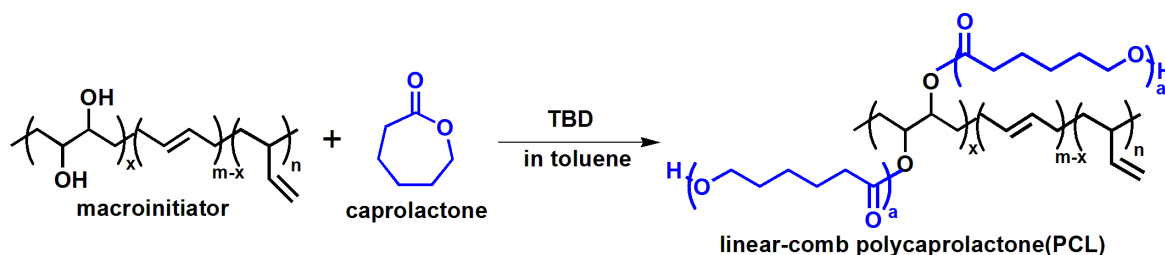
Table 1. Molecular Weight and Degree of Epoxidation of Macroinitiators

Sample	$M_n$ (Da) <sup>a</sup>	$M_w$ (Da) <sup>a</sup>	PDI <sup>a</sup>	E (mol%) <sup>b</sup>
HPB-1	6700	7400	1.11	19.3
HPB-2	6100	6600	1.08	23.7
HPB-3	6800	7600	1.12	27.4

<sup>a</sup>Measured by GPC in THF. <sup>b</sup> Degree of epoxidation

### Ring-opening polymerization of $\epsilon$ -CL

The ring-opening polymerization of  $\epsilon$ -CL was initiated by the side hydroxyl groups on HPB main chain and catalyzed by TBD at room temperature. The linear-comb poly( $\epsilon$ -caprolactone)s were synthesized by “graft from” strategy as shown in scheme 2 and the results are listed in Table 2. TBD is an effective organocatalyst for the ring-opening polymerization of  $\epsilon$ -caprolactone. Low loadings of TBD (0.5 mol% with respect to monomer) polymerized CL to near quantitative conversions, end group fidelity, and low polydispersities (<1.15) (Table 2). All samples of LC-PCLs (Table 2) were synthesized under the same reaction conditions except the macroinitiators. Apparently, the molecular weights of LC-PCLs increase with the epoxidation of macroinitiators increasing. The GPC curves (Figure 3) show the same tendency and all purified polymers exhibit a unimodal peak. The molecular weights of single arm of LC-PCLs are similar, so the difference in molecular weights of polymers originates from the different branching levels. It indicates that the branching level of the product can be regulated by adjusting the number of hydroxyl group on the macroinitiator.

Table 2. Results of ROP of  $\epsilon$ -CL Using different macroinitiators

sample	$M_n$ (KDa) <sup>a</sup>	$M_w$ (KDa) <sup>a</sup>	PDI <sup>a</sup>	$M_n^*$ (KDa) <sup>b</sup>	Yield(%) <sup>c</sup>
PCL-1 <sup>d</sup>	7.0	7.7	1.10	3400	59.4
PCL-2 <sup>e</sup>	11.3	12.1	1.07	4200	71.3
PCL-3 <sup>f</sup>	20.2	23.4	1.16	6200	72.0

Conditions:  $[M]/[OH](mol)=100$ ,  $[TBD]/[M](mol)=0.005$ ,  $C_M=1.0mol/L$ , 10h, toluene as solvent, 20 °C.

<sup>a</sup>Measured by GPC in THF. <sup>b</sup> $M_n^*$  means the molecular weight of single arm. Measured by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

<sup>c</sup>Calculated by the weight of monomer and product. <sup>d</sup>HPB-1 as the macroinitiator. <sup>e</sup>HPB-2 as the macroinitiator.

<sup>f</sup>HPB-3 as the macroinitiator.

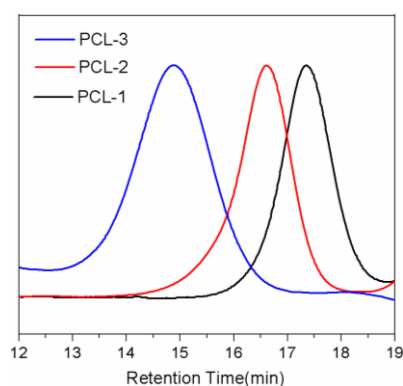


Figure 3. GPC curves of LC-PCLs samples in Table 2.

In this paper, we mainly investigated the polymerization of linear-comb highly-branched poly( $\epsilon$ -caprolactone) and the effect of different molecular weight of single arm on the polymer properties. Therefore, all polymers followed were synthesized by using the same macroinitiator (HPB-1 with 19.3 mol% epoxidation degree).

A series of linear-comb highly-branched poly( $\epsilon$ -caprolactone)s was synthesized by changing the proportion of monomer and hydroxyl group and the results are listed in Table 3. Obviously, both the molecular weight of single arm and polymers increase proportionally with the increase of the ratio of monomers to hydroxyl groups. The highest weight-average molecular weight in our experiments is  $27.6 \times 10^4$  g/mol. Significantly, the polydispersities (PDI) of all polymers with high molecular weight are narrow ( $<1.15$ ).



Table 3. Results of ROP of  $\epsilon$ -CL Using TBD

sample	[M]/[OH] (mol)	$M_n$ (KDa) <sup>a</sup>	$M_w$ (KDa) <sup>a</sup>	PDI <sup>a</sup>	$M_n^*$ (KDa) <sup>b</sup>	Yield(%) <sup>c</sup>
1-1	50	85	96	1.13	2.9	61.2
1-2	100	170	188	1.11	5.9	62.4
1-3	150	251	276	1.10	8.0	59.1

Conditions:[TBD]/[M](mol) = 0.005,  $C_M=1.0$  mol/L, 10h, toluene as solvent, 20 °C.

<sup>a</sup>Measured by GPC in THF.

<sup>b</sup> $M_n^*$  means the molecular weight of single arm. Measured by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

<sup>c</sup>Calculated by the weight of monomer and product.

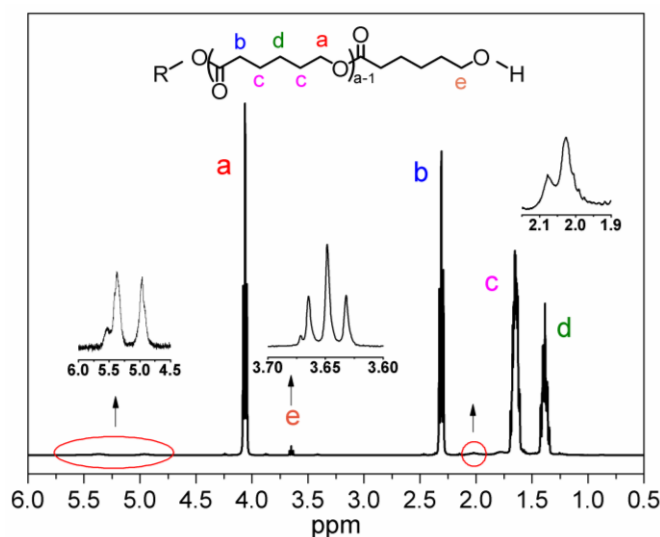


Figure 4. <sup>1</sup>H NMR spectrum of LC-PCL (sample 1-2 in Table 3).

Fig.4 shows the <sup>1</sup>H NMR spectrum of PCL using TBD. Each characteristic proton peak is observed and assigned to conform the structure of PCL describing in the literature.[35] The signals of methylene groups and methyne groups on the backbone chain are observed at 2.02 ppm and 4.96, 5.41 ppm, which implies that the PCL side chains have been grafted on the backbone chain (PB). The signals at 3.65 ppm stand for the methylene groups connecting with terminal hydroxyl groups. And the signals of the same protons on the other repeating units are at 4.06 ppm. The number of monomeric units of one arm can be calculated on the basis of the integral ratio of the above two signals. Furthermore, the molecular weight of one arm was obtained and summarized in Table 3.

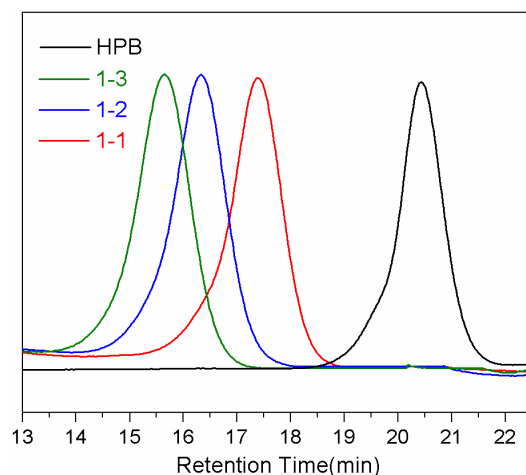


Figure 5. GPC curves of LC-PCLs samples in Table 3 and macroinitiator HPB-1.

The branched poly( $\epsilon$ -caprolactone)s were further characterized by GPC analysis. As shown in Figure 5, all purified polymers show a unimodal peak on their GPC charts and the peaks move forward obviously compared to macroinitiator. The molecular weight increases rapidly with the increase of the ratio of monomers to hydroxyl groups, while the polydispersity (PDI) remains narrow. To a certain extent, the polymerization steps were performed under good control.

### Effects of reaction conditions

Table 4. Effect of Catalyst loading on ROP of  $\epsilon$ -CL

sample	[TBD]/[M] (mol)	$M_n$ (KDa) <sup>a</sup>	$M_w$ (KDa) <sup>a</sup>	PDI <sup>a</sup>	$M_n^*$ (KDa) <sup>b</sup>	Yield (%) <sup>c</sup>
2-1	0.002	35	39	1.12	3.9	19.2
2-2	0.003	55	60	1.09	3.0	26.5
2-3	0.007	92	102	1.11	4.4	40.2
2-4	0.010	105	114	1.09	3.9	53.4
2-5	0.015	123	133	1.08	4.4	59.8
2-6	0.020	145	157	1.08	5.0	69.8

Conditions: [M]/[OH](mol)=150,  $C_M=1.0$ mol/L, 8h, toluene as solvent, 20 °C.

<sup>a</sup>Measured by GPC in THF.

<sup>b</sup> $M_n^*$  means the molecular weight of single arm. Measured by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

<sup>c</sup>Calculated by the weight of monomer and product.

We investigated the effect of different reaction factors on the ring-opening polymerization in an effort to optimize reaction system. First, we studied the influence of the content of catalyst on the ring-opening polymerization. It can be seen from Table 4 that the molecular weight of purified polymers and yield increase with increasing of catalyst loading. Different catalyst loadings result in different polymerization rates. It needs relatively long reaction time to polymerize completely under the condition of low catalyst loading, but long reaction time is

worthless for the ROP of  $\epsilon$ -CL. Also in the case of high catalyst loadings, transesterification is more noticeable than that of low catalyst loadings. Nevertheless, since this is a relatively slow process in comparison with the actual polymerization, this can easily be prevented by quenching the polymerization.[35] Thus, the purified polymers with high molecular weight, end group fidelity, and narrow polydispersities (minimal adverse transesterification during polymerization) can be obtained by controlling the loadings of catalyst.

Subsequently, we investigated the effect of reaction time on the ring-opening polymerization and the results were listed in Table 5. It shows that the molecular weight and yield both increase with a prolongation of reaction time. This indicates that ring-opening polymerization of  $\epsilon$ -CL needs a relatively long time which determined by the reactivity of monomer. Both GPC curves of the samples with different reaction time (Fig.6 (a)) are unimodal peaks. Fig. 6 (b) gives an obvious tendency that the molecular weight increases rapidly and then levels off with the extension of reaction time. It indicates that the molecular weight is likely to increase a little if continue to extend the reaction time. So 13h is enough for this polymerization reaction.

Table 5. Effect of Reaction Time on ROP of  $\epsilon$ -CL

Sample	time(h)	$M_n$ (KDa) <sup>a</sup>	$M_w$ (KDa) <sup>a</sup>	PDI <sup>a</sup>	$M_n^*$ (KDa) <sup>b</sup>	Yield(%) <sup>c</sup>
3-1	1	30	36	1.11	2.9	14.3
3-2	3	58	65	1.12	3.9	25.6
3-3	5	84	93	1.11	4.7	41.5
3-4	6	118	131	1.11	5.7	51.2
3-5	8	183	203	1.11	6.9	69.7
3-6	13	220	246	1.12	8.4	74.8

Conditions:  $[M]/[OH](mol)=200, [TBD]/[M](mol)=0.01, C_M=1.0mol/L, toluene$  as solvent, 20 °C..

<sup>a</sup>Measured by GPC in THF.

<sup>b</sup> $M_n^*$  means the molecular weight of single arm. Measured by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

<sup>c</sup>Calculated by the weight of monomer and product.

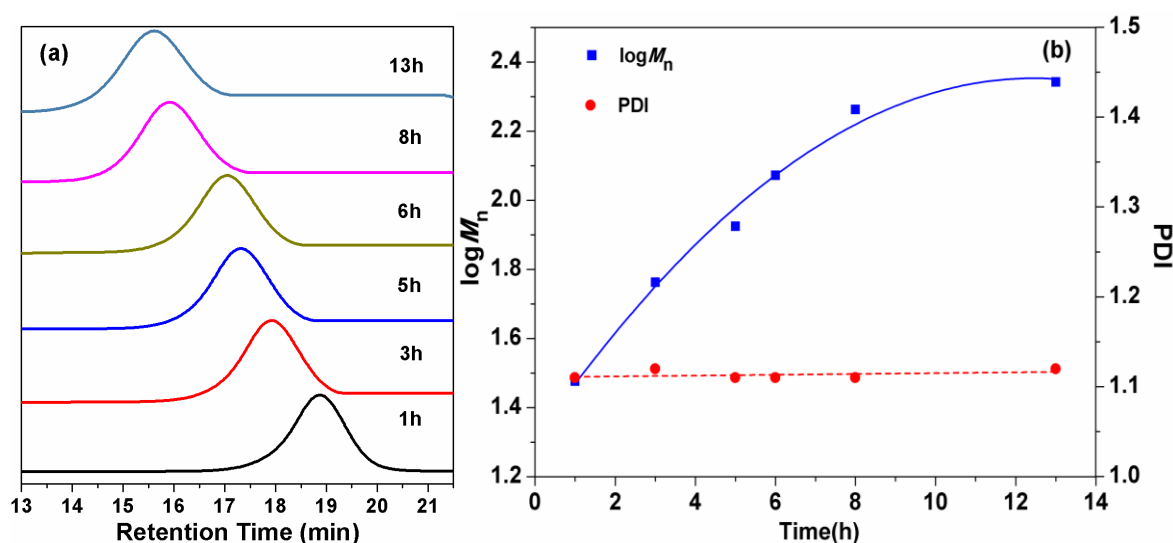


Figure 6. (a) GPC curves of LC-PCLs synthesized with different reaction times. (b) Relationships between reaction time and molecular weight/PDI of LC-PCLs.

Finally, the effect of monomer concentration on ROP of  $\epsilon$ -CL was studied. As can be seen, the molecular weight increases with increasing of monomer concentration (Table 6). In the case of low monomer concentration, the collision probability of components reduces greatly in the system resulting in low conversion at the same reaction time. We further conjecture that there will still be unreacted monomers in the system even after enough hours under the condition of low monomer concentration. The GPC curves and line chart ( $\log M_n$  to  $C_M$ ) (Fig. 7) imply similar tendency with Table 6. Because of the existence of transesterification, high monomer concentration is adverse to ROP of  $\epsilon$ -CL. So the monomer concentration between 1.0~2.0 mol/L is suitable.

Table 6. Effect of Monomer Concentration on ROP of  $\epsilon$ -CL

Sample	$C_M$ (mol/L)	$M_n$ (KDa) <sup>a</sup>	$M_w$ (KDa) <sup>a</sup>	PDI <sup>a</sup>	$M_n^*$ (KDa) <sup>b</sup>	Yield(%) <sup>c</sup>
4-1	0.5	69	77	1.11	3.7	22.4
4-2	1.0	122	134	1.10	6.3	56.1
4-3	1.5	151	166	1.10	7.1	71.1
4-4	2.0	190	213	1.12	8.6	83.4

Conditions:  $[M]/[OH](\text{mol})=100$ ,  $[TBD]/[M](\text{mol})=0.01$ , 13h, toluene as solvent, 20 °C.

<sup>a</sup>Measured by GPC in THF.

<sup>b</sup> $M_n^*$  means the molecular weight of single arm. Measured by  $^1\text{H NMR}$  in  $\text{CDCl}_3$ .

<sup>c</sup>Calculated by the weight of monomer and product.

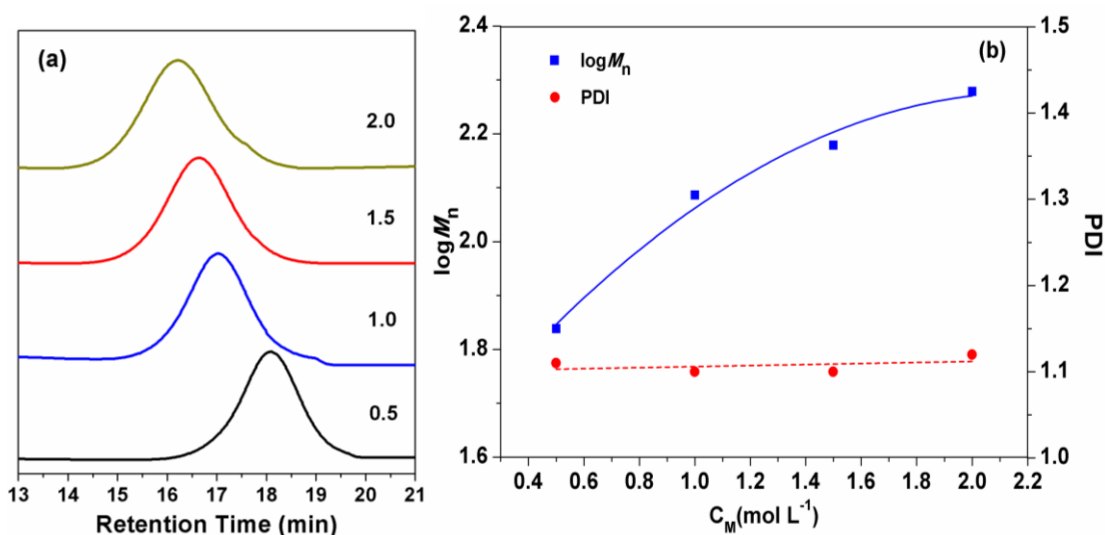
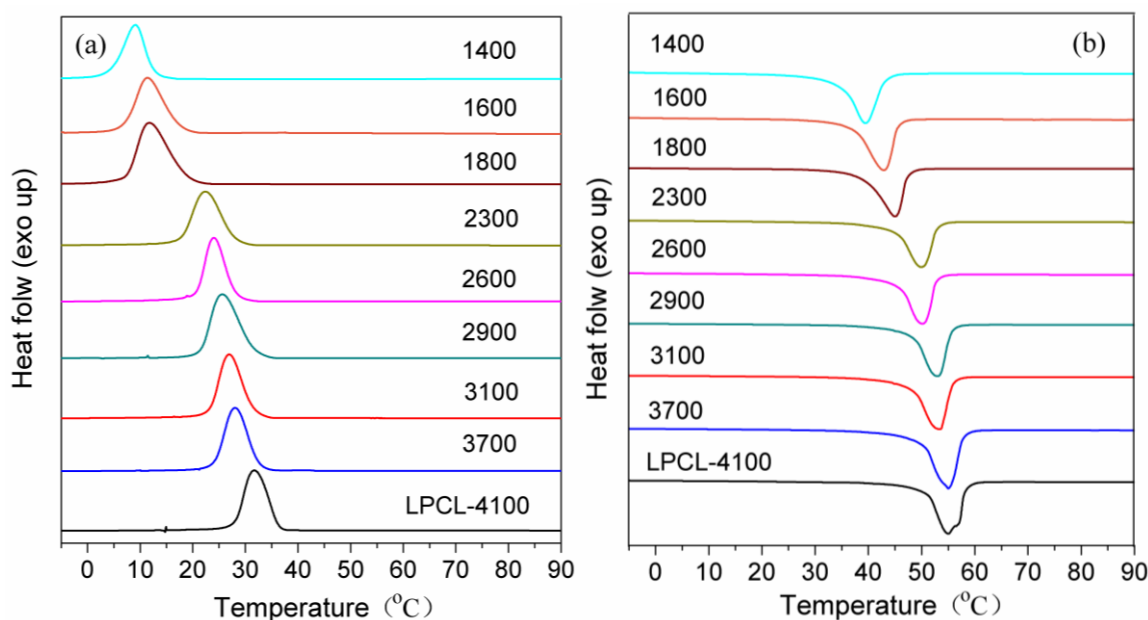


Figure 7. (a) GPC curves of LC-PCLs synthesized with different monomer concentrations. (b) Relationships between monomer concentration and molecular weight/PDI of LC-PCLs.

## Thermal properties

DSC traces were examined in order to study the thermal property of LC-PCLs with different side chain length. DSC traces (Fig. 8 a and b) clearly show  $T_c$ s and  $T_m$ s of LC-PCLs with different molecular weight of single arm

and linear polycaprolactone (L-PCL), which indicates that both the crystallization temperatures ( $T_c$ s) and melting temperatures ( $T_m$ s) increase with increasing of molecular weights of single arm. Fig. 8 (c) displays the same tendency that  $T_m$ s and  $T_c$ s both increase and then level off with increasing of molecular weight of single arm. This result is related to chain mobility. An increase of  $T_c$  implies a decreased difficulty in the crystallization process, since the crystallization proceeds during the cooling scan. This trend could be attributed to a decrease in nucleation density. The value of  $T_c$  is a function of the density of heterogeneities that can act like nuclei.[36] As will be seen below, evidences gathered from polarized optical microscopy indicate that LC-PCL with short side chain possesses a higher number of active heterogeneities per unit volume than that with long side chain. In Table 7 samples 1~8 stand for linear-comb poly( $\epsilon$ -caprolactone)s and sample 9 is linear poly( $\epsilon$ -caprolactone) homopolymer as a comparison. Table 7 gives an overview of crystallization and melting temperatures of some polymers prepared with similar molecular weights but varying molecular weights of single arm. It can be seen obviously that the melting temperature increases from 39.6 °C to 54.2 °C and the crystallization temperature increases from 9.1 °C to 29.1 °C with increasing of molecular weight of single arm. This means that the final crystallization and melting behaviors are not affected by the molecular weight of polymers, while they are strongly dependent on the molecular weight of single arm. Comparing samples 1~8 and 9, it is interesting that both  $T_c$ s and  $T_m$ s of branched PCLs are lower than those of linear PCL. It can be explained by that branching structure in LC-PCLs leads to the structural defects in the spherulites and results in lower crystallization and melting temperatures than those of linear PCL.[37]



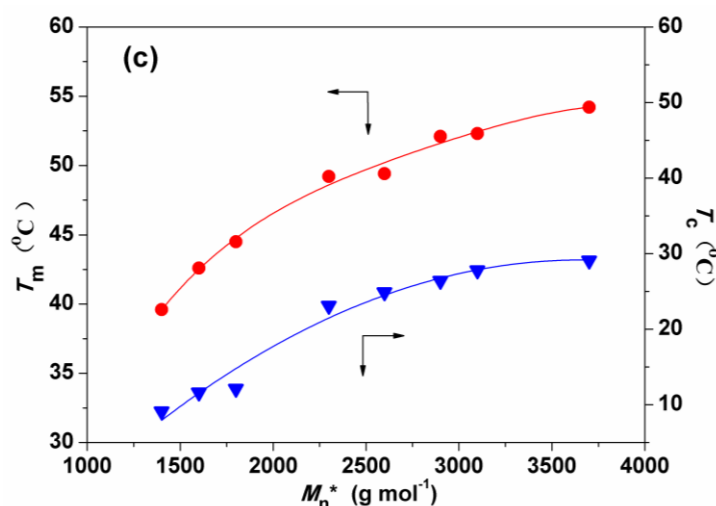


Figure 8. (a) Crystallization curves of PCLs with different side chain length. (b) Melting curves of PCLs with different side chain length. (c) The relationships between molecular weight of single arm and  $T_m/T_c$ .

Table 7. Thermal Parameters of PCLs with Different Side Chain Length

sample	$M_n$ (g mol <sup>-1</sup> ) <sup>a</sup>	$M_n^*$ (g mol <sup>-1</sup> ) <sup>b</sup>	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_c$ (°C)	$\Delta H_c$ (J/g)
5-1	46000	1400	39.6	57.4	9.1	58.4
5-2	53000	1600	42.6	68.7	11.6	67.5
5-3	54000	1800	44.5	60.6	12.1	58.6
5-4	42000	2300	49.2	67.1	23.1	66.6
5-5	42000	2600	49.4	66.9	24.9	67.2
5-6	50000	2900	52.1	71.6	26.4	70.5
5-7	61000	3100	52.3	75.0	27.8	74.3
5-8	66000	3700	54.2	78.1	29.1	76.4
5-9 <sup>c</sup>	4100	4100	54.0	85.4	32.9	84.2

<sup>a</sup>Measured by GPC in THF.

<sup>b</sup> $M_n^*$  means the molecular weight of single arm. Measured by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

<sup>c</sup>The sample is linear poly( $\epsilon$ -caprolactone).

Thermal stability of polymer is necessary in determining their use for many applications. Fig. 9 shows the TGA and DTG curves of linear poly( $\epsilon$ -caprolactone) homopolymer and linear-comb poly( $\epsilon$ -caprolactone). A sudden drop in the mass of the sample indicated the thermal degradation of the material. The curves show that thermal degradation began to occur only after the materials absorbed a certain amount of heat. The heat initiated the degradation process and breaks down the matrix structure of the material by cutting its molecular chain rupture or scission. Branched PCL starts to degrade at about 330 °C in a nitrogen atmosphere, and degradation is completed at about 450 °C. For branched PCL a mass loss of about 5% occurred at around 361 °C and the highest weight loss rate occurred at about 397 °C. Because the PCL side chains account for a large proportion and the PB main chain

accounts for a small proportion, PB main chain has little effect on the degradation of polymers. The degradation temperature of branched linear-comb PCL was close to which of linear PCL homopolymer. It implies that branched structure has no significant effect on the thermal stability of poly( $\epsilon$ -caprolactone).

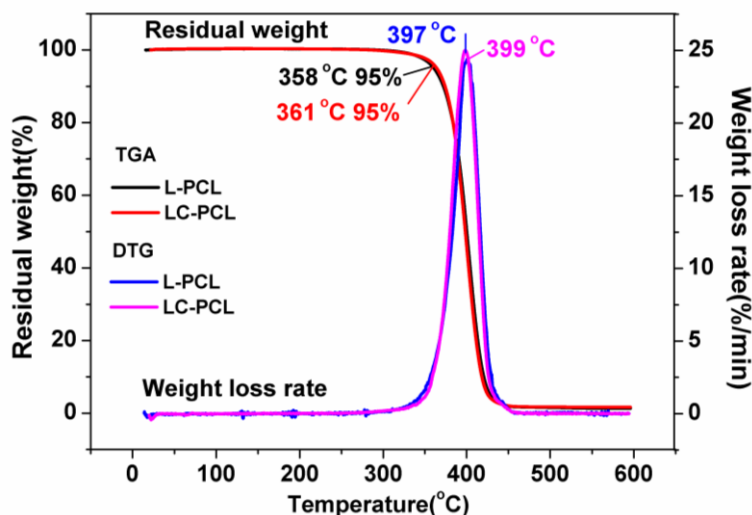


Figure 9. TGA and DTG curves of linear poly( $\epsilon$ -caprolactone) homopolymer (sample 5-9 in Table 5), and linear-comb poly( $\epsilon$ -caprolactone) (sample 5-8 in Table 5).

### Crystal structure and spherulitic morphology

The morphology as well as the crystallization behavior of crystalline-amorphous diblock copolymers has been studied extensively, and it can completely change the block copolymers morphology.[38-42] In order to check the crystallizability and crystal structure of linear-comb PCL, we examined WAXD patterns and polarized optical microscopy (POM) of LC-PCLs with different side chain lengths (Figs. 10 and 11). Each WAXD pattern has a couple of crystallographic reflections, which can be indexed satisfactorily to the crystal structure of PCL [43, 44]. The sharp crystalline peaks were observed at  $2\theta$  values of around  $21^\circ$  and  $24^\circ$  for all polymers. These two peaks are attributed to the diffraction from (110) and (200) lattice planes, respectively [45]. This indicates that the branched PCL certainly crystallize in the ordinary crystal form. A significant broadening of the reflections, however, cannot be detected among the WAXD patterns shown in Fig. 10 and it demonstrates that side chain length has no obvious effect on the crystal structure of branched PCL. The values of crystallite sizes and crystallinities of LC-PCLs with different side chain length are presented in Table 8. It shows that  $L_{hkl}$  of LC-PCL systematically decreases as side chain length increases. And crystallinity of LC-PCL increases with increasing of side chain length, which is consistent with the previous discussion that the enhancement effect of side chain length on the crystallization of LC-PCL.

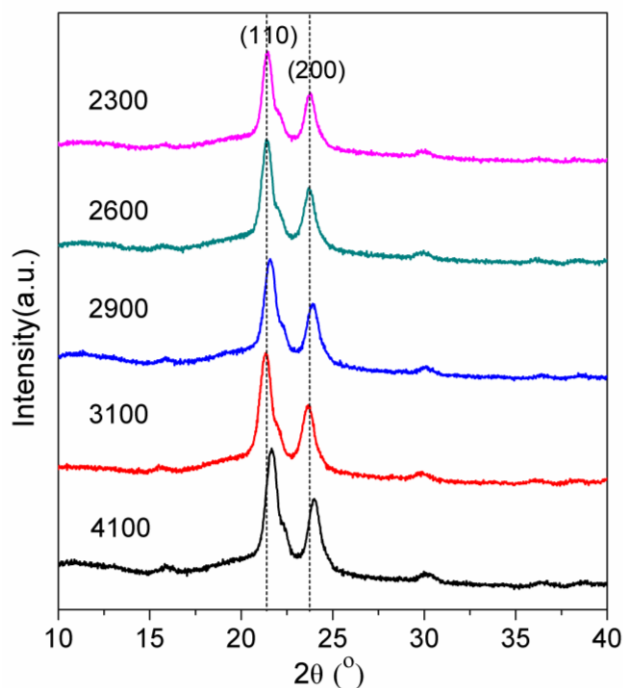


Figure 10. WAXD patterns of PCLs with different side chain length.

Table 8. Crystallite size of  $L_{110}$  and  $L_{200}$  and crystallinity of LC-PCLs with different side chain length

sample	$M_n^*$ (g mol <sup>-1</sup> ) <sup>a</sup>	$L_{110}$			$L_{200}$			$X_c(\%)$
		$2\theta^b$	$\beta^c$	$L_{hkl}(\text{nm})$	$2\theta^b$	$\beta^c$	$L_{hkl}(\text{nm})$	
5-4	2300	21.44	0.751	10.9	23.70	0.708	11.6	73.0
5-5	2600	21.42	0.769	10.6	23.68	0.744	11.0	76.1
5-6	2900	21.60	0.852	9.6	23.86	0.782	10.5	77.8
5-7	3100	21.35	0.856	9.5	23.61	0.792	10.3	78.8
5-9 <sup>d</sup>	4100	21.58	0.787	10.4	23.91	0.763	10.7	72.5

<sup>a</sup> $M_n^*$  means the molecular weight of single arm. Measured by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

<sup>b</sup>Bragg angle.

<sup>c</sup>Measured half-width of the experimental profile.

<sup>d</sup>The sample is linear poly( $\epsilon$ -caprolactone).

Fig. 11 shows the typical polarized photomicrographs of the spherulites crystallized from branched LC-PCLs and linear PCL at shown temperature and time. As seen in Fig. 11 (a-c), sample LC-PCL with  $M_n^*$  2300 g mol<sup>-1</sup> has just started to crystallize and sample LC-PCL with  $M_n^*$  3700 g mol<sup>-1</sup> has crystallized completely almost at the same crystallization temperature and time. This indicates that the crystallization of LC-PCL with long-side chain is much faster than that with short-side chain. Furthermore, it is obviously that the spherulites seem to be uniform in size and the spherulite size increases with the increase of molecular weight of single arm. Fig. 11 (b) and (c) shows experimental evidence that the nucleation process tends to be more instantaneous in the case of LC-PCL with  $M_n^*$  2900 g mol<sup>-1</sup> than in the case of LC-PCL with  $M_n^*$  3700 g mol<sup>-1</sup> crystallized from the melt, suggesting that the



nucleation density is higher for the LC-PCL with short side chain crystallized under the same conditions as the LC-PCL with long side chain examined.[36] Comparing Fig. 11 (a)(b)(c) and (d), it is clearly that the spherulite sizes of branched LC-PCLs are smaller than that of linear PCL, which can be explained by the structural defects resulted from branching structure.

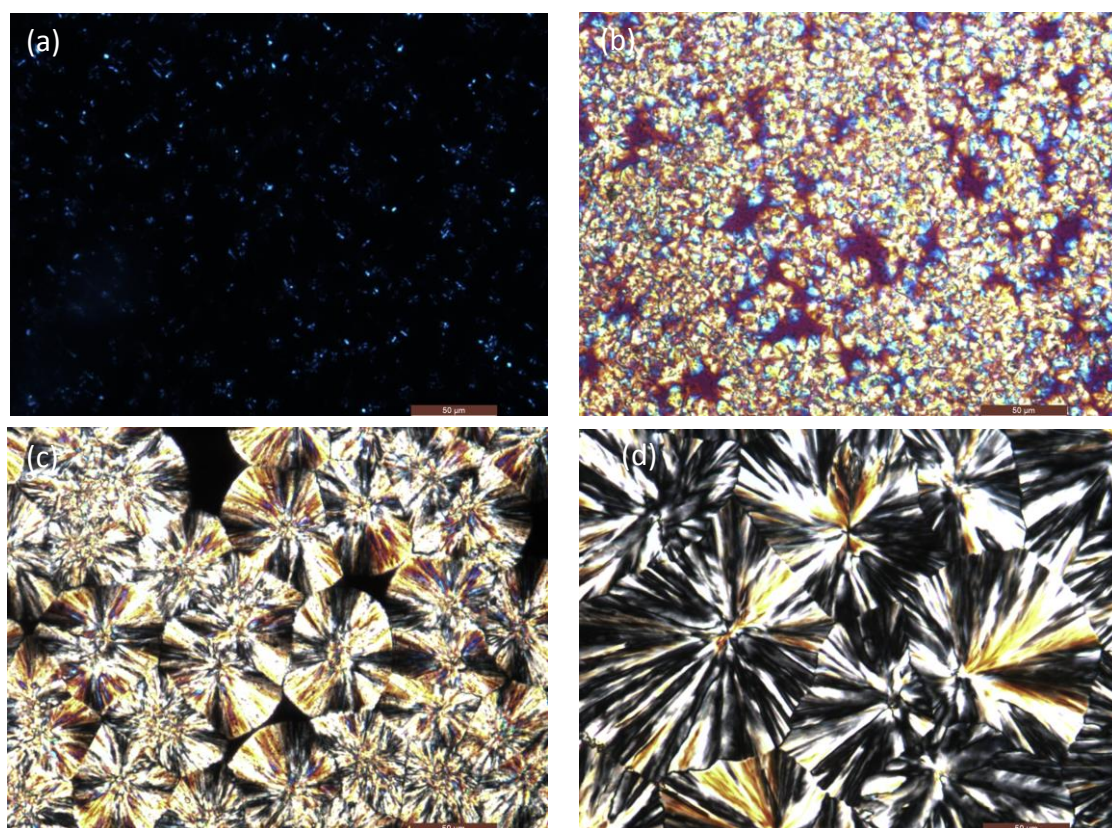


Figure 11. Polarized photomicrographs of PCLs isothermal crystallized at 44 °C for 22 min. (a) LC-PCL  $M_n^*$  2300 g mol<sup>-1</sup>; (b) LC-PCL  $M_n^*$  2900 g mol<sup>-1</sup>; (c) LC-PCL  $M_n^*$  3700 g mol<sup>-1</sup>; (d) L-PCL  $M_n$  4100 g mol<sup>-1</sup>.

## Conclusions

Highly branched linear-comb poly( $\epsilon$ -caprolactone)s with well-defined structure and high molecular weight were successfully synthesized by employing side hydroxyl groups of hydroxylated polybutadiene (HPB) as starting points for the grafting of branch chains and ring-opening polymerization of  $\epsilon$ -CL. The branched level, chain length, and molecular weight of branched LC-PCLs can be regulated by adjusting the number of hydroxyl groups on macroinitiator and monomer/hydroxyl group feed ratios. The simplicity of the reaction conditions, the ready availability of the catalyst, and the exquisite control over the polymerization were well demonstrated. The results of DSC, WAXD, and POM indicated that branched PCL crystallize in the ordinary crystal form similar to linear PCL and the final crystallization and melting behaviors are strongly dependent on the molecular weight of single arm. Both the crystallization temperatures ( $T_{cs}$ ) and melting temperatures ( $T_{ms}$ ) increase with the increase of molecular weights of single arm and both  $T_{cs}$  and  $T_{ms}$  of branched PCLs are lower than those of linear PCL.

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