Synthesis and Characterization of Resorcinarene-Centered Eight-Arm Poly(ε-caprolactone) Stars Catalyzed by Yttrium Complex

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ABSTRACT: Two novel multifunctional precursors with eight alcoholic hydroxyls were synthesized by derivatization of resorcinarene. Well-defined eight-arm star-shaped poly(ε-caprolactone)s (SPCLs) with reasonably narrow molecular weight distributions have been successfully prepared using the precursors as macro-initiators and yttrium tris(2,6-di-*tert*-butyl-4-methylphenolate) [$Y(DBMP)_3$] as catalyst at 40 °C. The molecular weight of SPCLs was characterized by end group ^1H NMR analyses and size-exclusion chromatography, which could be well controlled by the molar ratio of the monomer to the precursor. The polymerization is more controllable with the precursor holding longer hydrocarbon chains as R groups. Differential scanning calorimetry analyses suggested that the maximal melting point, the crystallization temperature, and the degree of crystallinities of SPCLs increased with the increasing of the molecular weight, and were significantly lower than that of the counterpart linear poly(ε-caprolactone) (LPCL). Furthermore, polarized optical microscopy indicated that LPCL showed fast crystallization rate with apparent Maltese cross pattern, whereas SPCL exhibited irregular spherulite and apparently slower crystallization rate. © 2008 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 46: 2108–2118, 2008

Keywords: macrocycles; poly(ε-caprolactone); rare earth catalyst; resorcinarene; ring-opening polymerization; star polymers

INTRODUCTION

Increasing attention is paid nowadays to the syntheses of star-shaped polymers because of their particular bulk and solution properties.[1] There are essentially two strategies to prepare star polymers: one can resort to linking a given number of linear chains to the same central core having certain functional groups ("arm-first" method)[2,3] or turn to growing branches from a multifunctional core that is able to initiate the monomer polymerization in multiple directions ("core-first" method).[4–6] The "core-first" method seems more attractive since it not only eliminates the tedious purification steps but also allows the functionalization of the star arm ends, though there are some drawbacks such as the design of multifunctional precursor of precise functionality. Star polymers based on small multifunctional initiators with precise arm numbers and lengths have been prepared using this method via living/controlled polymerization techniques such as atom transfer radical polymerization (ATRP),[7–12] reversible radical fragment transfer polymerization (RAFT),[13] and ring-opening polymerization (ROP).[14–19]

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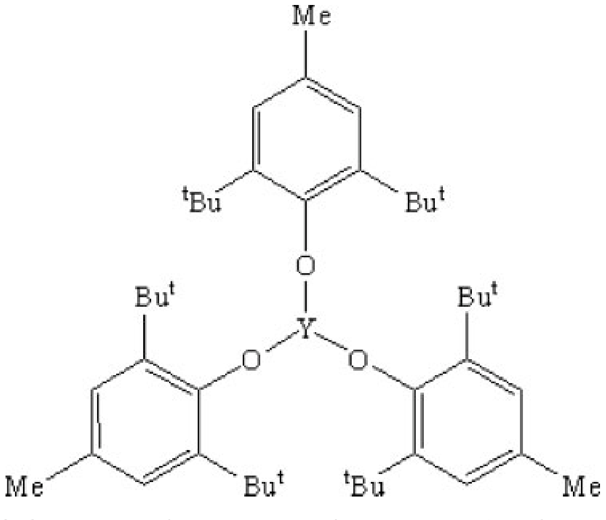
Macrocyclic compounds often provide several functional groups, which can be further modified to obtain star-like polymers. Calixarene-centered star polymers have been synthesized successfully using living/controlled polymerization techniques. Kennedy and co-workers[20] reported eight-arm poly (isobutylene) stars prepared by living cationic polymerization from calix[8]arene-based initiator. Sawamoto and co-workers[21] and Gnanou and co-workers[22–24] introduced the use of functionalized calix[n]arenes as ATRP initiators in the polymerization of methyl methacrylate, acrylates and styrene. Taton et al.[25] prepared eight-arm poly(ethylene oxide) stars based on octahydroxylated calix[8]arene precursor via anionic polymerization. Very recently, our research group described the synthesis of calix[6]arene-based amphiphilic polymers consisting of six PPO-block-PDTC arms through ring-opening polymerization.[26]

Resorcinarenes are another group of cyclic tetramers synthesized through an acid-catalyzed condensation between resorcinol and an aliphatic or aromatic aldehyde.[27] Generally speaking, resorcinarenes can be considered to contain two parts: one is the phenolic hydroxyl groups on the upper rim, and the other one is the R groups from the starting aldehyde on the lower rim. The syntheses of resorcinarene derivatives with various functional groups have been studied in detail, showing that they are useful building blocks in supramolecular chemistry.[28–31] It seems that resorcinarenes with eight phenolic OH groups are good starting material for the preparing of star polymers, but the rigid conformations and the high steric hindrance of initiating sites restrict their applications to star-like polymer syntheses. Thereby, compared with calixarenes, only a few publications concerned the use of resorcinarenes as core molecules to prepare well-defined star polymers over the past years. Tenhu and co-workers[32,33] reported the use of functionalized resorcinarenes as ATRP initiators in the polymerizations of *tert*-butyl acrylate and methyl methacrylate, but only four-arm star polymers were obtained due to high steric hindrance preventing the simultaneous reaction of all initiating sites. To the best of our knowledge, the synthesis of eight-arm star polymers based on resorcinarene cores via controlled ROP and using rare earth catalyst have not been reported.

Poly(ε-caprolactone) (PCL) is one of the most attractive and promising biodegradable aliphatic polyesters, which can be used as synthetic biomaterial or controlled drug release matrix due to its good drug permeability, biocompatibility, and nontoxicity.[34] PCLs with tailor made architectures have attracted much attention in relation to functional materials. Star-shaped poly(ε-caprolactone)s (SPCLs) have high molecular weight but relatively short chains, which lead to smaller hydrodynamic radius and lower viscosity comparing with linear poly(ε-caprolactone)s (LPCLs) with similar molecular weight, and are expected to display peculiar morphology, thermal property, and degradation performance.[35] Stannous octanoate [Sn(Oct)$_2$] is the most widely used catalyst for the preparation of SPCLs.[36–40] Nevertheless, high temperature (around 120 °C) is always needed for the polymerization, which leads to the unavoidable transesterification. In our continuing studies on the controlled ring-opening polymerization of lactones, lactides and cyclic carbonates, a series of rare earth phenolate complexes have been found to be efficient catalysts for CL homo- and copolymerization under mild conditions.[41–44]

The work presented here demonstrated for the first time the syntheses and characterizations of well-defined octaarmed SPCLs based on the resorcinarene cores in the presence of yttrium tris(2,6-di-*tert*-butyl-4-methylphenolate) [Y(DBMP)$_3$] (see Scheme 1) via controlled ring-opening polymerization. A series of SPCLs with well-controlled arm lengths have been successfully synthesized under mild conditions (40 °C). All the samples were characterized by nuclear magnetic resonance spectroscopy (NMR) and size-exclusion chromatography (SEC). Differen-



Scheme 1. The structure of yttrium tris(2,6-di-*tert*-butyl-4-methylphenolate) [Y(DBMP)$_3$].

tial scanning calorimetry (DSC) was used to investigate the thermal and crystallization behaviors of SPCLs. In the meantime, The crystalline morphology of SPCL was also investigated by polarized optical microscope (POM).

EXPERIMENTAL

Materials

ε-Caprolactone (99%; Acros) was distilled under reduced pressure prior to use. Methyl chloroacetate, potassium carbonate, potassium iodide (analytical reagent), and lithium aluminum hydride ($LiAlH_4$; 97%; Alfa) were used without further purifications. THF was distilled from the ketyl prepared from sodium and benzophenone. $Y(DBMP)_3$ was synthesized as we reported formerly.[41] Tetrahexylresorcinarene {2,8,14,20-tetrahexylpentacyclo [19.3.1.1^{3,7}.1^{9,13}.1^{15,19}] octacosa-1(25),3,5,7(28), 9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12, 16,18,22,24-octol} (1a) and tetraundecylresorcinarene {2,8,14,20-tetraundecylpentacyclo [19.3. 1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27), 15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22, 24-octol} (1b) were synthesized according to the procedure described in the literature.[45] Other reagents and solvents were purified by general methods.

Measurements

^1H NMR spectra were recorded on a Bruker Avance DMX500 spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. The molecular weight and molecular weight distribution were determined by size-exclusion chromatographic/multi-angle laser light scattering (SEC–MALLS). The SEC system consisted of a Waters degasser, a Waters 1525 HPLC pump with 717 plus autosampler, Waters 2410 RI detector and columns: Styragel, HT 3, HT 4, HT 5. The calibration was performed with commercial polystyrene standards. Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1.0 mL min^{-1} at 30 °C. The refractive-index increment (d_n/d_c) was determined with a Wyatt Optilab DSP differential refractometer at 690 nm, which was 0.064 mL g^{-1} for the SPCLs. DSC measurements were performed on a TA Q100 apparatus. The samples were heated from 0 to 100 °C, held for 2 min to erase the thermal history, then cooled to 0 °C at a rate of 20 °C min^{-1}, and finally heated to 100 °C at a rate of 10 °C min^{-1}. The intrinsic viscosities of PCLs were measured with Ubbelohde viscometer in DMF at 30.0 °C ± 0.1 °C. The morphologies of PCLs were monitored with an Olympus BX51 POM.

Syntheses of the Resorcinarene-Based Precursors

Octamethyl Tetrahexylresorcinarene Octaacetate 2a (General Procedure for 2a, 2b)

A mixture of tetrahexylresorcinarene (1.65 g, 2 mmol), methyl chloroacetate (1.72 g, 16 mmol), K_2CO_3 (2.76 g, 20 mmo1), KI (12.7 mg, 0.1 mmol) and anhydrous acetone (100 mL) was stirred under argon atmosphere and refluxed for 48 h. After removing acetone, the residue was suspended in $Na_2S_20_3$ aqueous solution (5%, 30 mL) for 30 min, and then extracted with dichloromethane (15 mL × 3). The organic extract was dried over magnesium sulfate, filtered and concentrated to 10 mL. Upon addition of methanol, 2a precipitated to give 2.40 g pale yellow powder (1.71 mmol, 86% yield). MS for $C_{76}H_{104}O_{24}$: $m/z = 1424$ $(M + Na)^+$. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.85 (t, 12H, $CH_2(CH_2)_4CH_3$), 1.25–1.32 (bs, 32H, $CH_2(CH_2)_4CH_3$), 1.85(s, 8H, $CH_2(CH_2)_4CH_3$), 3.76 (s, 24H, CH_2COOCH_3), 4.28 (s, 16H, CH_2COOCH_3), 4.59 (t, 4H, CH (methine)), 6.22 (s, 4H, ArH, upper), 6.62 (s, 4H, ArH, lower).

Octamethyl Tetraundecylresorcinarene Octaacetate 2b

Following the general procedure described above, compound 2b was obtained from tetraundecylresorcinarene in 87% yield. MS for $C_{96}H_{144}O_{24}$: $m/z = 1704$ $(M + Na)^+$. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.87 (t, 12H, $CH_2(CH_2)_9CH_3$), 1.23–1.33 (bs, 72H, $CH_2(CH_2)_9CH_3$), 1.85(s, 8H, $CH_2(CH_2)_4CH_3$), 3.76 (s, 24H, CH_2COOCH_3), 4.28 (s, 16H, CH_2COOCH_3), 4.59 (t, 4H, CH (methine)), 6.21 (s, 4H, ArH, upper), 6.61 (s, 4H, ArH, lower).

Octa-2-hydroxyethoxytetrahexylresorcinarene 3a

A solution of 2a (1.40 g, 1 mmol) in 40 mL of dry THF was added dropwise to a stirred suspension of 97% $LiAlH_4$ (0.46 g, 12 mmol) in the 40 mL of dry THF. The reaction mixture was stirred for 30 min under argon atmosphere at room temperature and then 50 °C for 2 h. The excess of

$LiAlH_4$ was destroyed by careful addition of water. Dilute hydrochloric acid was added to the mixture to salt out the metal-salt (PH = 5–6). The filtrate was dried over magnesium sulfate, filtered, and evaporated. The white crude product was recrystallized from EtOH/water. Yield: 70%. MS for $C_{68}H_{104}O_{16}$: $m/z = 1200$ $(M + Na)^+$. ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 0.87$ (t, 12H, $CH_2(CH_2)_4CH_3$), 1.25–1.33 (bs, 32H, $CH_2(CH_2)_4CH_3$), 1.85 (s, 8H, $CH_2(CH_2)_4CH_3$), 3.00 (s, 8H, OCH_2CH_2OH), 3.82 (t, 32H, OCH_2CH_2OH), 4.53 (t, 4H, CH (methine)), 6.30 (s, 4H, ArH, upper), 6.71 (s, 4H, ArH, lower).

Octa-2-hydroxyethoxytetraundecylresorcinarene 3b

A solution of 2b (1.68 g, 1 mmol) in 50 mL of dry THF was added dropwise to a stirred suspension of 97% $LiAlH_4$ (0.46 g, 12 mmol) in the 50 mL of dry THF. The reaction mixture was stirred for 30 min under argon atmosphere at room temperature and then 50 °C for 2 h. The excess of $LiAlH_4$ was destroyed by careful addition of water and the solvent evaporated under reduced pressure. The residue was taken up in chloroform and washed successively with dilute sulfuric acid and water. The organic phase was dried over magnesium sulfate, filtered, and evaporated. The white crude product was recrystallized from EtOH/water. Yield: 73%. MS for $C_{88}H_{144}O_{16}$: $m/z = 1480$ $(M + Na)^+$. ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 0.87$ (t, 12H, $CH_2(CH_2)_9CH_3$), 1.25–1.33 (bs, 72H, $CH_2(CH_2)_9CH_3$), 1.85 (s, 8H, $CH_2(CH_2)_9CH_3$), 3.00 (s, 8H, OCH_2CH_2OH), 3.82 (t, 32H, OCH_2CH_2OH), 4.53 (t, 4H, CH (methine)), 6.30 (s, 4H, ArH, upper), 6.70 (s, 4H, ArH, lower).

Polymerizations

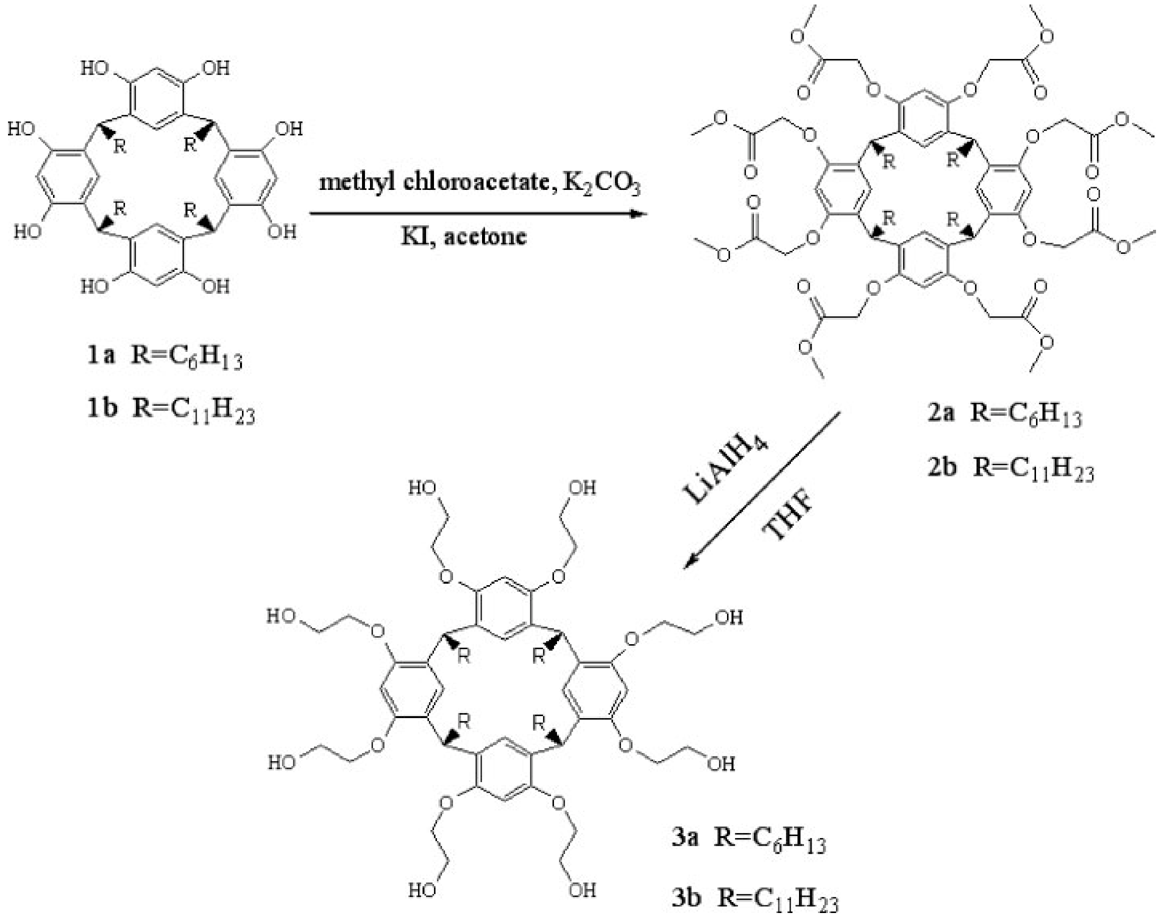
All the polymerizations were carried out in 20-mL ampoules with Schlenk technique under inert atmosphere. A typical polymerization procedure was as follows: 0.118 g 3a (0.8 mmol of OH group) was transferred into a flamed-dried ampoule. Then 1.67 mmol $Y(DBMP)_3$ in 6.3 mL THF was injected into the ampoule and aged for 30 min at 30 °C. Finally, 1.82 g CL (16.0 mmol) was added to the ampoule via a syringe. The ampoule was put into a water bath at 40 °C. After 4 h, the mixture was poured into a large amount of methanol, and the polymer precipitated from methanol, filtered and dried in vacuum to constant weight.

RESULTS AND DISCUSSION

Syntheses and Characterizations of Octafunctional Precursors

Two resorcinarene derivatives with eight 2-hydroxyethoxy groups incorporated onto the upper rim had been synthesized by a simple experimental procedure (see Scheme 2). Generally speaking, for the preparing of well-defined star-shaped polymers with "core-first" method, precursors must have good solubilities to ensure all the initiating sites could simultaneously contribute to the polymerization. R groups on the lower rim of the resorcinarene derivatives highly influence their solubilities and conformations in solution. In our attempts to prepare SPCLs, octafunctional resorcinarene precursors holding methyls and phenyls as R groups had been tried to trigger the ring-opening polymerization of CL, but failed to obtain any polymers due to their poor solubilities and probably high rigid conformations in polymerization solution. It seems that conformationally mobile hydrocarbon chains such as C_6H_{13} and $C_{11}H_{23}$ would increase the solubility of the derivative resorcinarene. Indeed, 1a and 1b had been chosen as the starting material and the octamethyl resorcinarene octaacetates (2a and 2b) were synthesized in high yields. Then, reaction of 2a and 2b with $LiAlH_4$ produced the octafunctional precursors (3a and 3b) without column chromatography purification.

The ^1H NMR spectra of the octafunctional precursors (3a and 3b) were presented in Figure 1. The protons attached to the aromatic rings gave double signals (H^g and H^h), illustrating the aromatic groups lay spatially in C_2-symmetric structures. The relatively broad signals from both 3a and 3b refer to the structures with slow conformational interconversion leading to the possible coexistence of several conformers. The C_2-symmetric conformers interconvert through the C_{4v} structures,[46,47] and this interconversion is slower when hydrogen bonds are weak or absent. The signals of the alcoholic hydroxyl groups could be clearly detected at 3.0 ppm (H^f), which indicates the presence of weak intramolecular hydrogen bonds leading to the slower interconversion of conformers. All these findings suggest that when the phenolic hydroxyl groups of resorcinarenes are converted into alcoholic hydroxyl groups, the intramolecular hydrogen bonds become weaker, and the structures become more flexible, which could provide suffi-



Scheme 2. Synthetic route for the preparation of two resorcinarene-based cores.

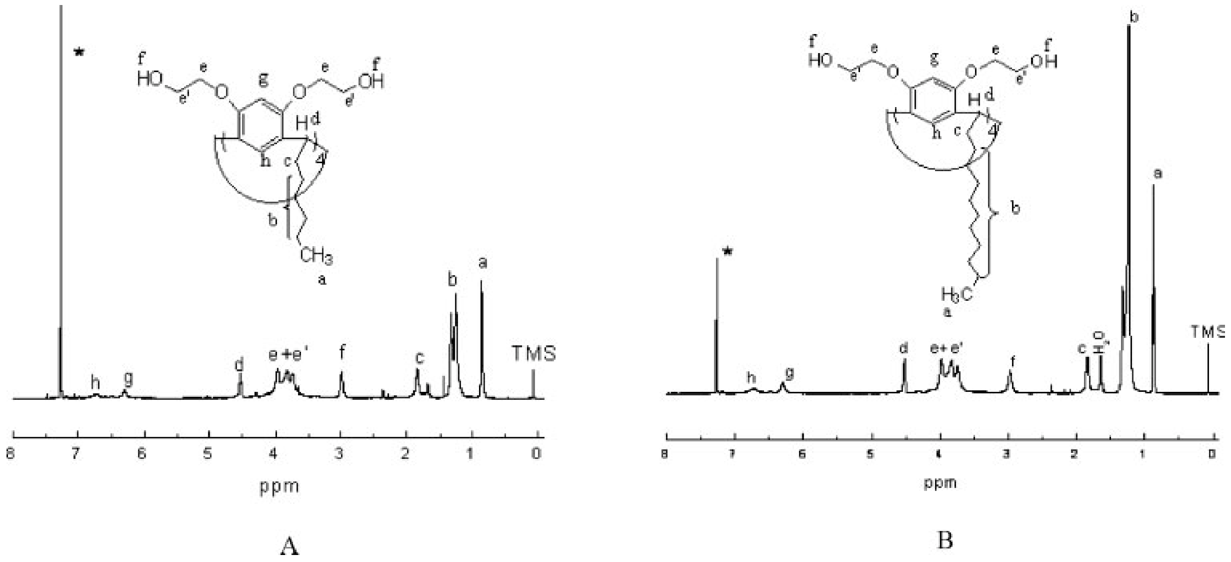
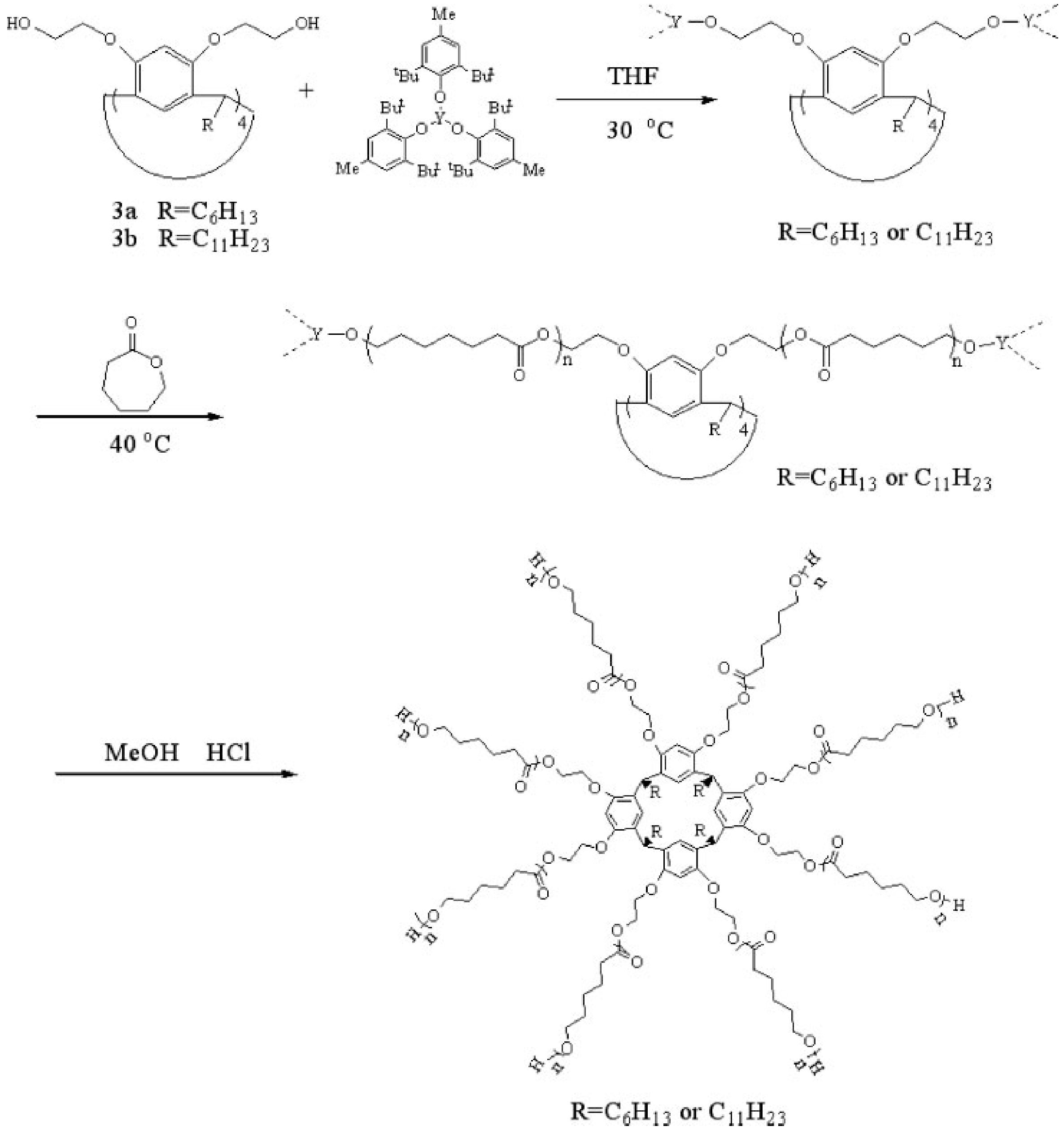


Figure 1. ^{1}H NMR spectra (500 MHz) of octafunctional precursor 3a (A) and 3b (B) in $CDCl_3$. The signals originating from solvent are marked with asterisks.



Scheme 3. "Core-First" synthetic strategy for a poly(ε-caprolactone) star by ROP.

cient space to permit simultaneous initiating of all functional sites in the polymerization.

Synthesis and Characterization of Eight-Arm Star-Shaped Poly(ε-caprolactone)s

The synthesis of SPCLs was carried out by the ring-opening polymerization of CL with various molar ratios of CL to octafunctional precursors in THF at 40 °C as shown in Scheme 3. In the aging step, only five of the eight hydroxyls per precursor had been metalated by yttrium (see experimental part). However, all of the eight functional sites could simultaneously initiate the polymerization of CL monomers because of the rapid exchange between the dormant hydroxyls and active alkoxy yttrium relative to the rate of polymerization. Under this condition, the initiating of linear chains would be maximally reduced, and well-defined eight-arm poly(ε-caprolactone) stars were successfully prepared. Figure 2 exhibits the ^{1}H NMR spectra of SPCL2 based on 3a and SPCL8 based on 3b, in

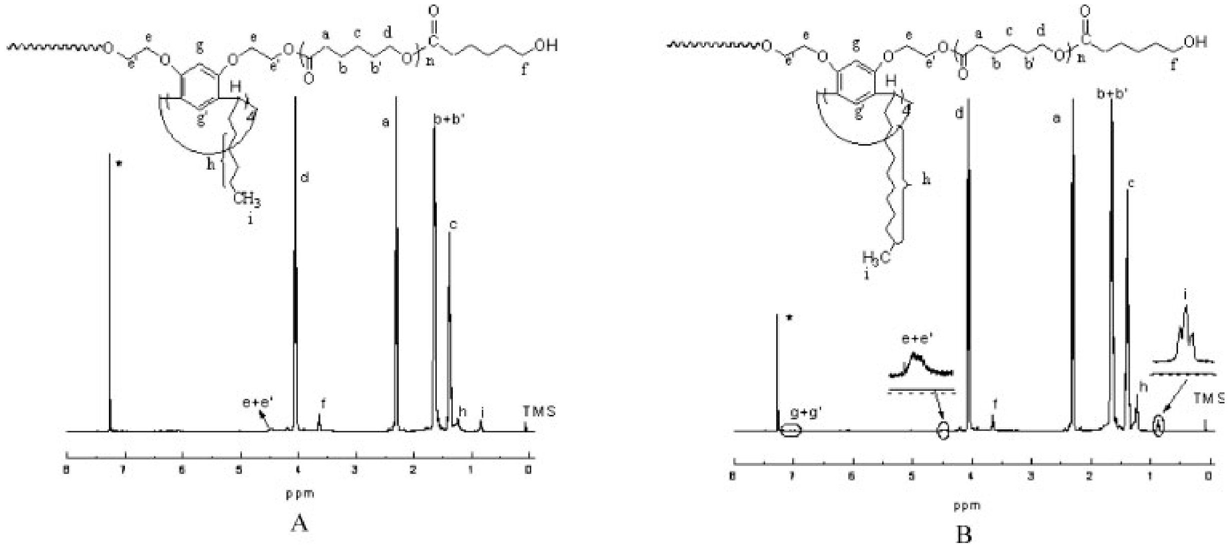


Figure 2. ^{1}H NMR spectra (500 MHz) of SPCL2 (A) and SPCL8 (B) in $CDCl_3$. The signals originating from solvent are marked with asterisks.

which the peak at about 4.5 ppm ($H^{e'}$) shows the direct links between PCL arms and octafunctional core, and the signal of methyl group due to octafunctional core (H^i) was also detected at around 0.87 ppm. Furthermore, the ratio of peak areas of H^i and H^f (H^i/H^f) is exactly 3/4, which clearly demonstrated the eight-arm star structure of the samples prepared. From the data in Table 1, the molecular weights obtained from ^{1}H NMR spectra are close to the values calculated by observed conversion and $[CL]_0$/[Precursor] except SPCL1. The polymerizations with precursor 3b are more controllable than that with 3a, which may be related to the better solubility of 3b holding the longer hydrocarbon chains as R groups than that of 3a.

As a comparison, LPCL was also prepared using *n*-butanol as initiator under similar condi-

Table 1. Ring-Opening Polymerization Using Precursors 3a and 3b for SPCLs

Run	Polymer[a]	[M]/[Precursor] (molar ratio)	[η] (dL/g)	Conv (%)	$M_{n,Cal}$ (g mol^{-1})[b]	$M_{n,NMR}$ (g mol^{-1})[c]	$M_{n,MALLS}$ (g mol^{-1})[d]	$M_{n,SEC}$ (g mol^{-1})[e]	PDI
1	SPCL1	55	0.146	90.3	6800	9200		18,800	1.2_8
2	SPCL2	98	0.162	92.8	11,500	12,600		20,200	1.3_2
3	SPCL3	175	0.196	93.9	19,900	20,600	19,700	25,300	1.4_3
4	SPCL4	200	0.209	95.5	23,000	26,000		32,300	1.4_6
5	SPCL5	240	0.210	94.6	27,100	26,300		33,600	1.4_7
6	SPCL6	327	0.301	96.0	37,000	36,500	28,100	55,000	1.5_0
7	LPCL[f]	55	0.224	93.4	5900	5800		22,000	1.3_4
8	SPCL7	55	0.129	91.2	7200	7600		17,700	1.2_6
9	SPCL8	92	0.135	93.8	11,300	11,500		18,700	1.3_9
10	SPCL9	162	0.214	93.1	18,700	19,800	18,900	27,000	1.4_7
11	SPCL10	207	0.235	94.5	23,800	24,800	23,700	35,500	1.4_9
12	SPCL11	245	0.236	95.8	28,200	28,500		37,600	1.4_8
13	SPCL12	304	0.311	95.2	34,500	36,500	35,100	58,000	1.4_5

Polymerization conditions: THF, $[CL]_0 = 2.0$ mol/L, 40 °C, 4 h.

[a] SPCL1-6 were based on precursor 3a, SPCL7-12 were based on precursor 3b.

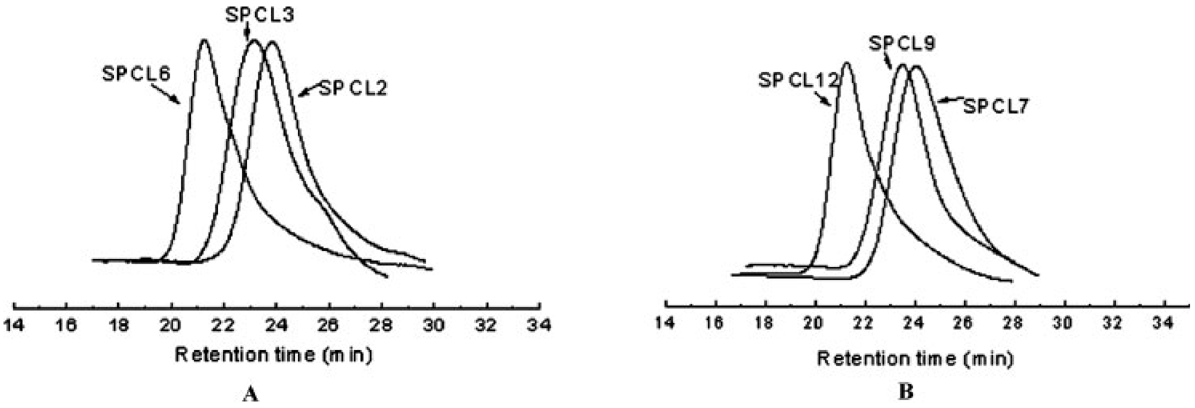
[b] Calculated from the feeding molar ratio of $[CL]_0$/[Precursor] and conversion.

[c] Calculated from equation: $M_n^{nmr} = \frac{I_d}{I_i} \times \frac{3}{4} \times 114 + M_{precursor}$ (except LPCL).

[d] Measured by connecting a multi-angle laser light scattering detector to the SEC.

[e] Measured by SEC with polystyrene standards.

[f] The LPCL was initiated by *n*-butanol.

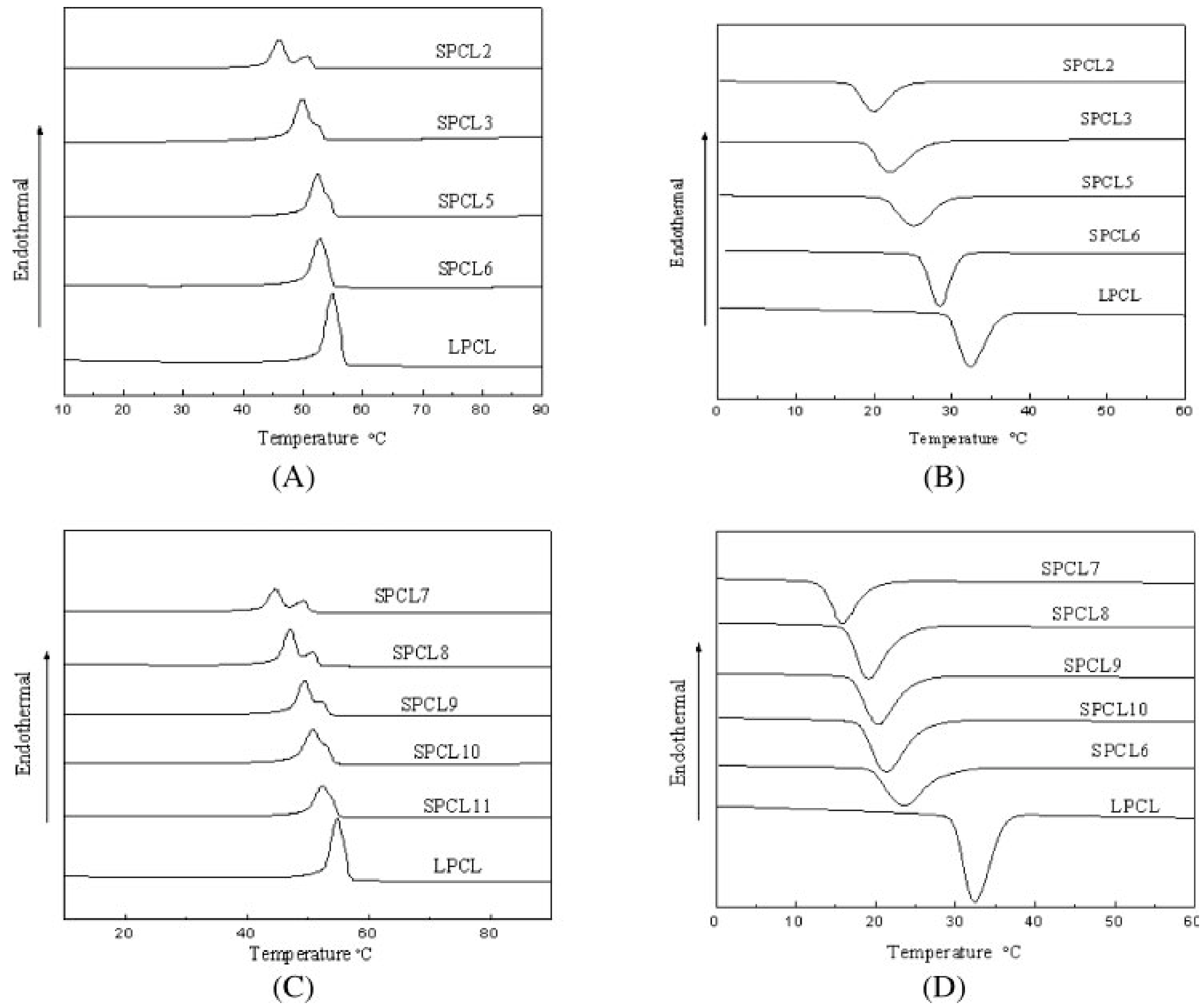


A

B

Figure 3. SEC traces of two series of SPCLs: SPCLs based on precursor 3a (A), SPCLs based on precursor 3b (B).

tions (Run 7, Table 1). The molecular weight of LPCL was calculated by similar method. LPCL and SPCL7 have similar molecular weight (only CL unit), but the viscosity of LPCL is significantly higher than SPCL7s (Table 1), which also verifies the star architecture of the product prepared.



(A)

(B)

(C)

(D)

Figure 4. The DSC curves of SPCLs. Second heating run (A,C), cooling run (B,D).

Table 2. Thermal Behaviors of SPCLs and LPCL Determined by DSC

Run	Polymer	[a]T_{m1} (°C)	[b]T_{m2} (°C)	[a]ΔH_{m1} (J/g)	[b]ΔH_{m2} (J/g)	[a]X_{c1} (%)	[b]X_{c2} (%)
1	SPCL1	54.7	46.1	69.3	53.9	49.7	38.6
2	SPCL3	57.2	49.9	78.9	55.7	56.6	39.9
3	SPCL6	60.4	54.8	88.5	58.3	63.4	41.8
4	SPCL7	51.3	44.7	63.0	40.6	34.2	29.1
5	SPCL9	56.6	49.5	79.2	59.4	56.8	42.6
6	SPCL12	57.4	52.4	80.2	59.3	57.5	42.5
7	LPCL	58.6	54.9	94.4	68.6	67.7	49.2

[a] Data from the first heating run.
[b] Data from the second heating run.

SEC traces (Fig. 3) show that the SPCLs prepared have single and reasonably narrow molecular weight distributions (≤ 1.5). However, the tailing detected in the low molecular weight region for the SPCLs with high molecular weight (SPCL6 and SPCL12) could be attributed to a small amount of linear PCL originating from the chain transfer or backbiting of the alkoxide active centers. The results of the actual molar masses of the SPCLs measured by connecting a multi-angle laser light scattering detector to the SEC have confirmed the values obtained from ^{1}H NMR (Table 1), which indicates that the molecular weight of SPCLs can be well controlled by adjusting the molar ratio of the monomer to the precursor. However, the actual molar masses of SPCL6 is smaller than the designed value, which may be ascribed to the poor solubility of the macro-initiator resulting in ill-defined structure.

Thermal and Crystallization Behavior of SPCLs

The thermal and crystallization behavior of SPCLs were investigated by DSC measurements. In the meantime, the data of LPCL was also included as a comparison. The DSC curves of the samples in the cooling run, and the second heating run were showed in Figure 4. The melting temperature (T_m) and the crystallization temperature (T_c) of the polymers were influenced by their architectures. Both T_m and T_c of SPCLs are obviously lower than that of LPCL with similar molecular weight. For SPCLs, T_m and T_c increase with increasing arm length. The lower crystallization temperature (T_c) suggests that the crystallization of the chains in SPCLs is slower than in the counterpart LPCL. These observations could be attributed to two factors: first, the increased free end-groups and branching points of the star polymers rendered the crystallization more difficult; second, resorcinarene core could constitute an obstacle to the crystallization arrangement as in SPCLs, which had been evidenced by the appearance of bimodal melting in the second heating DSC scan, and thus reduced the rate of crystallization.[48] The degree of crystallinity (X_c) of SPCLs can be calculated from DSC analyses with the enthalpy of fusion of 139.6 J/g for perfect crystalline PCL.[49] The results summarized in Table 2 suggest that SPCL has much lower X_c than that of its linear analogue.

A POM was used to observe the crystalline morphology for both SPCL7 and LPCL, as presented in Figure 5. The isothermal crystallization temperature at 45 °C was chosen between T_c and T_m for the two samples. Within a rather short crystallization time (260 s), LPCL presented apparent Maltese cross patterns showing a fast crystallization rate. At the crystallization time of 410 s, the spherulities enlarged significantly. However, although SPCL7 had similar molecular weight with LPCL, it showed irregular spherulite even at the crystallization time of 1250 s. Its crystallization rate was apparently slower than that of LPCL. In all, these results indicate that the star architectures highly affect the spherulite morphology and the spherulite growth rate of PCL, which is consistent with the observations on DSC measurement.

CONCLUSIONS

Novel octafunctional resorcinarene precursors 3a and 3b were successfully prepared and used for the synthesis of eight-arm SPCLs by rare earth complex catalyst via ring-opening polymerization. Well-defined star polymers with reasonably narrow molecular weight distributions

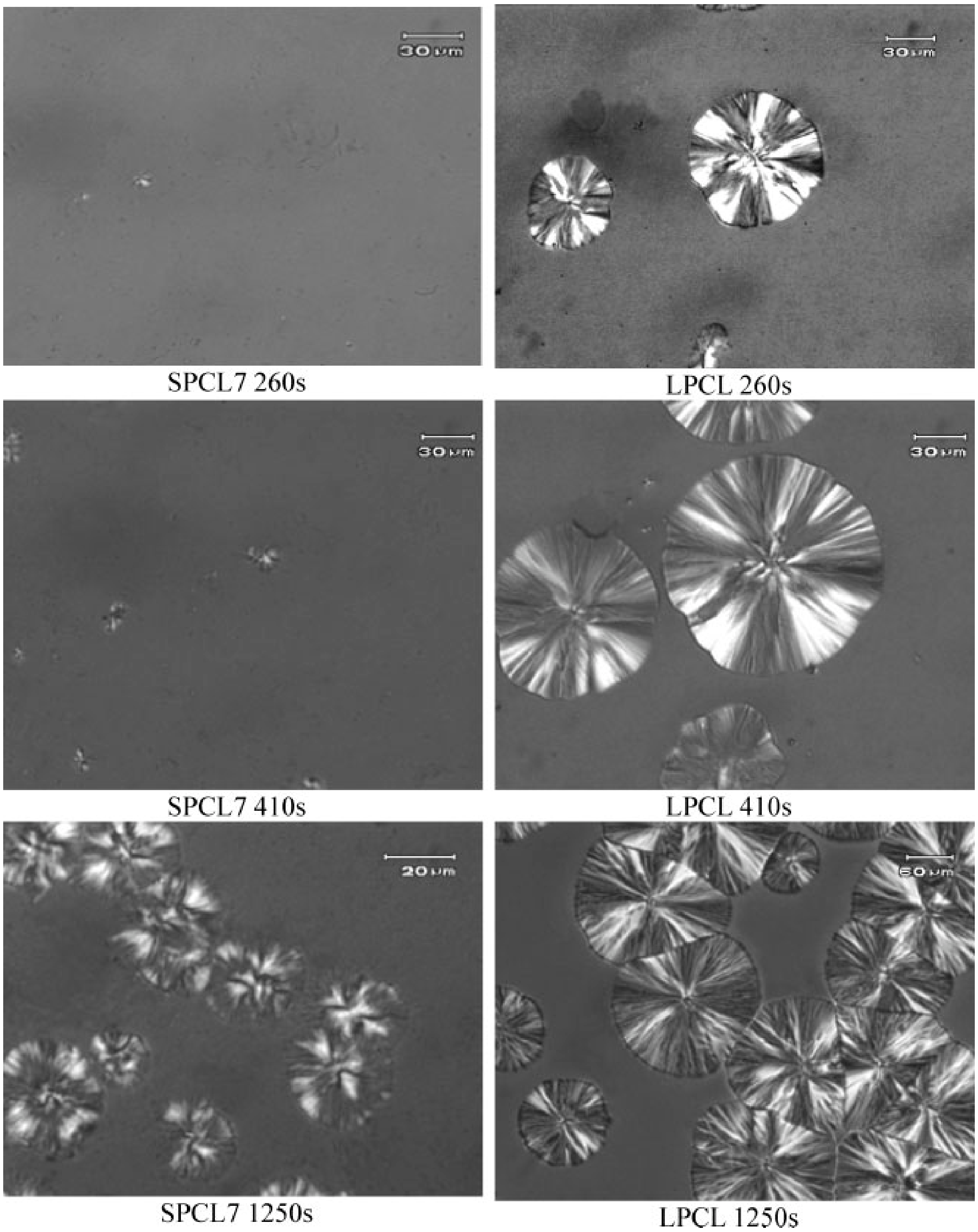


Figure 5. POM photomicrographs of PCL polymers crystallized at 45 °C.

were obtained, indicating controlled polymerizations. The microstructure, molecular weight, thermal, and crystallization behaviors of the SPCLs prepared were examined in detail.

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