

A Novel Initiating System for Ring-Opening Polymerization of ϵ -Caprolactone: Synthesis of Triarm Star-Shaped Poly(ϵ -caprolactone)

Weipu Zhu, Xiaowei Tong, Weihui Xie, Zhiquan Shen

Key Laboratory of Macromolecule Synthesis and Functionalization of Ministry of Education, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

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ABSTRACT: The rare earth compound, scandium trifluoromethanesulfonate [$\text{Sc}(\text{OTf})_3$], has been used as a water-tolerant catalyst for the synthesis of star-shaped poly(ϵ -caprolactone)s (SPCLs) with trimethylol propane as trifunctional initiator in solvent at 40°C. Triarm SPCLs have been successfully prepared. The molar mass of SPCLs were determined by end-group ^1H NMR analyses, which could be well controlled by the molar ratio of the monomer to the initiator, and were independent of the amount of $\text{Sc}(\text{OTf})_3$ used. Differential scanning calorimetry analyses suggested that the maximal melting point, the cold crystallization temperature, and the degree of

crystallinities of SPCLs increased with the increasing of the molar mass and were lower than the linear poly(ϵ -caprolactone) (LPCL) with similar molar mass. Furthermore, polarized optical microscopy indicated that LPCL showed fast crystallization rate and good spherulitic morphology with apparent Maltese cross pattern, whereas SPCLs exhibit much lower crystallization rate and poor spherulitic morphology. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1943–1948, 2010

Key words: star polymers; polyesters; water-tolerant catalyst; trimethylol propane; ring-opening polymerization

INTRODUCTION

Poly(ϵ -caprolactone) (PCL) is one of the important biomaterials attributing to its biodegradability and biocompatibility, which has been increasingly investigated worldwide in biomedical, pharmaceutical, and environmental applications.¹ Many catalysts such as stannous,^{2,3} calcium,^{4,5} aluminum,^{6,7} and zinc^{8–10} compounds have been developed to prepare PCL by ring-opening polymerization (ROP) of ϵ -caprolactone (CL). PCLs with complex macromolecular architectures have attracted great attention in relation to functional materials. Among them, star-shaped poly(ϵ -caprolactone)s (SPCLs) have high molar mass but relatively short chains, which lead to smaller hydrodynamic radius and lower viscosity comparing to linear poly(ϵ -caprolactone)s (LPCLs) with similar molar mass, and are expected to display

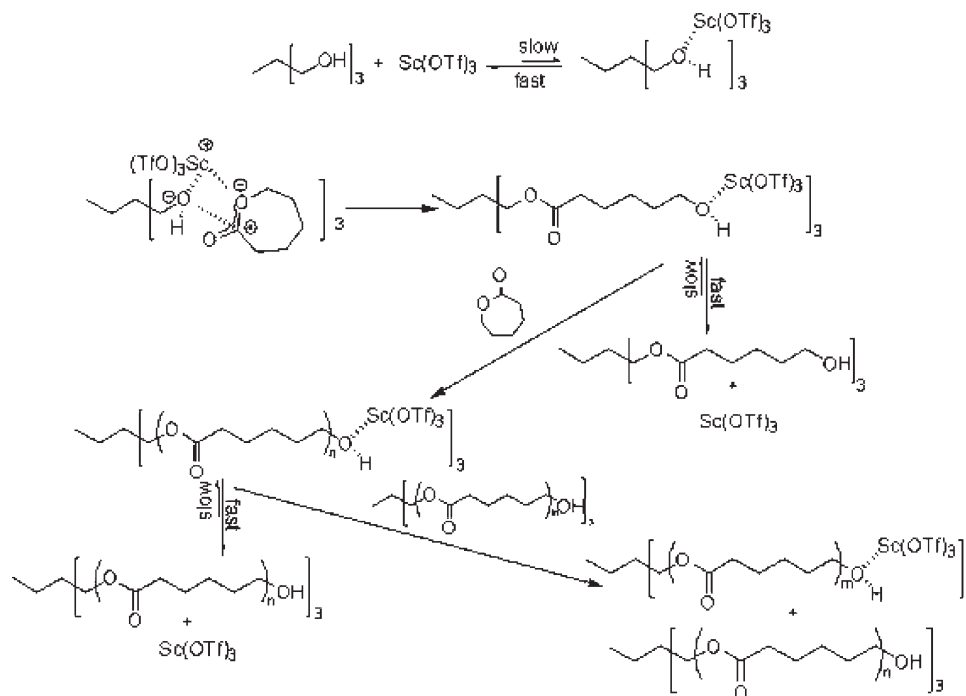
peculiar morphology, thermal property, and degradation performance.¹¹

ROP of CL by use of multifunctional alcohol initiators has been proved to be a suitable approach to prepare SPCLs. Stannous octanoate [$\text{Sn}(\text{Oct})_2$] is the most widely used catalyst for SPCLs.^{12–17} Nevertheless, high temperature (around 120°C) is always needed for the polymerization. Furthermore, $\text{Sn}(\text{Oct})_2$ is extremely air and moisture sensitive. So exploring new catalysts for preparing SPCLs is still necessary. In our continuing studies on the synthesis of SPCLs, a series of rare earth complexes, such as rare earth phenolates, SmI_2 and $\text{Sm}(\text{PPh}_2)_2$ have been used as efficient catalysts preparing well-defined SPCLs with multifunctional alcohol under mild conditions.^{18–21} Metal triflates are newly reported efficient cationic catalysts for lactones and lactides polymerizations.^{22–24} Known from other common catalysts, the activity of metal triflates would not be restrained by moisture and air. Moller et al.,²⁵ Zhou et al.,²⁶ and Nomura et al.^{27,28} reported the ROP of CL using scandium triflate [$\text{Sc}(\text{OTf})_3$] as catalyst preparing LPCLs with controlled molar mass and very narrow molar mass distribution at room temperature. However, there is no reference concerning the preparation of SPCLs with metal triflates. In this article, $\text{Sc}(\text{OTf})_3$ has been first employed as catalyst for preparing triarm SPCLs using trimethylol propane (TMP) as initiator under

Correspondence to: W.-P. Zhu (carrols@163.com) or Z.-Q. Shen (zhiquan_shen@163.com).

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Scheme 1 Conceivable mechanism of ROP of CL with TMP as initiator and Sc(OTf)₃ as catalyst preparing SPCL.

mild condition (40°C). A series of SPCLs with well-controlled arm length have been successfully synthesized. One Sc(OTf)₃ molecule could produce a large number of PCL arms as shown in Scheme 1. The influence of the star architecture on the thermal and crystallization behavior of the polymer was also studied in detail.

MATERIALS AND METHODS

Materials

CL (Acros, Belgium) and *n*-butanol (Shanghai Chemical, China) were distilled under reduced pressure prior to use. Sc(OTf)₃ was synthesized from Sc₂O₃ (Yaolong, Shanghai, China) and trifluoromethanesulfonic acid (Shanghai Ever-thriving Trading, Shanghai, China) according to the method in the literature.²⁹ The product was dried *in vacuo* (200°C/0.5 mmHg for 40 h) to give anhydrous Sc(OTf)₃. TMP (Shanghai Chemical) was recrystallized from alcohol with toluene as precipitator. Other reagents and solvents were purified by general methods.

Measurements

The intrinsic viscosities of PCLs were measured with Ubbelohde viscosimeter (Nirun Intelligent Technology Co. Ltd., Shanghai, China) in DMF at 30.0°C ± 0.1°C. ¹H NMR spectra were recorded on a Bruker Avance DMX500 spectrometer (Germany) in CDCl₃ with tetramethylsilane as internal standard. Size-

exclusion chromatographic (SEC) measurements calibrated to commercial polystyrene standards were performed on a Waters 150-C apparatus (Milford, MA) with columns: Styragel HT 3, HT 4, HT 5, and Waters 2410 RI detector in tetrahydrofuran (THF) (1.0 mL min⁻¹) at 25°C. Differential scanning calorimetry (DSC) measurements were performed on a TA Q100 apparatus (New Castle, DE). The samples were heated from 0°C to 80°C, held for 2 min to erase the thermal history, then cooled to 0°C at a rate of 20°C/min, and finally heated to 80°C at a rate of 10°C/min. The morphologies of PCLs were monitored with an Olympus BX51 (Tokyo, Japan) polarized optical microscope (POM).

Polymerizations

Polymerization was carried out in a 20-mL ampoule. The initiator, the catalyst, and the solvent were added into the container with designed amounts and aged for 15 min at 40°C before the CL monomer was injected into the ampoule. The ampoule was put into a water bath at 40°C. After the desired polymerization time, the mixture was poured into a large excess of ethanol, and the polymer precipitated from ethanol, filtered, and dried in vacuum to constant weight.

RESULTS AND DISCUSSION

Syntheses and characterizations

The syntheses of SPCLs were carried out by the ROP of CL with various molar ratios of CL,

TABLE I
Syntheses of SPCLs with Trimethylol Propane as Initiator and $\text{Sc}(\text{OTf})_3$ as Catalyst

| Run | Polymer | TMP/CL (mol %) | $\text{Sc}(\text{OTf})_3/\text{CL}$ (mol %) | $[\eta]$ (dL/g) | Conversion (%) | M_n^{Cal} (kg/mol) ^b | M_n^{NMR} (kg/mol) ^c | M_n^{SEC} (kg/mol) ^d | MWD ^d |
|-----|-------------------|-------------------|--|--------------------|-------------------|---|---|---|------------------|
| 1 | SPCL1 | 4.0 | 0.5 | 0.069 | 93.0 | 2.8 | 3.0 | 4.7 | 1.41 |
| 2 | SPCL2 | 3.0 | 0.5 | 0.081 | 98.8 | 3.9 | 4.2 | | |
| 3 | SPCL3 | 2.0 | 0.5 | 0.108 | 95.0 | 5.6 | 5.3 | 6.9 | 1.58 |
| 4 | SPCL4 | 1.0 | 0.5 | 0.155 | 88.1 | 10.2 | 10.7 | 9.4 | 1.44 |
| 5 | SPCL5 | 0.5 | 0.5 | 0.219 | 94.2 | 21.6 | 18.6 | 14.9 | 1.40 |
| 6 | ³ LPCL | 2.0 | 0.5 | 0.134 | 90.8 | 5.2 | 4.7 | | |
| 7 | SPCL6 | 2.0 | 0.1 | 0.105 | 91.2 | 5.3 | 5.1 | 6.6 | 1.41 |
| 8 | SPCL7 | 2.0 | 1.0 | 0.118 | 99.5 | 5.8 | 5.3 | 7.0 | 1.49 |

Polymerization conditions: toluene/THF (4/1), $[\text{CL}] = 1.0$ mol/L, 40°C , 72 h.

^a The LPCL was initiated by *n*-butanol.

^b Calculated from the feeding molar ratio of CL/TMP and conversion.

^c Calculated from eq. (1).

^d Measured by SEC.

$\text{Sc}(\text{OTf})_3$, and TMP in solvent (THF/toluene = 1/4) at 40°C as shown in Table I. Figure 1 exhibits the ^1H NMR spectrum of SPCL3, in which the single peak at around 4.0 ppm (H^c) shows the direct links between PCL arm and TMP core. The signal of methyl group due to TMP core (H^a) and PCL arm end-group (H^h) were also detected at 0.9 and 3.6 ppm. The intensity ratio of H^h to H^a is equal to 2. The ^1H NMR spectrum clearly demonstrated the triarm star structure of the product prepared.

The intrinsic viscosities of SPCLs (Runs 1–5, Table I) indicate the influences of CL/TMP values on the molar mass. As the amount of TMP increased, molar mass decreased. The molar mass of SPCLs can be calculated from the intensities of H^g and H^a (136 stands for the molecule weight of TMP):

$$M_n^{\text{NMR}} = \frac{I_g}{I_a} \times \frac{3}{2} \times 114 + 136 \quad (1)$$

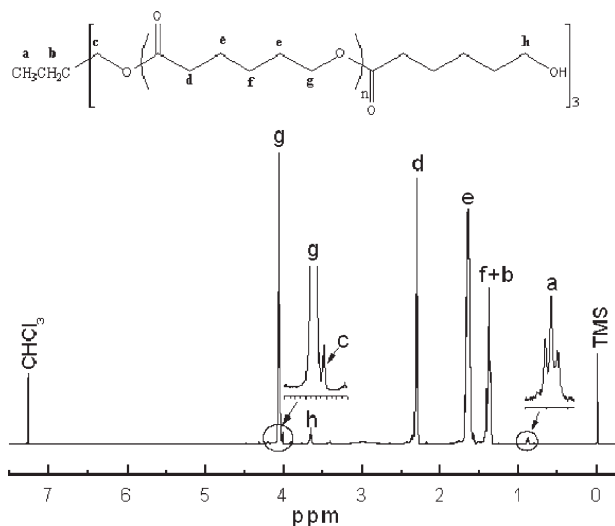


Figure 1 ^1H NMR spectrum of SPCL3.

From the data in Table I (Runs 1–5), it is clear that the molar mass obtained from ^1H NMR spectra are close to the values calculated by observed conversion and CL/TMP value. These results indicate that the molar mass of SPCLs can be well controlled by altering the molar ratio of monomer to the initiator. The SEC patterns of SPCLs were shown in Figure 2. The molar mass calibrated by polystyrene also decreased with the increase of TMP amount. The back biting reaction during the polymerization process may lead to rather broad molar mass distributions.^{19–21,30,31}

As a comparison, LPCL was also prepared using *n*-butanol as initiator under similar conditions (Run 6, Table I). The molar mass of LPCL is calculated by a similar method. LPCL and SPCL3 have similar molar mass, but the viscosity of LPCL is significantly higher than SPCL3's, which also verifies the star

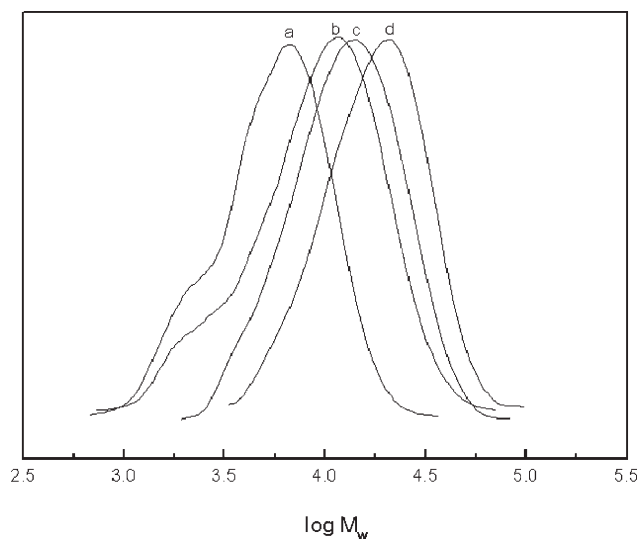


Figure 2 SEC curves of SPCL1 (a), SPCL3 (b), SPCL4 (c), and SPCL5 (d).

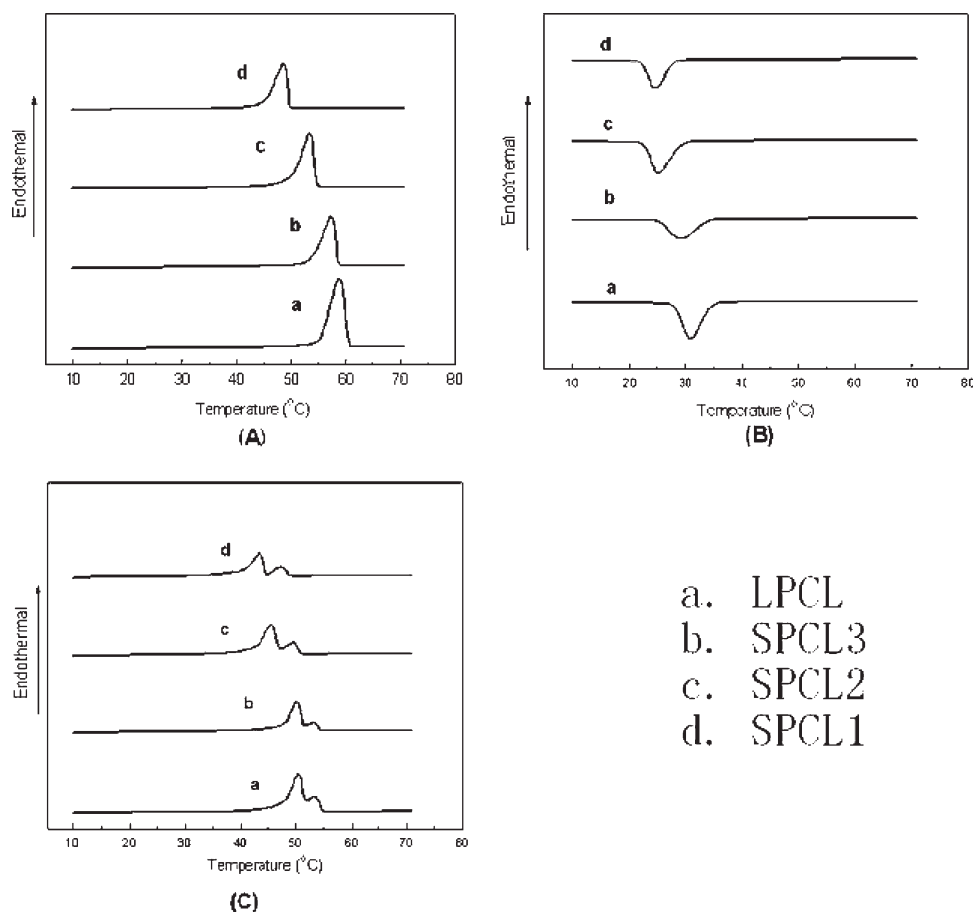


Figure 3 The DSC curves of LPCL (a), SPCL3 (b), SPCL2 (c), SPCL1 (d); first heating run (A), cooling run (B), and second heating run (C).

architecture of the products prepared. The value of g' was defined to be the viscosity ratio of star polymer to linear polymer, having the same molar mass:

$$g' = \frac{[\eta]_{\text{star}}}{[\eta]_{\text{liner}}} \quad (2)$$

According to review by Douglas et al.,³² g' could be calculated by the arm number (f) of star polymer from following equation:

$$g' = \left(\frac{3f-2}{f^2}\right)^{0.58} \frac{1-0.276-0.015(f-1)}{1-0.276} \quad (3)$$

In this work, SPCL3 and LPCL have similar molar mass. The g' values calculated from eqs. (2) and (3) are 0.81 and 0.83, respectively. They are very close also suggesting the triarm architecture of the products.

The feeding molar ratio of CL to TMP could control the molar mass of SPCL. As shown in Table I (Run 3, 7, 8), the $\text{Sc}(\text{OTf})_3/\text{CL}$ values ranged from 0.1 to 1.0% have no apparent influence on the yield, viscosity, and molar mass of SPCLs.

Thermal and crystallization behavior of SPCLs

DSC analyses were used to investigate the melting and crystallization behaviors of the SPCLs, while the data of LPCL was also included as a comparison. The DSC curves of the samples in the first heating run, the cooling run, and the second heating run were shown in Figure 3. The melting temperature (T_m) and the cold 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 molar mass. SPCLs having longer arm lengths show higher T_m and T_c . 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.³³ The results summarized in Table II suggest that SPCL has lower X_c than that of its linear analogue and thermal history has more effect on the X_c of SPCLs than LPCL. This may be attributed to the higher end group concentration of SPCLs.

Figure 4 displays the morphologies of SPCL1, SPCL3, and LCPL by POM. The isothermal crystallization temperature at 45°C was chosen between T_c

TABLE II
Thermal Behaviors of SPCLs and LPCL Determined by DSC

| Run | Polymer | T_{m1} ($^{\circ}\text{C}$) ^a | T_{m2} ($^{\circ}\text{C}$) ^b | ΔH_{m1} (J/g) ^a | ΔH_{m1} (J/g) ^b | X_{c1} (%) ^a | X_{c2} (%) ^b |
|-----|---------|--|--|------------------------------------|------------------------------------|---------------------------|---------------------------|
| 1 | SPCL1 | 48.7 | 43.6 | 90.9 | 67.8 | 65.1 | 48.6 |
| 2 | SPCL2 | 53.3 | 45.8 | 95.6 | 67.4 | 68.5 | 48.3 |
| 3 | SPCL3 | 57.3 | 50.2 | 102.8 | 68.1 | 73.6 | 48.8 |
| 4 | LPCL | 58.9 | 50.5 | 118.0 | 108.6 | 84.5 | 77.8 |

^a Data from the first heating run.

^b Data from the second heating run.

and T_m for all samples. Within a rather short crystallization time (180 s), LPCL presented good spherulitic morphology and Maltese cross patterns showing a fast crystallization rate. At the crystallization time of 360 s, the spherulites enlarged significantly.

Although SPCL3 has similar molar mass with LPCL, it shows spherulite with poor morphology until a quite long crystallization time of 440 s. Its crystallization rate was apparently slower than that of LPCL. SPCL1 appeared to be more difficult

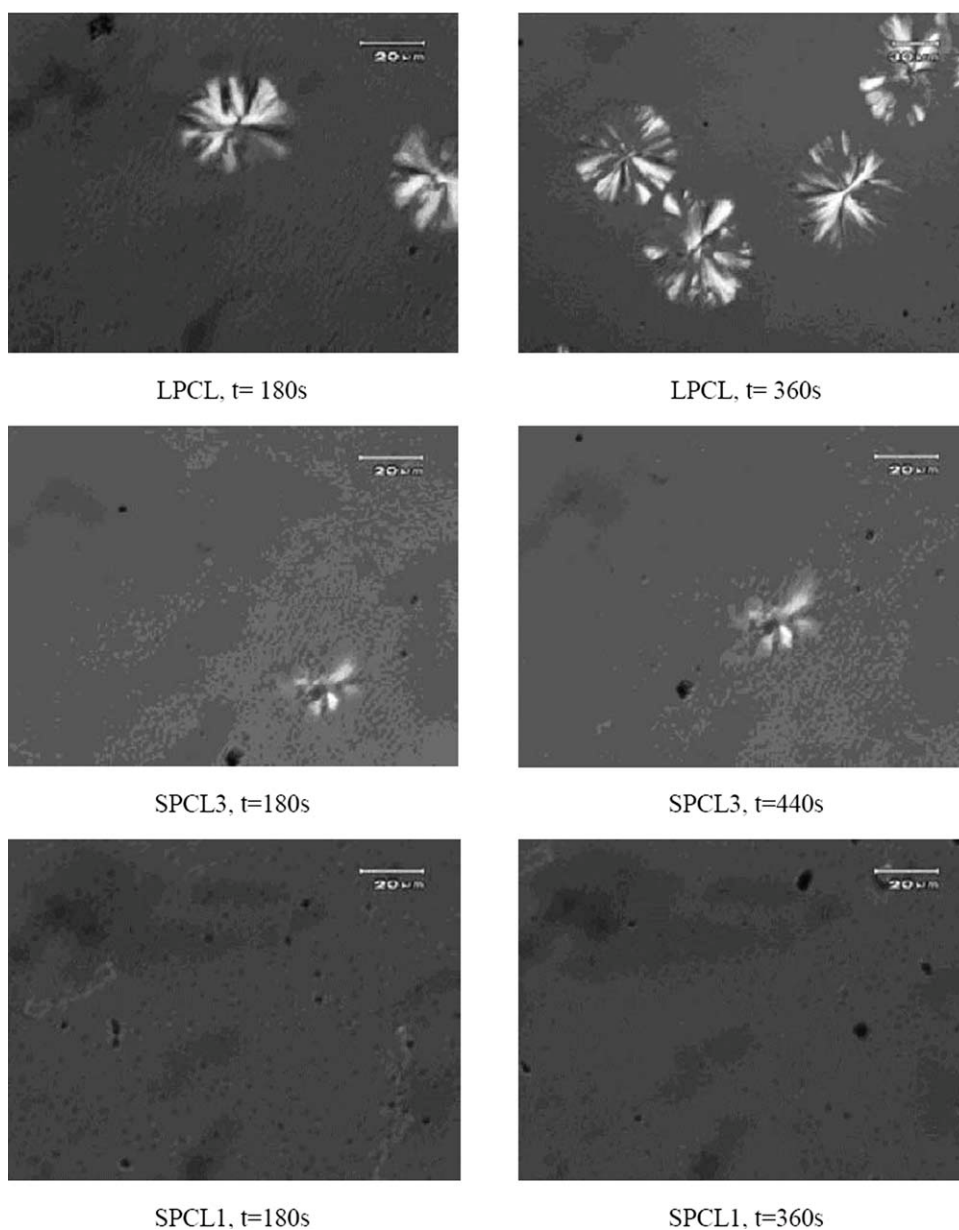


Figure 4 POM photomicrographs of PCL polymers crystallized at 45°C.

to crystallize than SPCL3 due to the decreased molar mass.

CONCLUSIONS

In this article, $\text{Sc}(\text{OTf})_3$ has been first employed as catalyst to synthesize SPCL with TMP as core molecule. The arm length of the star polymer can be controlled by adjusting the molar ratio of the monomer to the initiator. The microstructure, molar mass, thermal and crystallization behavior of the star polymers prepared were examined. $\text{Sc}(\text{OTf})_3$ and multifunctional alcohol is expected to be a new kind of moisture and air-tolerant initiating system for the ROP of lactones and lactides preparing star-shaped or hyperbranched biodegradable polymers under mild conditions. Further research work is in progress.

References

- Uhrich, K. E.; Cannizzaro, S.; Langer, R. S.; Shakesheff, K. M. *Chem Rev* 1999, 99, 3181.
- Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* 2000, 33, 689.
- Kowalski, A.; Libiszowski, J.; Biela, T.; Cypriak, M.; Duda, A.; Penczek, S. *Macromolecules* 2005, 38, 8170.
- Zhong, Z.; Dijkstra, P. J.; Brg, C.; Westerhausen, M.; Feijem, J. *Macromolecules* 2001, 34, 3863.
- La Gatta, A.; De Rosa, A.; Laurienzo, P.; Malinconico, M.; De Rosa, M.; Schiraldi, C. *Macromol Biosci* 2005, 5, 1108.
- Ko, B. T.; Lin, C. C. *Macromolecules* 1999, 32, 8296.
- Muraki, T.; Fujita, K.; Oishi, A.; Tuguchi, Y. *Polym J* 2005, 37, 847.
- Majoumo-Mbe, F.; Smolensky, E.; Lonneck, P.; Shpasser, D.; Eisen, M. S.; Hey-Hawkins, E. *J Mol Catal A Chem* 2005, 240, 91.
- Chen, H. Y.; Huang, B. H.; Lin, C. C. *Macromolecules* 2005, 38, 5400.
- Libiszowski, J.; Kowalski, A.; Duda, A. E.; Penczek, S. *Macromol Chem Phys* 2002, 203, 1694.
- Stridsberg, K. M.; Ryner, M.; Albertsson, A. C. *Adv Polym Sci* 2002, 157, 41.
- Wang, J. L.; Dong, C. M. *Macromol Chem Phys* 2006, 207, 554.
- Choi, J.; Kim, I. K.; Kwak, S. Y. *Polymer* 2005, 46, 9725.
- Wang, J. L.; Wang, L.; Dong, C. M. *J Polym Sci Part A: Polym Chem* 2005, 43, 5449.
- Dong, C. M.; Qiu, K. Y.; Cu, Z. W.; Feng, X. D. *Macromolecules* 2001, 34, 4691.
- Corbin, P. S.; Webb, M. P.; Mcalvin, J. E.; Fraser, C. L. *Biomacromolecules* 2001, 2, 223.
- Gou, P. F.; Zhu, W. P.; Ning, X.; Shen, Z. Q. *J Polym Sci Part A: Polym Chem* 2008, 46, 6455.
- Xi, X. J.; Jiang, L. M.; Ling, J.; Sun, W. L.; Shen, Z. Q. *J Appl Polym Sci* 2006, 102, 175.
- Zhu, W. P.; Chen, W.; Shen, Z. Q. *Chin J Catal* 2007, 28, 547.
- Gou, P. F.; Zhu, W. P.; Shen, Z. Q. *Acta Polym Sin* 2007, 10, 967.
- Gou, P. F.; Zhu, W. P.; Shen, Z. Q. *J Polym Sci Part A: Polym Chem* 2008, 46, 2108.
- Funabashi, M.; Kunioka, M. *Macromol Symp* 2005, 224, 309.
- Kunioka, M.; Wang, Y.; Onozawa, S. *Macromol Symp* 2005, 224, 167.
- Zhu, W. P.; Tong, X. W.; Xie, W. H.; Shen, Z. Q. *Chem J Chin Univ Chin* 2007, 28, 1186.
- Moller, M.; Kange, R.; Hedrick, J. L. *J Polym Sci Part A: Polym Chem* 2000, 38, 2067.
- Zhou, J.; Kaga, A.; Takasu, A.; Inai, Y.; Hirabayashi, T. *Polym J* 2003, 35, 757.
- Nomura, N.; Taira, A.; Tomioka, T.; Okada, M. *Macromolecules* 2000, 33, 1497.
- Nomura, N.; Taira, A.; Nakase, A.; Tomioka, T.; Okada, M. *Tetrahedron* 2007, 63, 8478.
- Kobayashi, S.; Hachiya, I. *J Org Chem* 1994, 59, 3590.
- Penczek, S.; Cypriak, M.; Duda, A.; Kubisa, P.; Slomkowski, S. *Prog Polym Sci* 2007, 32, 247.
- Zhu, W. P.; Xie, W. H.; Tong, X. W.; Shen, Z. Q. *Eur Polym J* 2007, 43, 3522.
- Douglas, J. F.; Roovers, J.; Freed, K. F. *Macromolecules* 1990, 23, 4168.
- Youan, B. B.; Benoit, M. A.; Rollmann, B.; Riveau, G.; Gillard, J. *J Microencapsul* 1999, 16, 601.