

Synthesis of Star-Shaped Poly(ϵ -caprolactone) by Samarium-Based Tetrafunctional Initiator and Its Dilute-Solution Properties

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ABSTRACT: An *in situ*-generated tetrafunctional samarium enolate from the reduction of 1,1,1,1-tetra(2-bromoisobutyryloxymethyl)methane with divalent samarium complexes [Sm(PPh₂)₂ and SmI₂] in tetrahydrofuran has proven to initiate the ring-opening polymerization of ϵ -caprolactone (CL) giving star-shaped aliphatic polyesters. The polymerization proceeded with quantitative conversions at room temperature in 2 h and exhibited good controllability of the molecular weight of polymer. The resulting four-armed poly(ϵ -caprolactone) (PCL) was fractionated, and the dilute-solution properties of the fractions were studied in

tetrahydrofuran and toluene at 30°C. The Mark–Houwink relations for these solvents were $[\eta] = 2.73 \times 10^{-2} M_w^{0.74}$ and $[\eta] = 1.97 \times 10^{-2} M_w^{0.75}$, respectively. In addition, the unperturbed dimensions of the star-shaped PCL systems were also evaluated, and a significant solvent effect was observed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 175–182, 2006

Key words: star polymers; ring-opening polymerization; fractionation of polymers divalent samarium complex; dilute-solution properties

INTRODUCTION

In recent years the synthesis of aliphatic polyesters with star architectures has attracted increasing interest from both theoretical and practical points of view.^{1–8} Methods for preparing star-shaped polymers can be divided into two categories. One is based on the reaction of the propagating end of linear polymers with appropriate terminators or crosslinking agents. The other is by the polymerization starting from multifunctional initiators, which is more promising for preparing star polymers with a well-defined number of arms. Hedrick et al.² and Qiu et al.³ reported the synthesis of star-shaped polymers from ϵ -caprolactone using multifunctional alcohols with stannous or aluminum catalysts. However, comparatively little work has been conducted on multifunctional initiation with transition-metal catalysts, especially lanthanide complexes.⁹

In a preliminary study we developed ring-opening polymerization (ROP) of lactones with *in situ*-formed samarium enolates as an initiator and synthesized star-shaped poly(ϵ -caprolactone) with a well-defined

structure under mild reaction conditions.¹⁰ The advantages of this synthetic procedure are that the initiation species was readily available from the reduction of multifunctional 2-bromoisobutyric ester with samarium(II) complexes without isolation and the initiator had satisfactory stability. The high efficiency of the samarium-based initiators for the ROP of cyclic esters may be related to the strong coordination between the propagating site and the monomer because of the characteristic oxophilicity of lanthanide metals.

This article focuses on the dilute-solution property of the obtained star-shaped PCL as well as describing its polymerization features and structural characterization. The Mark–Houwink constants, K and a , and the unperturbed dimensions of these star-shaped polyesters were evaluated in toluene and tetrahydrofuran for the first time.

EXPERIMENTAL

Materials

ϵ -Caprolactone (CL; Aldrich Chemicals Co., Milwaukee, WI) was dried over calcium hydride and distilled under reduced pressure. Pentaerythritol was used after recrystallization from ethanol. Toluene (Tol) and tetrahydrofuran (THF) were dried over a benzophenone-sodium complex for 3 days and distilled prior to use. A 0.1M THF solution of SmI₂ was prepared as described previously.¹¹ Sm(PPh₂)₂ was synthesized as a dark green powder by the reaction of SmI₂ with 2 equiv of KPh₂

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(ACROS) in THF by a procedure reported previously.¹² 1,1,1,1-Tetra(2-bromo-isobutyryloxy-methyl) methane was prepared according as previously reported.¹⁰

Synthesis of star-shaped poly(ϵ -caprolactone)

The polymerization was carried out using Schlenk techniques in a dry nitrogen atmosphere. In a typical process, a solution of $\text{Sm}(\text{PPh}_2)_2$ or SmI_2 (0.1 mol/L, 0.35 mmol) was added to a dried Schlenk tube containing 1,1,1,1-tetra(2-bromo-isobutyryloxymethyl) methane (0.029 g, 0.043 mmol) at ambient temperature. After 15 min the given amount of monomer was injected into the resulting suspension, and then the mixture was stirred for a certain time. The polymerization reaction was terminated with methanol containing a small amount of hydrochloric acid. The product was then dissolved in CH_2Cl_2 and recovered by precipitation in excess methanol. Finally, the purified polymer samples were dried *in vacuo* at 30°C for 48 h.

Fractionation of PCL samples

A series of six fractions of star-shaped PCL were prepared by successive fractionation from butanone solutions with *n*-hexane as the nonsolvent according to the method of Koleske and Lundberg.¹³

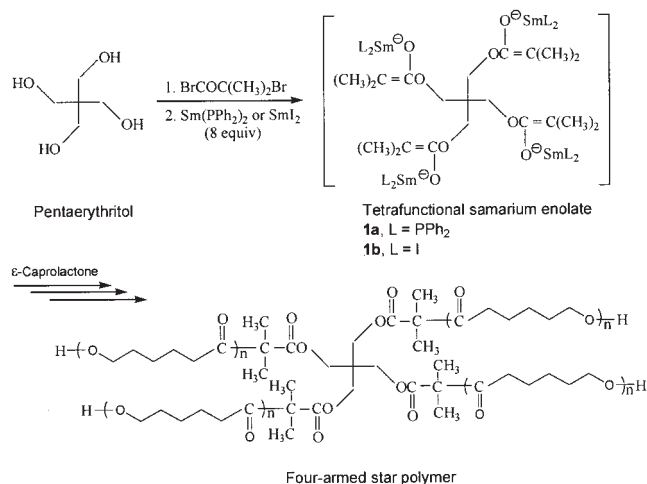
Measurements

NMR spectra were recorded on a Bruker Avance DMX-500 NMR instrument with tetramethylsilane (TMS) as an internal reference in CDCl_3 . The sample concentrations were 20–30 mg/mL for ^1H -NMR and 15–200 mg/mL for ^{13}C -NMR. Number-average molecular weights (M_n) and polydispersity indexes (M_w/M_n) were determined by gel permeation chromatography (GPC) on a Waters 208 GPC apparatus equipped with two consecutive polystyrene gel columns, ultraviolet and 18-angular light scattering detectors. Analyses were performed in THF at a flow rate of 1.0 mL/min with an injected volume of 0.5 mL. The sample concentration was about 0.2%. Differential scanning calorimetry (DSC) curves were taken on a Perkin-Elmer DSC Pyris-1 apparatus from 0°C to 80°C at a heating rate of 10°C/min. Viscosity measurements were made in THF and in toluene with an Ubbelohde type viscometer at 30°C. Intrinsic viscosity ($[\eta]$) was determined by extrapolating the plots of η_{sp}/c and $\ln(\eta_r/c)$ versus concentration (c). The correlation coefficient was greater than 0.99 for all runs.

Results and discussion

Polymerization features

Scheme 1 illustrates the synthetic procedure of four-armed PCL by the ROP of ϵ -caprolactone initiated with



Scheme 1

tetrafunctional samarium enolates. The initiator system formed *in situ* by the reduction of 1,1,1,1-tetra(2-bromoisobutyryloxymethyl)methane with $\text{Sm}(\text{PPh}_2)_2$ or SmI_2 at room temperature in THF; in this process a yellow-colored suspension appeared, indicating the formation of trivalent samarium enolates (**1a** and **1b**). After centrifugal separation, the supernatant solution of the reaction mixture was found to be active for polymerization, whereas the isolated solid was inactive. This means that the initiating species dissolved in the reaction medium. The suspension substance was probably a side product such as samarium(III) bromide, which was not harmful to the polymerization and could be removed during the purification of the polymer samples.

Table I summarizes the conditions and results of polymerization of CL with *in situ*-formed samarium enolates **1a** and **1b**. All polymerization reactions were quite fast. In fact, a complete monomer conversion was achieved within 30 min for the SmI_2 -forming samarium enolate system (**1b**). Comparatively, the **1a**-initiating polymerization proceeded somewhat slowly and hence was easier to handle (see runs 2 and 6, Table I). Furthermore, the polymer obtained by **1a** had a higher molecular weight. This may be ascribed to the relatively stable propagating species of the **1a** system because of the presence of the bulky and "soft" phosphido ligands at active sites.¹² Generally, the ligands that had better electron-donating ability and/or were sterically demanding hampered the coordination of the monomer and slowed the polymerization process.

In an attempt to determine if the polymerization system had a living character, a polymerization experiment in which monomer was added in two batches (runs 5 and 8, Table I) was conducted. It was found that the growing polymer chain was active for the further polymerization of the second batch of the monomer. Not only was a quantitative polymer yield observed after completion of the polymerization of the

TABLE I
Polymerization of ϵ -CL with *In Situ*-Formed Tetrafunctional Samarium Enolates (**1**) at Room Temperature in THF^a

Run	Samarium enolate	$[\epsilon\text{-CL}]_0$ (mol/L)	$[\epsilon\text{-CL}]_0/[1]_0$ (molar ratio)	Conv. (%)	M_w^b (10^4)	M_w/M_n^b
1	1a	4.6	1000	100	6.31	2.16
2	1a	3.3	1000	56.6	4.42	1.24
3	1a	2.5	800	100	7.20	2.15
4	1a	2.5 ^c	1200 ^d	97.5	9.72	2.04
5	1b	4.6	1000	100	4.81	1.97
6	1b	3.16	1000	100	2.52	2.64
7	1b	2.5	800	100	3.87	1.64
8	1b	2.5 ^c	1200 ^d	99	5.73	2.10

^a $[1]_0 = 0.01$ mmol/mL. Polymerization time = 2 h.

^b Determined by GPC.

^c The initial concentration of 1st batch monomer.

^d Monomer addition was done in two batches: 1st batch = 8 mmol, reaction time = 2 h; 2nd batch = 4 mmol; the total reaction time = 6 h.

second batch monomer, but also the molecular weight increased, as shown in Table I (runs 3 and 4).

Figure 1 shows the dependence of both monomer conversion and molecular weight (M_w) on the polymerization time of the **1a** initiating system at 4°C as well as the corresponding plot of M_w versus monomer conversion. As is clear from Figure 1, molecular weight and monomer conversion had a good linear relationship. These results indicated that control of the molecular weight of the polymerization system could be achieved.

The formation of a four-armed architecture was verified initially by comparing the real molecular weight [obtained from static light-scattering measurement (SLS)] of the synthesized star-shaped PCL with that of its linear homologs.¹⁰ For example, SLS measurement showed that the star-shaped and linear PCLs had molecular weights of 54,500 and 17,500, respectively,

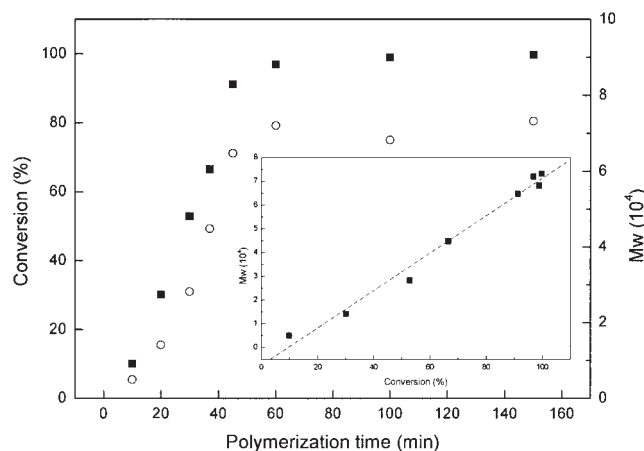


Figure 1 Dependence of the monomer conversion (■) and M_w (○) on the reaction time for the ROP of CL initiated by the tetrafunctional samarium enolate (**1a**) in THF at 4°C. The inset shows the plot of M_w versus the monomer conversion for this polymerization.

whereas the GPC technique showed their molecular weights to be similar ($M_w \approx 49,000$).

To obtain more structural information, the PCLs were analyzed by an NMR technique. ¹H-NMR proved that all the PCL arms possessed a —CH₂OH group at the terminating chain end,¹¹ which also means the initiation of polymerization with *in situ*-generated samarium enolates by ring cleavage at the O-acyl bond (see Scheme 1). The ¹³C-NMR spectrum and assignment of peaks are presented in Figure 2. In the spectrum, the intensity of signals assigned to the ϵ -oxycaproyl unit, in the middle of the PCL arms, was strong, whereas both the end ϵ -oxycaproyl unit and the core residue produced very weak signals. From

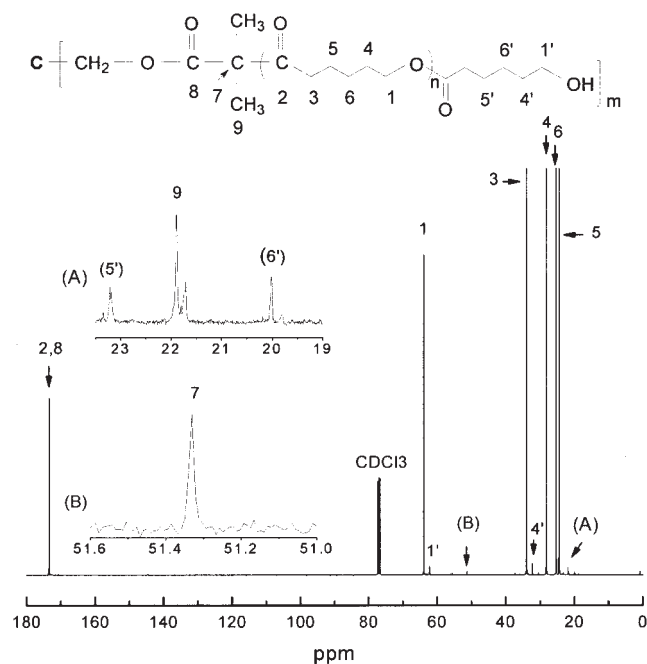


Figure 2 ¹³C-NMR spectrum of hydroxyl-terminated multiarmed PCL.

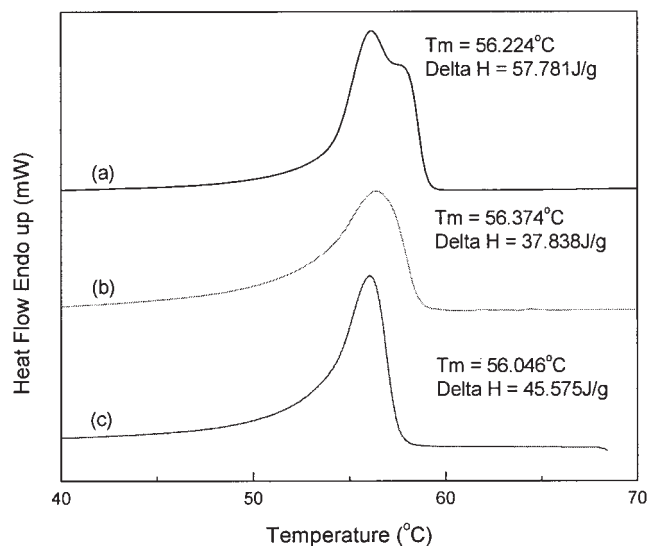


Figure 3 DSC thermogram of the star-shaped polymer of CL: (a) $M_n = 30,640$, $M_w/M_n = 1.187$; (b) $M_n = 112,450$, $M_w/M_n = 1.06$; (c) $M_n = 65,880$, $M_w/M_n = 1.288$.

comparing it to the model compound, diethyl dimethylmalonate,¹⁴ the peaks at 21.8 and 51.32 ppm were assigned to C_9 and C_7 in the initiating unit, respectively. In view of the four initiating sites in the enolate having equivalent reactivity, it would be expected that all active sites participated in the initiation reaction. Consequently, the resultant polyester should have had the desired star-shaped architecture, that is, four PCL arms with terminal hydroxyl groups, as shown in Scheme 1. The single ^{13}C -NMR signal of C_7 may provide support for this conclusion. In addition, the minor signal peaks at 23.2 and 20.1 may correspond to the C_5 and C_6 in the terminal ϵ -oxycaproyl unit.

It should be noted that the present system produced PCL with a relatively broad polydispersity (M_w/M_n), especially when higher monomer concentrations were

applied or when the monomer was added in two batches (see Table I). A possible explanation of such broad polydispersity is that the star-shaped polymer contained PCL arms of different lengths. That may be related to the rapid increase in viscosity in the initial stage of polymerization reaction.

Figure 3 shows the typical DSC traces of star-shaped PCL of different molecular weights. These samples exhibited almost same melting temperatures ($\sim 56^\circ\text{C}$) independent of their molecular weights. The lower melting temperature suggests that the crystallization behavior of the star-shaped PCL and its linear counterpart differed somewhat.⁶

Dilute-solution properties of star-shaped PCL

The hydrodynamic properties and unperturbed dimensions of linear PCL were reported several decades ago.¹³ However, to the best of our knowledge, few studies have investigated the solution properties of star-shaped PCLs, and the corresponding Mark-Houwink constants are not available in the literature. In this study, the dilute-solution properties of star-shaped PCLs with a broad and narrow molecular weight distribution, respectively, were investigated.

Table II shows the results of the experimental measurement of both polydisperse four-armed star-shaped PCL with an M_w/M_n of 1.8–2.4 and fractionated PCL with an $M_w/M_n < 1.3$. The values of the Huggins parameter, k' and $(k' + k'')$, are listed in the last columns of Table II. For the fractionated PCL (F1–F6), the Huggins constants fell in the range of 0.3–0.4, except for sample F6 in THF, indicating that the two solvents were good solvents for the star-shaped PCL. The average k' was 0.34 and 0.38 for the THF and toluene systems, respectively. In contrast, $(k' + k'')$ was close to 0.5 for the fractionated samples. Consequently, one-point determination can be used to

TABLE II
Experimental Hydrodynamic Properties for both Polydisperse and Fraction Star-Shaped Poly(ϵ -caprolactone)s at 30°C

Sample	$M_w \times 10^{-4}$	M_w/M_n	$[\eta]$ (mL/g)		k'^a		$k' + k''^a$	
			THF	Toluene	THF	Toluene	THF	Toluene
1	8.65	1.94	105.86	85.79	0.39	0.43	0.52	0.54
2	8.36	2.18	102.98	82.03	0.34	0.49	0.49	0.56
3	6.66	2.19	89.97	75.33	0.33	0.40	0.49	0.52
4	6.46	2.32	88.27	71.72	0.52	0.56	0.58	0.59
5	3.47	2.34	57.90	46.24	0.21	0.48	0.43	0.53
6	2.98	1.85	53.61	43.64	0.21	0.46	0.43	0.55
F1	11.92	1.06	142.85	127.21	0.41	0.39	0.53	0.52
F2	11.74	1.19	146.06	127.74	0.32	0.37	0.48	0.51
F3	9.20	1.25	126.43	109.00	0.38	0.40	0.51	0.52
F4	8.48	1.29	119.71	102.18	0.34	0.31	0.49	0.49
F5	5.65	1.06	87.68	76.02	0.31	0.40	0.47	0.51
F6	3.64	1.19	60.55	52.56	0.25	0.40	0.46	0.50

^a K' , Huggins parameter; K'' , the constant from Kraemer equation $\ln \eta r/c = [\eta] - K''[\eta]^2 c$.

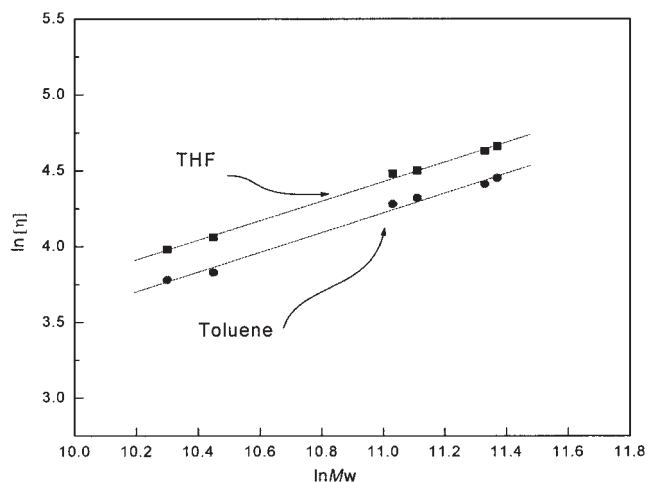


Figure 4 Intrinsic viscosity (mL/g) as a function of the molecular weight of polydisperse star-shaped PCL in THF (■) and in toluene (●) at 30°C.

estimate their intrinsic viscosity.¹⁵ For the unfractionated samples, both k' and $(k' + k'')$ showed little irregularity.

The intrinsic viscosity determined for the polydisperse star PCL at 30°C is shown as a function of molecular weight (Fig. 4). These data may be represented by eqs. (1) and (2).

$$[\eta] = 6.93 \times 10^{-2} M_w^{0.65} \quad (\text{in THF}) \quad (1)$$

$$[\eta] = 5.30 \times 10^{-2} M_w^{0.65} \quad (\text{in toluene}) \quad (2)$$

A similar plot is depicted in Figure 5 for the fractionated PCL samples, and the corresponding Mark-Houwink equations can be deduced as

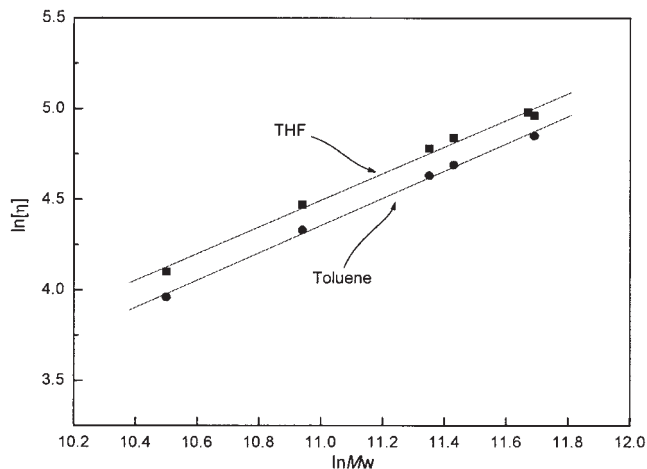


Figure 5 Intrinsic viscosity (mL/g) as a function of the molecular weight of fractionated star-shaped PCL in THF (■) and in toluene (●) at 30°C.

$$[\eta] = 2.73 \times 10^{-2} M_w^{0.74} \quad (\text{in THF}) \quad (3)$$

$$[\eta] = 1.97 \times 10^{-2} M_w^{0.75} \quad (\text{in toluene}) \quad (4)$$

Equations (1) and (2) show that the a values of the polydisperse star PCLs in both solvents were much smaller than those of the fractionated samples, although they had a similar molecular weight range (see Table II). We consider the polydispersity of molecular weight to possibly be responsible for this difference. That is, the hydrodynamic property of star-shaped PCL with a higher molecular weight was likely similar to that of its linear counterpart. However, the effect of star-shaped architecture on the hydrodynamic properties may be more pronounced for the component of the polydisperse samples with a relatively low molecular weight. Thus, the low-molecular-weight component was probably a main contributor to the decreased hydrodynamic volume of the polydisperse star PCL systems. In addition, it is noteworthy that the Mark-Houwink constant a observed in toluene almost equaled that in THF regardless of the polydisperse or fractionated samples. This suggests the PCL arms were equally flexible in toluene and in THF.

A number of graphical procedures are available for obtaining unperturbed dimensions of polymer molecules from intrinsic viscosity and molecular weight measurements in theta solvents. In general, all these methods involve determination of the constant K_θ for the expression:

$$[\eta]_\theta = K_\theta M^{1/2} \quad (5)$$

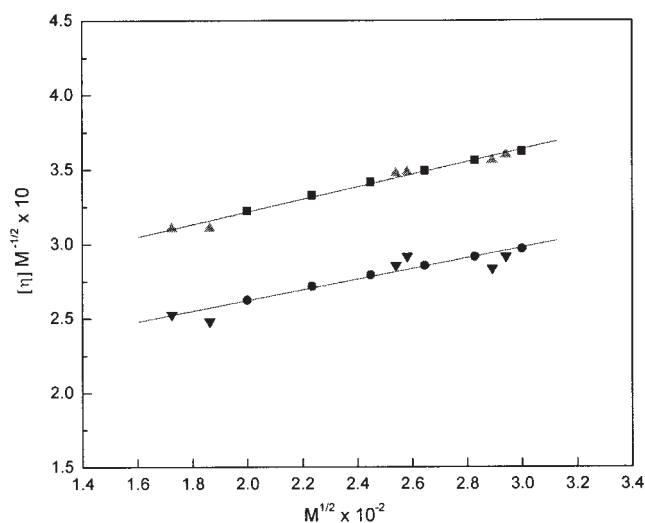


Figure 6 Plot of the Stockmayer-Fixman expression [eq. (7)] for polydisperse star PCL in THF (■) and in toluene (●) obtained with smoothed data; for comparison, the experimental data in THF (▲) and in toluene (▼) are shown.

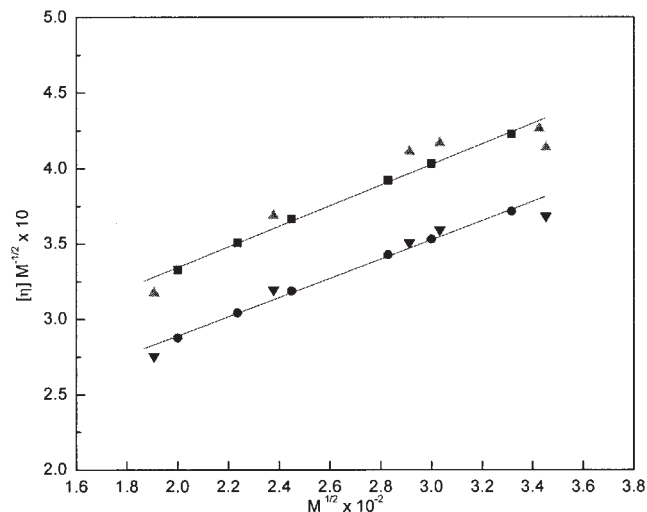


Figure 7 Plot of the Stockmayer–Fixman expression [eq. (7)] for fractionated star PCL in THF (■) and in toluene (●) obtained with smoothed data; for comparison, the experimental data in THF (▲) and in toluene (▼) are shown.

In this expression K_θ is defined as

$$K_\theta = \Phi_0 \langle r^2 \rangle_0 / M^{3/2} \quad (6)$$

where Φ_0 is the asymptotic value of the Flory constant and $\langle r^2 \rangle_0$ is the unperturbed mean-square end-to-end distance. In the calculations, the values used for Φ_0 were 2.7×10^{23} ($M_w/M_n < 1.3$) and 2.1×10^{23} ($1.8 < M_w/M_n < 2.4$) for the well-fractionated and unfractionated samples, respectively,¹⁶ where $\langle r^2 \rangle_0$ is expressed in square centimeters and $[\eta]$ is expressed in cubic centimeters per gram.

The Stockmayer–Fixman expression¹⁷ has a relatively simple form and is given by

$$[\eta]M^{-1/2} = K_\theta + 0.51\phi_0 BM^{1/2} \quad (7)$$

where B is a constant related to the specific volume of the polymer, the molar volume of the solvent, and the Flory interaction parameter. With this expression, it was possible to obtain the K_θ , with which it was pos-

TABLE III
Comparison of Calculated K_θ of Polydisperse Star and fractionated Poly(ϵ -caprolactone) from Smoothed $[\eta]$ - M Data Obtained in Two Solvents

Solvent	K_θ (mL \times mole ^{1/2} g ^{-3/2})	
	Polydisperse star PCL	Fractionated star PCL
THF	0.238	0.198
Toluene	0.191	0.162

sible to calculate $\langle r^2 \rangle_0$ through eq. (6). Furthermore, the unperturbed dimension, $[\eta]_\theta$, could be calculated using eq. (5), and the molecular expansion factor, α , could then be calculated with the following equation:

$$\alpha = ([\eta]/[\eta]_\theta)^{1/3} \quad (8)$$

To facilitate the calculations, the same expression was used on smoothed data obtained by selecting molecular weights and calculating intrinsic viscosities using eqs. (1), (2), (3), and (4). Because these values were in good agreement, it was decided to use the smoothed data for the determinations. Graphical representations of eq. (7) are shown in Figures 6 and 7, and the K_θ values obtained are summarized in Table III.

K_θ , which is an important indicator of the flexibility of a polymer coil, is also called the short-distance interaction parameter. A small K_θ indicates good flexibility for a specific polymer chain at theta conditions. As evident from Table III, the polydisperse samples had a relatively large K_θ value, which may have been a result of the low-molecular-weight fractions that had relatively poor flexibility from the presence of a star-shaped structure. This situation is similar to that discussed above. It is also notable that the K_θ values calculated for star PCL in toluene were about 20% lower than those for star PCL in THF.

Tables IV and V show the $[\eta]_\theta$, $\langle r^2 \rangle_0$, and expansion factor, α , values, which were calculated from eqs. (5), (6), and (8), respectively. It can be seen that the values of $\langle r^2 \rangle_0$ for polydisperse and fractionated star

TABLE IV
Unperturbed Dimensions of the Polydisperse Star PCL Calculated from K_θ Evaluated from Eq. (7)

$M_w \times 10^{-4}$	$[\eta]$ (mL/g) ^a		$[\eta]_\theta$ (mL/g)		α		$\langle r^2 \rangle_0 \times 10^{14}$ (cm ²)	
	THF	Toluene	THF	Toluene	THF	Toluene	THF	Toluene
4	64.43	52.51	47.60	38.20	1.11	1.11	434.80	375.49
5	74.40	60.72	53.12	42.63	1.12	1.12	540.80	468.51
6	83.68	68.37	58.18	46.69	1.13	1.14	648.96	562.21
7	92.43	75.58	62.86	50.45	1.14	1.14	757.12	655.92
8	100.74	82.45	67.18	53.92	1.14	1.15	865.28	749.62
9	100.74	89.02	71.26	57.20	1.15	1.16	973.44	843.32

^a Calculated from eqs. (1) and (2).

TABLE V
Unperturbed Dimensions of the Fractionated Star PCL Calculated from K_θ Evaluated from Eq. (7)

$M_w \times 10^{-4}$	$[\eta]$ (mL/g) ^a		$[\eta]_\theta$ (mL/g)		α		$\langle r^2 \rangle^0 \times 10^{14}$ (cm ²)	
	THF	Toluene	THF	Toluene	THF	Toluene	THF	Toluene
4	66.57	57.52	39.60	32.40	1.19	1.21	325.44	284.26
5	78.45	68.04	44.27	36.22	1.21	1.23	406.80	355.32
6	89.72	78.06	48.50	39.68	1.23	1.25	488.16	426.38
8	110.88	96.94	56.00	45.82	1.26	1.28	650.88	568.52
9	120.92	105.93	59.40	48.60	1.27	1.30	732.24	639.58
11	140.16	123.21	65.67	53.73	1.29	1.32	894.96	781.71

^a Calculated from eqs. (3) and (4).

PCLs in the two solvents differed by about 7%. The dependence of the solvent on unperturbed dimensions reflects the change in the short-range interactions of an isolated macromolecule in solution. This effect is understandable for the aliphatic polyester with flexible chains.¹⁸ The expansion factor, α , obtained in toluene was somewhat greater than that in THF for the fractionated samples, but they were of the magnitude expected for polymer molecules in good solvents.

On the basis of this observation, we concluded that the characteristic parameters of unperturbed star-shaped PCL chains are a function of the solvent. The effect of the solvent on the conformation of star PCL chains seems to be connected to the nature of the solvent as well as to the interaction of the solvent molecule with the main chain. It is remarkable that the unperturbed star PCL chains were more extended in THF, whereas in toluene both K_θ and $\langle r^2 \rangle_0$ exhibited lower values. In the latter system the interaction with the polymer chains was probably stronger.

The freely rotating state is a hypothetical state of the chain in which the bond angle restrictions are retained, but the steric hindrances to internal rotation are released. The mean-square end-to-end distance of the freely rotating chain, $\langle r^2 \rangle_{0f}$ is given by following equation:¹⁹

$$\langle r^2 \rangle_{0f} = nl^2[(1 + \cos\theta)/(1 - \cos\theta)] \quad (9)$$

TABLE VI
Steric Factors, Flexibility Parameters, and Flory's Characteristic Ratios of Star Poly(ϵ -caprolactone)s

Sample	σ^a		$A \times 10^9$ (cm) ^b		C_∞^c	
	THF	Tol	THF	Tol	THF	Tol
Polydisperse Star PCL	1.93	1.79	10.4	9.68	7.43	6.43
Fractionated Star PCL	1.67	1.56	9.02	8.43	5.59	4.88
Linear PCL ^a	1.37	—	7.99	—	4.38	—

^a $S = [\langle r^2 \rangle_0 / \langle r^2 \rangle_{0f}]^{1/2}$

^b $A = (\langle r^2 \rangle_0 / M)^{1/2}$

^c $C = \langle r^2 \rangle_0 / nl^2$

^d according to ref. 15.

where n is the number of carbon atoms in the chain, l is the bond length, and θ is the valence bond angle. According to Koleske et al.,¹³ $\langle r^2 \rangle_{0f}$ can be calculated, assuming the ester group may be counted as two carbon atoms and taking $l = 1.54 \text{ \AA}$ and $\theta = 109.5^\circ$. Then the steric factor, σ , flexibility parameter, A , and Flory's characteristic ratio, C_∞ , were readily obtained to describe the chain characteristics of star-shaped PCLs (Table VI). The corresponding data for linear PCL are listed together for comparison. Among these parameters, the Flory's characteristic ratio, C_∞ , was the most intrinsic expression for flexibility. From the results, it can be seen that the flexibility of star-shaped PCL coils was somewhat poor compared to that of their linear counterparts in the same conditions.

CONCLUSIONS

Star-shaped PCLs with a well-defined architecture were prepared by the ring-opening polymerization of ϵ -caprolactone with an *in situ*-formed multifunctional samarium enolate. The novel catalyst system exhibited high activity, and the ring-opening polymerization behaved like a quasi-living characteristic. The Mark-Houwink relations both for well-fractionated four-armed PCLs of $M_w/M_n < 1.3$ and polydisperse samples of M_w/M_n of 1.8–2.4 were established in THF and toluene, respectively. Investigation of the dilute-solution property indicated that the unperturbed dimensions of the star-shaped PCL chains had a significant solvent effect. The star-shaped PCL chains were more flexible in toluene than in THF solution, which was similar to the results for linear PCLs. However, the flexibility of the star-shaped polyester coils was somewhat poorer than that of their linear counterparts in the same conditions.

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