

## Synthesis and Characterization of Star-Branched Poly( $\epsilon$ -caprolactone)

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**ABSTRACT:** Three-dimensional star-branched poly( $\epsilon$ -caprolactone) was synthesized by combining ring-opening polymerization and “living” free-radical polymerization. The “arm-first” approach was used. In the first step the functionalized poly( $\epsilon$ -caprolactone) was synthesized as the side chains. Then a difunctional monomer, divinylbenzene (DVB), was used as end-linking agent to synthesize star-branched polymers *via* “living” free radical polymerization. The star-branched poly( $\epsilon$ -caprolactone) with divinylbenzene core was characterized by gel permeation chromatography (GPC), proton nuclear magnetic resonance (<sup>1</sup>H NMR), and differential scanning calorimetry (DSC).

**KEY WORDS** Poly( $\epsilon$ -caprolactone) / Ring-Opening Polymerization / “Living” Free-Radical Polymerization / Divinylbenzene /

The synthesis of polymers with star-like or branched architecture has attracted much attention in recent years due to their special properties that arise from three-dimensional compact shape of the macromolecules. These architectures were usually synthesized through two approaches, *i.e.*, the “arm-first” and the “core-first” methods. The “arm-first” approach involves the synthesis of the precursor arms with functional terminus followed by end-linking using a multifunctional agent. The advantage of the “arm-first” technique is that it can control the molecular structure of the arms that are usually synthesized by living anionic, cationic, and free radical polymerizations. For example, high molecular weight star-shaped polystyrenes were synthesized by living/controlled radical polymerization of styrene and subsequent linking by DVB or 1,1'-(methylene-4,1-phenylene)bismaleimide (BMI).<sup>1–4</sup>

Polycaprolactone (PCL) is an important environment-friendly polymer. Many publications deal with the macromolecular engineering of PCL.<sup>5</sup> Various star-shaped polymers containing PCL segment such as homopolycaprolactone,<sup>6,7</sup> poly( $\epsilon$ -caprolactone)-*b*-poly(DL-lactic acid-*alt*-glycolic acid),<sup>8</sup> poly[(trimethylene carbonate)-*co*-( $\epsilon$ -caprolactone)],<sup>9</sup> poly(CL-*b*-LA)<sup>10,11</sup> and multi-arm star block copolymers based on  $\epsilon$ -caprolactone<sup>12</sup> have been successfully synthesized. These star-shaped polymers were synthesized mainly by initiation of multifunctional alcohol with aluminum or stannous catalysts. These branched copolymers show some intrinsic properties (*e.g.*, high branching functionality, low viscosity and so on).

In this paper, we report the synthesis of star-branched poly( $\epsilon$ -caprolactone) possessing large number of arms. In the first step, a 2,2,6,6-tetramethylpiperidine-1-oxyl

(TEMPO)-terminated poly( $\epsilon$ -caprolactone) was synthesized as the arms. Then this kind of poly( $\epsilon$ -caprolactone) was used to initiate the polymerization of styrene and DVB to form the cores, a nucleus of polydivinylbenzene with rays of linear PCL chains. The living end of arms are capable of initiating the polymerization of a second monomer to make star-branched block copolymers.<sup>13,14</sup> The resulting star-branched PCLs have many arms, 40–50 or even more. The DSC measurement shows some special properties of the products.

### EXPERIMENTAL

#### *Materials*

$\epsilon$ -Caprolactone (Aldrich, 99%) was distilled over calcium hydride under reduced pressure before use. 2,2,6,6-Tetramethylpiperidine-1-oxyl was purchased from Acros and used as received. Divinyl benzene, benzoyl peroxide (BPO), aluminum triisopropoxide and styrene were purchased from Shanghai chemical reagent company. Divinyl benzene, styrene, and aluminum tri(isopropoxide) were distilled before use.

#### *Measurement*

The molecular weight and the polydispersity index,  $d = M_w/M_n$ , were determined by gel permeation chromatography (GPC) using three Waters Styragel columns (pore size: 10<sup>2</sup>, 10<sup>3</sup>, and 10<sup>4</sup> Å in series), in tetrahydrofuran (THF) at a flow rate of 1 mL min<sup>-1</sup> at 40 °C. The elution time was detected by a Waters 410 RI detector. The columns were calibrated by narrow polystyrene standard. <sup>1</sup>H NMR measurement was carried out on a Bruker (400 MHz) NMR instrument using CDCl<sub>3</sub> as the solvent, and tetramethylsilane (TMS) as

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the standard.

$T_m$  was obtained by DSC analysis on a NETZSCH DSC 204 instrument. The sample was cooled from 25 °C to -10 °C, and heated from -10 °C to 100 °C at a rate of 5 °C min<sup>-1</sup> to eliminate the thermal history. Then the sample was cooled to -10 °C and rescanned to 100 °C at a rate of 5 °C min<sup>-1</sup>.

#### Synthesis of TEMPO-Terminated Poly( $\epsilon$ -caprolactone)

The alcohol **1** and TEMPO-terminated PCL **2** were synthesized according to the ref 15 and 16, respectively. Alcohol **1** (138.5 mg, 0.5 mmol) was dissolved in dry toluene (10 mL) and then mixed with a solution of aluminum tri(isopropoxide) (0.27 mL in dry toluene, 0.03 mmol) in a flask, which was previously flamed and argon-purged three times. The reaction mixture was stirred at room temperature for 10 min and then evaporated to dryness. Another 10 mL toluene was injected into the flask. The mixture was then stirred for 10 min and evaporated to dryness again. Afterwards 20 mL dry toluene and 0.2 mL  $\epsilon$ -caprolactone (0.20 g, 1.8 mmol) were added to the flask respectively. The reaction mixture was stirred at 40 °C for 16 h. Then 0.25 mL acetic acid was added to the mixture to terminate the reaction. The mixture was precipitated into cold heptane, redissolved in tetrahydrofuran and reprecipitated into cold heptane to give the purified TEMPO-terminated PCL, **2**, as a white solid.

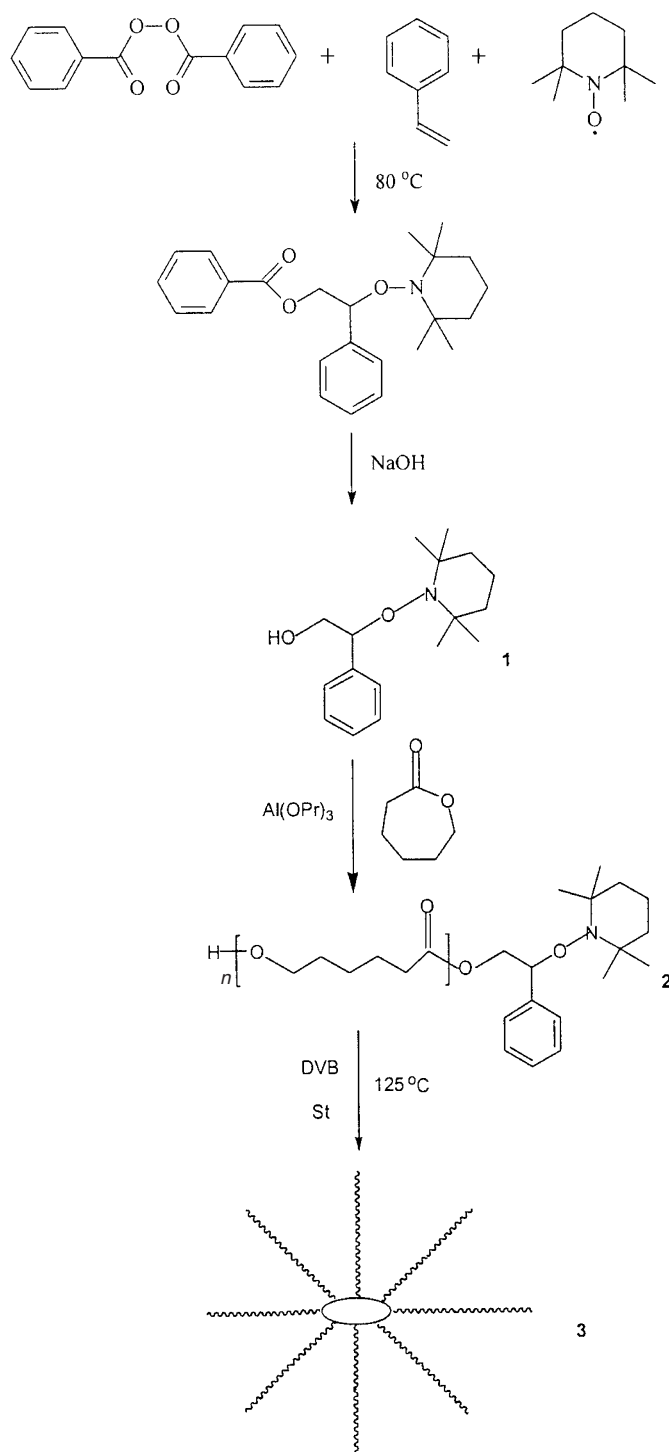
#### Synthesis of Star-Branched Poly( $\epsilon$ -caprolactone)

In a typical experiment, 0.14 g ( $3.4 \times 10^{-5}$  mol) TEMPO-terminated poly( $\epsilon$ -caprolactone), 0.077 g ( $5.9 \times 10^{-4}$  mol) DVB, 0.033 g ( $3.2 \times 10^{-4}$  mol) St and 2.8 mL xylene were added to a well-dried flask. The mixture was stirred at room temperature for 10 min. Then the mixture was added to a number of small well-dried schlenk tubes. The mixture was degassed through three freeze-pump-thaw cycles, purged by the purified argon for 15 min and then placed in an oil bath at 125 °C. The resulting polymer was precipitated into methanol to get the star-branched PCL, **3**.

## RESULTS AND DISCUSSION

The overall synthetic strategy is outlined in Scheme 1. We followed the same method used by Hawker<sup>15,16</sup> *et al.* to synthesize the alcohol **1** and TEMPO-terminated poly( $\epsilon$ -caprolactone) **2**. This structure is different from that polymeric TEMPO prepared by Yoshida *et al.* using anionic polymerization of  $\epsilon$ -caprolactone initiated by TEMPO associated aluminum alkoxide.<sup>17</sup>

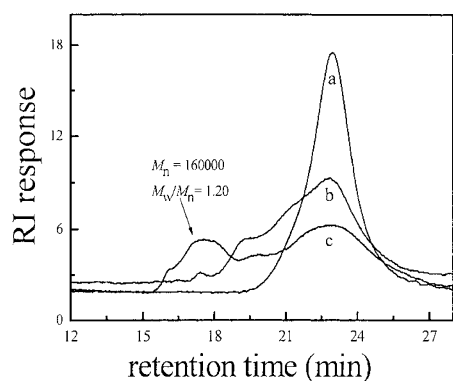
The hydroxy group in double headed initiator



**Scheme 1.**

**1** was used as the initiating center for the ring-opening polymerization of cyclic lactones. Aluminum tri(isopropoxide) was used as the promoter.<sup>18–20</sup> TEMPO-terminated poly( $\epsilon$ -caprolactone) with controlled molecular weight and low polydispersity was synthesized. Then the alkoxyamine group was utilized to initiate the nitroxide-mediated “living” free radical polymerization of vinyl monomers.

TEMPO-terminated poly( $\epsilon$ -caprolactone) was prepared at 40 °C for 16 h catalyzed by aluminum



**Figure 1.** GPC curves of TEMPO-terminated poly( $\epsilon$ -caprolactone) (a), star-branched poly( $\epsilon$ -caprolactone) at the polymerization time of 6 d (b) (Star 2 in Table I), and 15 d (c) (Star 3 in Table I).

tri(isopropoxide). For example, polymerization of 56 equiv. of  $\epsilon$ -caprolactone initiated by **1** gave poly( $\epsilon$ -caprolactone) with molecular weight of 4100 and polydispersity of 1.25.

To investigate the stability of the main chain of TEMPO-terminated poly( $\epsilon$ -caprolactone), we performed a blank experiment in which the PCL was heated in xylene at 125 °C for 12 d. No change was observed in comparison with the starting GPC curve. Therefore TEMPO-terminated poly( $\epsilon$ -caprolactone), **2**, can be used to synthesize star-branched poly( $\epsilon$ -caprolactone). The GPC curves in Figure 1 confirmed that the reaction between TEMPO-terminated poly( $\epsilon$ -caprolactone) and divinylbenzene forms a star-branched structure. The molecular weight of the star-branched polymer increased with the reaction time. For example, TEMPO-terminated poly( $\epsilon$ -caprolactone), divinylbenzene (15.0 equiv.) and styrene (8.0 equiv.) were dissolved in xylene (10 wt%) and heated at 125 °C. A star-branched poly( $\epsilon$ -caprolactone) was obtained with molecular weight of 160000 and  $M_w/M_n = 1.20$ , which corresponds to the controlled knitting of 40–50 linear chains into a single star. It is very difficult to separate the resulting star-branched polymer from the remaining PCL, which requires specially chosen size exclusion chromatography column.

The results in Table I show that the molecular weight of the resulting star polymers increases along with the reaction time and the ratio of DVB/PCL, indicating a higher incorporation ratio of the TEMPO-terminated poly( $\epsilon$ -caprolactone) as arms.

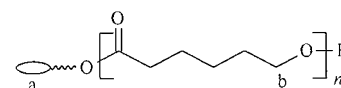
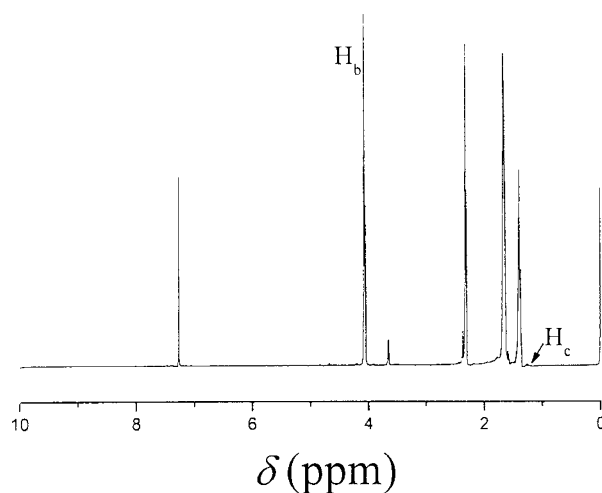
A typical  $^1\text{H}$  NMR spectrum of the TEMPO-terminated poly( $\epsilon$ -caprolactone) was shown in Figure 2a. Two small signals appeared at 1.24 and 1.29 ppm which are assigned to the methyl groups of TEMPO. The ratio of the integral areas below  $H_b$  and  $H_c$  is 9.4 : 1. The functionality of PCL chain by

**Table I.** Results from the experiments of star-branched poly( $\epsilon$ -caprolactone)<sup>a</sup>

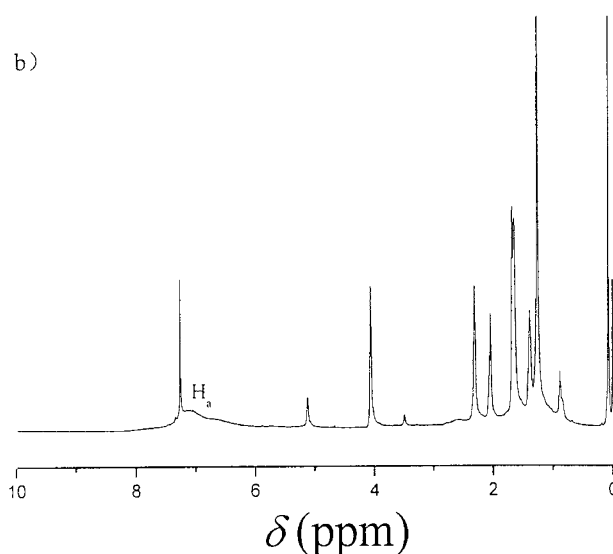
Batch	Reactant Ratio PCL/DVB/St	Reaction Time	$M_n$	$M_w/M_n$
		$d$		
Star 1	1/15/8	3	32500	1.1
Star 2	1/15/8	6	107000	1.1
Star 3	1/15/8	15	160000	1.2
Star 4	1/30/8	3	112000	1.2
Star 5	1/30/8	12	793000	1.6

<sup>a</sup>The  $M_n$  of TEMPO-terminated poly( $\epsilon$ -caprolactone) is 4100 and the polydispersity is 1.25. The values of  $M_n$  and  $M_w/M_n$  are only for the star polymer parts in GPC profiles.

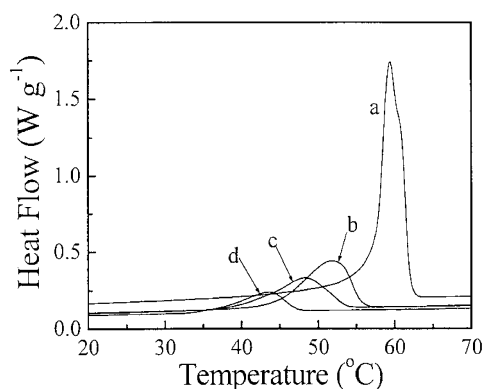
a)



b)



**Figure 2.**  $^1\text{H}$  NMR spectra of TEMPO-terminated poly( $\epsilon$ -caprolactone) (a) and star-branched poly( $\epsilon$ -caprolactone) (b) (Star 3 in Table I).



**Figure 3.** Comparison of DSC curves for a commercial homo-PCL (a), star-branched PCL (b), (c), and (d). The reaction was conducted 6 d (b), 12 d (c), and 18 d (d), respectively (Molar ratio of PCL/DVB/St = 1/17/8).

TEMPO moiety can be estimated by NMR measurement and the degree of polymerization of the arms,  $DP = 4100/114.14 \approx 36$ :

$$\begin{aligned} \text{TEMPO}\% &= DP/(12/2) \times (A_{\text{Hc}}/A_{\text{Hb}}) \\ &= 36/6 \times 9.4 \approx 56.4\% \end{aligned}$$

The formation of the star-branched architecture was confirmed by  $^1\text{H}$  NMR. In Figure 2a, the aromatic protons from trace amount of phenyl ring (e.g., from alcohol **1**) in the starting poly( $\epsilon$ -caprolactone) is negligible. However, the star polymer shows obviously signals between 7.2–7.8 ppm that come from divinyl benzene and styrene units in the product (Figure 2b).

Differential Scanning Calorimetry was utilized to investigate the melting points of linear homo-PCL ( $M_w = 53000$ ) and star-branched copolymer (Figure 3). The melting point of the star-branched poly( $\epsilon$ -caprolactone) decreases with reaction time. This could be due to the increase of PCL arm numbers. The increased arms probably disrupt the orderly pattern of the crystal. This observation is consistent with star-shaped poly( $\epsilon$ -caprolactone) synthesized by Takeshi Endo.<sup>6</sup> Accordingly, the heat of fusion ( $\Delta H_m$ ) of the star copolymer is smaller than that of homo-PCL (Table II), indicating a lower crystallinity. This is because the crystallization is disturbed by a large number of end groups and branch units within one star molecule.<sup>21</sup> There is also a gradual decrease in  $\Delta H_m$  with reaction time, due to the increase of arm numbers with reaction time.

Figure 3 also shows that the melting peak is broadened as the degree of branching increases. The same phenomena was also observed for star-shaped PEO.<sup>22</sup> It can be conjectured that at the same experimental conditions, the branching effect might be an important factor in determining the melting process. With the increase of branching arms, there may be more defects in the star-branched poly( $\epsilon$ -caprolactone), which leads to the

**Table II.** DSC results of homo-PCL and star-branched PCL

Samples	$T_m$ °C	$\Delta H_m$ J g <sup>-1</sup>
Homo-PCL	60.0	75.4
Star-PCL (6 d) <sup>a</sup>	51.8	24.8
Star-PCL (12 d) <sup>a</sup>	48.2	18.3
Star-PCL (18 d) <sup>a</sup>	43.6	10.3

<sup>a</sup>Molar ratio of PCL/DVB/St is 1/17/8.

broadening of the melting range.<sup>23</sup>

## CONCLUSION

In this paper, we report the successful synthesis of star polymers by the “arm-first” technique *via* living free radical polymerization using a preformed PCL macroinitiator in the presence of a divinyl coupling reagent, as proven by GPC,  $^1\text{H}$  NMR, and DSC. This star-branched polymer consists of a nucleus of polydivinylbenzene and rays of linear PCL chains. The resulting polymers have condensed architecture, and therefore, exhibit special physical properties such as low melting point.

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