

Functionalized Multiarm Poly(ϵ -caprolactone)s: Synthesis, Structure Analysis, and Network Formation

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ABSTRACT: The purpose of this research was to synthesize and characterize a novel class of four-arm, star-shape biodegradable polymers having double-bond functionality as a precursor for free-radical polymerization, with unsaturated monomers or macromers or photocrosslinking for network formation. The synthesis involved two basic steps. First, hydroxyl-functionalized four-arm poly(ϵ -caprolactone)s (PPCL-OH) were synthesized by the ring-opening polymerization of ϵ -caprolactone in the presence of pentaerythritol and stannous octoate. Second, double-bond-functionalized four-arm poly(ϵ -caprolactone)s (PPCL-Ma) were synthesized by reacting PPCL-OH with maleic anhydride in the melt at 130°C. Quantitative conversion of hydroxyl func-

tionality in PPCL-OH to double-bond functionality was achieved for low molecular weight PPCL-OH. Both the PPCL-OH and the PPCL-Ma were characterized by FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, SEC, and DSC. The capability of the double-bond-functionalized four-arm poly(ϵ -caprolactone)s (PPCL-Ma) to form network structures was preliminarily shown by photocrosslinking PPCL-Ma. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2296–2306, 2002

Key words: biodegradable; photocrosslinking; poly(ϵ -caprolactone)s; ring-opening polymerization; functionalization of polymers

INTRODUCTION

There has been an increased interest in star-shape polymers in recent years.^{1–8} Star-shape polymers have more than two to three linear polymeric arms attached to a center core and usually exhibit interesting properties because of their unique shape, high density, and functionality. For example, when compared to linear polymers of the same molecular weight and composition,⁹ star-shape polymers showed a smaller hydrodynamic radius and lower solution viscosity.

There are many methods to synthesize star-shape polymers. For example, amphiphilic star-shape polymers of vinyl ethers with hydroxyl or carboxylic group were synthesized by reacting linear living polymers with bifunctional vinyl compounds.^{10,11} Many reaction methods, such as chain-coupling reactions,¹² stable free-radical polymerization,¹³ living free-radical polymerization,^{14–16} and chain-transfer polymerization,^{17,18} have recently been reported.

Poly(ϵ -caprolactone)s (PCLs) are important biomedical materials because of their biodegradability, bio-

compatibility, and large molecular pore size for high permeability.^{19,20} PCLs have been widely used to make controlled-release drug-delivery devices.^{21,22} Delivery systems based on PCLs reach a longer drug-delivery time and can be decomposed into nontoxic low molecular weight species that can be metabolized by the organisms.

Star-shape poly(ϵ -caprolactone)s should be of great interest and may have significant potential in biomedical applications because of higher density of PCL per unit volume, which may be able to provide a greater degree of drug release through diffusion and biodegradation mechanisms. In our previous study,²³ we reported the synthesis and structural analysis of functionalized three-arm poly(ϵ -caprolactone)s; in that study we suggested that such three-arm poly(ϵ -caprolactone) star polymers could be used as precursors of free-radical polymerization with unsaturated monomers or macromers.

In this study, hydroxyl-terminated four-arm poly(ϵ -caprolactone)s (PPCL-OH) were synthesized by ring-opening polymerization by use of pentaerythritol as the center core. PPCL-OHs were then converted to maleic acid monoester functionalized poly(ϵ -caprolactone)s (PPCL-Ma), and the molecular weight dependency on conversion yields was examined. The chemical structure of both PPCL-OH and PPCL-Ma were studied by FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, size-exclusion chromatography (SEC), and DSC. The potential of star-shape polymers as precursors for subsequent

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free-radical polymerization with unsaturated monomers or macromers was tested by photocrosslinking PPCL-Ma to form a network structure.

EXPERIMENTAL

Materials

ϵ -Caprolactone (CL) from Aldrich Chemicals (Milwaukee, WI) was purified by drying with CaH_2 for 3 days and distilling under vacuum at 100°C . Pentaerythritol (99+%; Aldrich) was dried over P_2O_5 in vacuum at room temperature for 2 days. Maleic anhydride (99%), photoinitiator 2,2-dimethoxy-2-phenylacetophenone (99%, Aldrich), and stannous octoate (95%; Sigma, St. Louis, MO) were used without further purification. Toluene (Mallinckrodt Baker, Paris, KY) and dioxane (99.8%, anhydrous; Aldrich) were dried by refluxing over benzophenone–Na complex and distilled in an atmosphere of dry argon. Chloroform (Mallinckrodt Baker) was extracted with water for three times to remove residual alcohol, dried with anhydrous MgSO_4 overnight, and distilled in an atmosphere of dry argon. Petroleum ether (35–60°C grade; Mallinckrodt Baker) was used without purification. Borosilicate (Pyrex) pressure reaction tubes (Scientific Group, Vineland, NJ) were used for melt polycondensation.

Preparation of hydroxyl-functionalized four-arm poly(ϵ -caprolactone)s (PPCL-OH)

PPCL-OHs were synthesized by the ring-opening polymerization of ϵ -caprolactone in the presence of pentaerythritol and stannous octoate (0.1 wt % of ϵ -caprolactone) in a borosilicate pressure polymerization tube. After repeatedly vacuuming and refilling with dry argon, the polymerization tube with reactants was sealed in vacuum and reacted in an oil bath at 130°C for 48 h. The resulting raw product was dissolved in chloroform and poured gently into excess petroleum ether to precipitate PPCL-OH. After being filtered and dried, the powdery precipitates were washed with distilled water four times and dried over P_2O_5 in vacuum at room temperature until a constant weight was obtained. PPCL-OHs of different molecular weights were obtained by varying the molar feed ratio of ϵ -caprolactone monomer to pentaerythritol from 5 : 1 to 40 : 1.

A linear high molecular weight PCL was synthesized by the same method but without pentaerythritol and reducing the amount of stannous octoate to 0.05 wt % of ϵ -caprolactone. This high molecular weight PCL was used as a control for thermal property analyses.

Preparation of double-bond-functionalized four-arm poly(ϵ -caprolactone)s (PPCL-Ma)

PPCL-Ma samples were prepared by reacting hydroxyl-terminated four-arm poly(ϵ -caprolactone)s (PPCL-OH) with 5 equivalents of maleic anhydride by continuously stirring the melt at 130°C under N_2 atmosphere in a round-bottom three-neck flask for 1 day. The reaction mixture was dissolved in chloroform and the solution was gently poured into six times petroleum ether to precipitate PPCL-Ma. The powdery precipitates obtained were stirred in 500 mL of distilled water for 4 h to remove excess maleic anhydride. After filtration, the precipitates were washed four times with distilled water and dried over P_2O_5 in vacuum at room temperature to a constant weight.

Photocrosslinking of double-bond-functionalized four-arm poly(ϵ -caprolactone)s

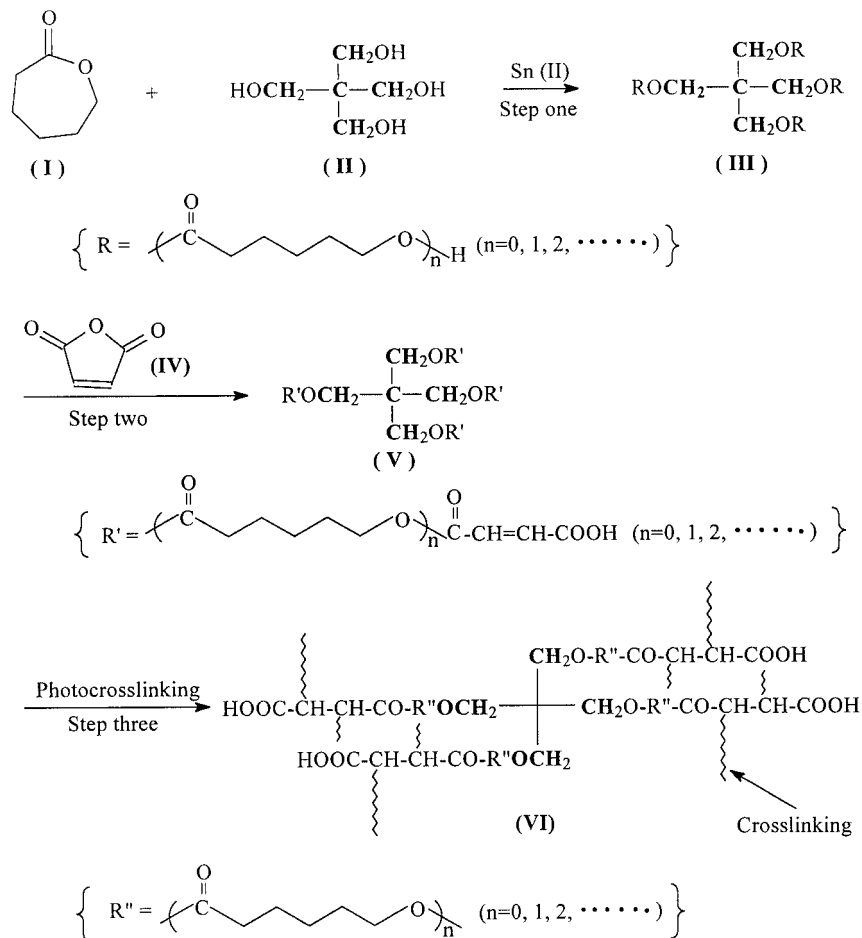
A preliminary test of the capability of double-bond-terminated four-arm PPCL-Ma to form a network structure by photocrosslinking was made. PPCL-Ma was dissolved in dioxane to make 5% w/v solution and photoinitiator [2,2'-dimethoxy-2-phenyl acetophenone (4 wt % of PPCL-Ma)] was added and stirred rapidly for a few minutes to ensure proper dissolution. The solution was then poured onto a glass plate and irradiated with 365-nm wavelength UV lamp (model UVL-18, 8 W, handheld; UVP, Upland, CA) for 5 h. The resulting film was dried in vacuum at room temperature for 1 day.

Characterization

FTIR spectra of the synthesized polymers were obtained from thin-film samples on a Nicolet Magna-IR 560 spectrometer (Nicolet Instruments, Madison, WI). Thin-film samples were prepared by casting a THF solution of a sample (1 mg/mL) onto a KBr crystal disk and further drying in a vacuum oven at room temperature overnight to remove any residual solvent. Omnic software was used for data acquisition and presentation.

^1H - and ^{13}C -NMR spectra of samples were recorded on a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) operating at 300 MHz in deuterated chloroform with tetramethylsilane (TMS) as the internal reference. The sample concentrations were 20–30 mg/mL for ^1H -NMR and 150–200 mg/mL for ^{13}C -NMR. Chemical shifts were reported in parts per million (ppm).

The SEC measurements were carried out with THF as eluent (1.0 mL/min) using a Waters 510 HPLC pump (Waters, Milford, MA), U6K injector, three PSS SDV columns (linear, 10^4 and 100 \AA) in series, and a Milton ROM differential refractometer. The sample



Scheme 1 Synthesis of double-bond-functionalized four-arm poly(ϵ -caprolactone) (IV) from ϵ -caprolactone monomer (I), pentaerythritol core (II), four-arm hydroxyl-terminated poly(ϵ -caprolactone) (III), and maleic anhydride (IV). Photocrosslinking of the double-bond-functionalized four-arm poly(ϵ -caprolactone) (IV) into four-arm poly(ϵ -caprolactone) network (VI).

concentration was 5–10 mg/mL of THF. The columns were calibrated with polystyrene standards having a narrow molecular weight distribution.

The thermal property was measured by using a differential scanning calorimeter (DSC 2920; TA Instruments, New Castle, DE) under nitrogen purging at a heating rate of 10°C/min, from -50 to 120°C . The heat of fusion (ΔH_f) was determined by integrating the normalized area of melting endotherms, and the degrees of crystallinity (χ_c) of PPCL-OH, PPCL-Ma, and its networked polymers were calculated according to the following equation:

$$\chi_c = (\Delta H_f / \Delta H_f^*) \times 100\%$$

where ΔH_f is the heat of fusion of a testing sample and ΔH_f^* is the theoretical heat of fusion of PCL (135 J/g).²⁴

RESULTS AND DISCUSSION

Scheme 1 illustrates the synthesis of the hydroxyl-functionalized four-arm poly(ϵ -caprolactone) (PPCL-

OH, III) by ring-opening polymerization of ϵ -caprolactone (I) initiated by pentaerythritol (II) with stannous octoate catalyst, the incorporation of a double bond into the chain ends of the hydroxyl-functionalized four-arm poly(ϵ -caprolactone) (PPCL-Ma, V), and the subsequent photocrosslinking of PPCL-Ma into a network of four-arm poly(ϵ -caprolactone)s (VI).

Synthesis and characterization of hydroxyl-functionalized four-arm poly(ϵ -caprolactone)s (PPCL-OH, III)

The ring-opening polymerization of ϵ -caprolactone in the presence of pentaerythritol and stannous octoate was a very effective method to synthesize the hydroxyl-terminated four-arm poly(ϵ -caprolactone). The yield was more than 95% (Table I). As described in our previous study,²³ stannous octoate was the most frequently used catalyst for the polymerization of lactone, such as ϵ -caprolactone, lactide, and glycolide, because of its high catalytic efficiency.

In the present study, pentaerythritol served two roles in the polymerization of ϵ -caprolactone. First,

TABLE I
Effect of Feed Molar Ratio on the Yield and Molecular Weight of Hydroxyl-Terminated Multiarm Poly(ϵ -caprolactone)/(PPCL-OH)

Sample	Feed molar ratio (CL/OH) ^a	Yield (%)	M_n^b ($\times 10^3$)	M_w^b ($\times 10^3$)	M_p^b ($\times 10^3$)	Polydispersity (M_w/M_n)
PPCL-OH-1 ^c	5/1	95.7	4.29	5.99	6.07	1.40
PPCL-OH-2 ^c	10/1	96.9	7.23	10.6	11.0	1.45
PPCL-OH-3 ^c	20/1	96.4	17.3	24.1	24.3	1.39
PPCL-OH-4 ^c	40/1	96.6	28.9	41.3	40.5	1.43
PCL ^d	—	98.9	108	268	139	2.48

^a CL/OH means the molar ratio of ϵ -caprolactone monomer to hydroxyl group. CL/OH = 4 \times mole of ϵ -caprolactone/mole of pentaerythritol.

^b M_n and M_w are the number-average and weight-average molecular weights, respectively, and were determined by GPC with PS standards. M_p stands for the molecular weight at the top of the highest peak on the GPC trace.

^c Synthesized by the ring-opening polymerization of ϵ -caprolactone in the presence of pentaerythritol and stannous octoate.

^d Linear poly(ϵ -caprolactone) synthesized by the ring-opening polymerization of ϵ -caprolactone using stannous octoate as catalyst and absence any alcohol.

pentaerythritol controls the number of arms of star-shape polymers and becomes the core of the four-arm PPCL-OH. Hydroxyls of pentaerythritol and stannous octoate form a complex alcohol-catalyst system.^{25,26} This complex formation with hydroxyls made the chain growth of ϵ -caprolactone much easier. Second, pentaerythritol also controls the molecular weight of PPCL-OH by its feed molar ratio to ϵ -caprolactone monomer (Table I). The molecular weight of PPCL-OH increased with an increase in the molar feed ratio of pentaerythritol to ϵ -caprolactone. The desirable molecular weight of PPCL-OH could be obtained by varying the feed molar ratio. For example, as the feed molar ratio of ϵ -caprolactone (CL) to the hydroxyl group (OH) of pentaerythritol increased 8 times (from 5 : 1 for PPCL-OH-1 to 40 : 1 for PPCL-OH-4), the number-average molecular weight of PPCL-OH increased 6.8 times (from 4290 of PPCL-OH-1 to 28,900 of PPCL-OH-4).

The FTIR spectra of PPCL-OH-1 and PPCL-OH-4 are shown in Figure 1. There was no distinct difference in FTIR spectra between PPCL-OH-1 and PPCL-OH-4, except the broad peak from 3060 to 3570 cm^{-1} , for hydroxyls. The intensity of the OH peak of PPCL-OH-1 was slightly stronger than that of PPCL-OH-4, which was attributed to the reduction in the relative content of the hydroxyl groups in the pentaerythritol core of PPCL-OH-4 because of its higher molecular weight ($M_w = 41,300$), compared to that of PPCL-OH-1 ($M_w = 5990$), attained at a higher CL/OH feed molar ratio (i.e., more hydroxyl groups in pentaerythritol reacted with CL monomers at such a high feed molar ratio). The other main absorption peaks were assigned as follows: 2945 and 2866 cm^{-1} for the CH_2 stretching; 1725 cm^{-1} for the stretching of carbonyl; 1246 and 1195 cm^{-1} for the C—O stretching.

The $^1\text{H-NMR}$ spectra of PPCL-OH in CDCl_3 are shown in Figure 2 and peaks were assigned as follows. Chemical shifts (in ppm): 3.94–4.12 (H_1 and H_2); 3.64–

3.69 (H_1 , for the end group of PCL arms); 3.44–3.49 (H_2 , for the methylene adjacent to the residual hydroxyl group of pentaerythritol); 2.15–2.05 (H_3); 1.51–1.76 (H_4 and H_5); 1.27–1.47 (H_6). The $-\text{CH}_2\text{-OH}$ end groups of PCL arms were always found in all PPCL-OHs at 3.64–3.69 ppm, and the intensity of this peak decreased with an increase in the feed molar ratio of CL to OH (Fig. 2, spectra a–d). The residual hydroxyl groups of pentaerythritol in PPCL-OH (3.44–3.49 ppm for H_2) could always be observed over the entire range of the feed molar ratio of CL/OH (5 : 1 to 40 : 1),

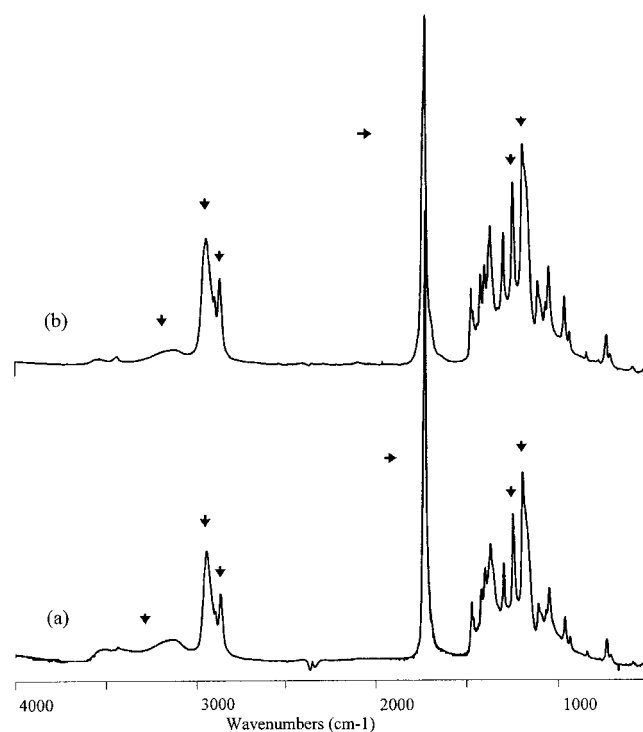


Figure 1 FTIR spectra of hydroxyl-terminated multiarm poly(ϵ -caprolactone) (PPCL-OH): (a) PPCL-OH-1; (b) PPCL-OH-4.

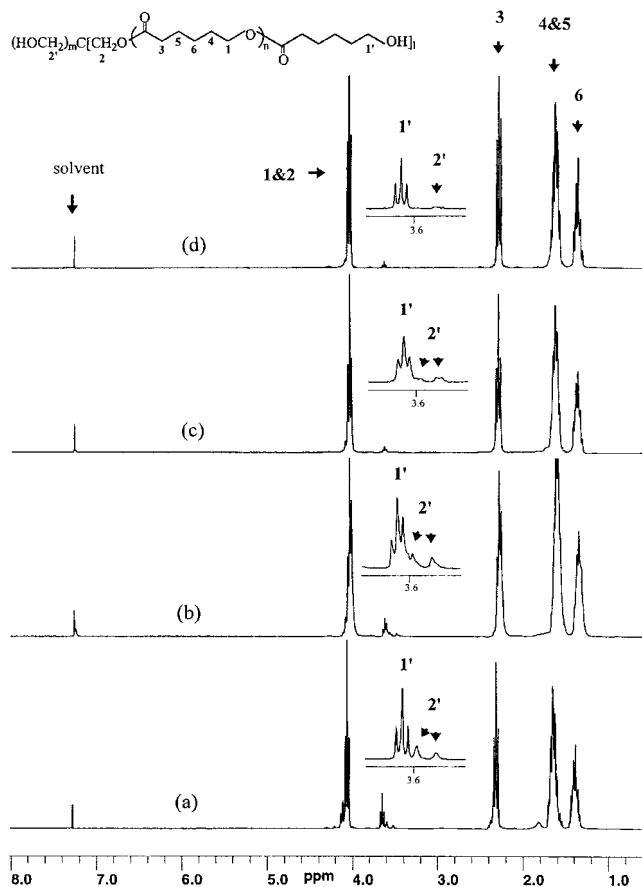


Figure 2 $^1\text{H-NMR}$ spectra (in CDCl_3) of hydroxyl-terminated multiarm poly(ϵ -caprolactone) (PPCL-OH): (a) PPCL-OH-1; (b) PPCL-OH-2; (c) PPCL-OH-3; (d) PPCL-OH-4.

although they decreased with increases in the feed molar ratio of CL/OH (Table II; e.g., from 28.8 to 7.3%). These data indicate that even at a feed molar ratio of ϵ -caprolactone monomer to pentaerythritol as high as 40 : 1, it was difficult to convert all of the four hydroxyls of pentaerythritol to the PCL arms. Such a difficulty is illustrated by the presence of the trace

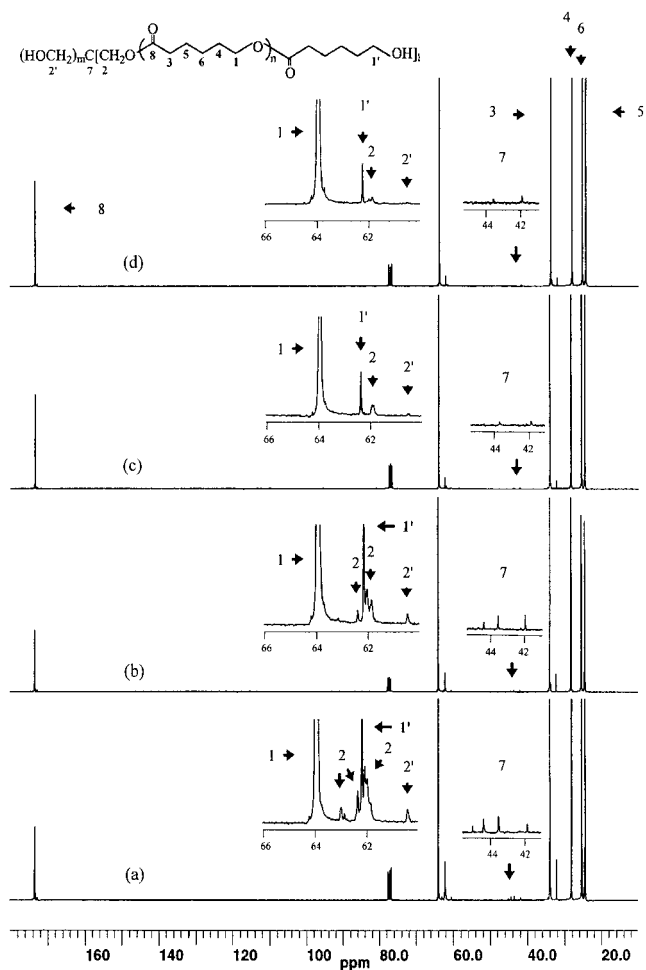


Figure 3 $^{13}\text{C-NMR}$ spectra (in CDCl_3) of hydroxyl-terminated multiarm poly(ϵ -caprolactone) (PPCL-OH): (a) PPCL-OH-1; (b) PPCL-OH-2; (c) PPCL-OH-3; (d) PPCL-OH-4.

proton signals from the free $-\text{OH}$ groups of the core material (pentaerythritol).

The $^{13}\text{C-NMR}$ spectra of PPCL-OH are shown in Figure 3 and peaks were assigned as follows: the

TABLE II
Relationship of the Feed Molar Ratio and the Residual Hydroxyls of Pentaerythritol in Hydroxyl-Terminated Multiarm Poly(ϵ -caprolactone) (PPCL-OH)

Sample	Feed molar ratio (CL/OH) ^a	Molar ratio of α/β ^b	Residual hydroxyls of pentaerythritol (%)
PPCL-OH-1 ^c	5/1	2.47/1	28.8
PPCL-OH-2 ^c	10/1	3.19/1	23.9
PPCL-OH-3 ^c	20/1	4.51/1	19.1
PPCL-OH-4 ^c	40/1	12.69/1	7.3

^a CL/OH means the molar ratio of ϵ -caprolactone monomer to hydroxyl group. CL/OH = 4 \times mole of ϵ -caprolactone/mole of pentaerythritol.

^b α is the PCL arm end group $-\text{CH}_2\text{OH}$; β is the residual hydroxyl group $-\text{CH}_2\text{OH}$, and the ratio α/β was calculated according to the integrated areas of $\text{H}_{1'}$ and $\text{H}_{2'}$ in the $^1\text{H-NMR}$ spectra.

^c Synthesized by the ring-opening polymerization of ϵ -caprolactone in the presence of pentaerythritol and stannous octoate.

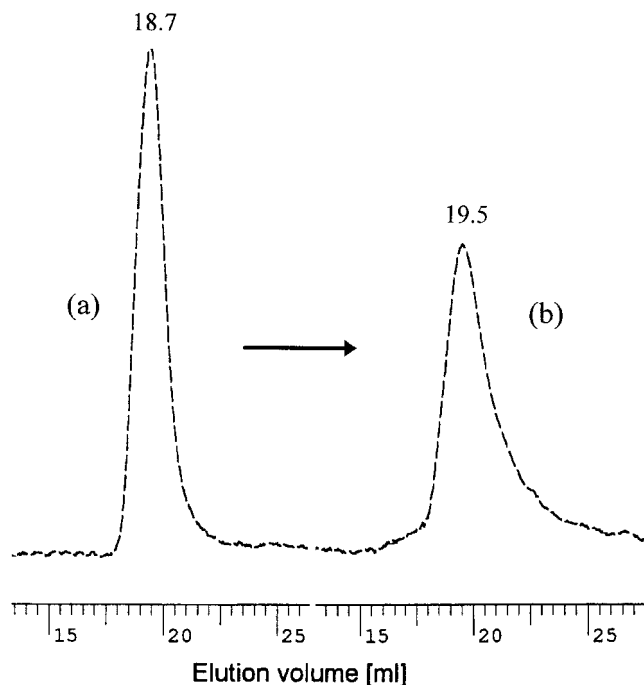


Figure 4 Size-exclusion chromatograph of hydroxyl-terminated multiarm poly(ϵ -caprolactone) (PPCL-OH) and double-bond-functionalized multiarm poly(ϵ -caprolactone) (PPCL-Ma): (a) PPCL-OH-4; (b) PPCL-Ma-4.

multipeaks at 172.69–174.05 ppm for carbon 8 (C_8); 33.93 ppm for C_3 (not the end ϵ -oxycaproyl unit); 32.18 ppm for C_3 (the end ϵ -oxycaproyl unit of PCL arms); 28.18 ppm for C_4 ; 25.37 ppm for C_6 ; 24.40 ppm for C_5 .

Because of the different number of PCL arms attached to pentaerythritol core (different type of pentaerythritol carbons), the signal of the carbonyl carbon C_8 of ϵ -oxycaproyl unit adjacent to these pentaerythritol carbons showed as small peaks between 172.69 and 174.05 ppm.

Although the ^{13}C signals of the ϵ -carbon (C_1) in the ϵ -oxycaproyl unit were in the same region of the methylene carbon in pentaerythritol, they still could be assigned by comparing the data with the ^{13}C -NMR

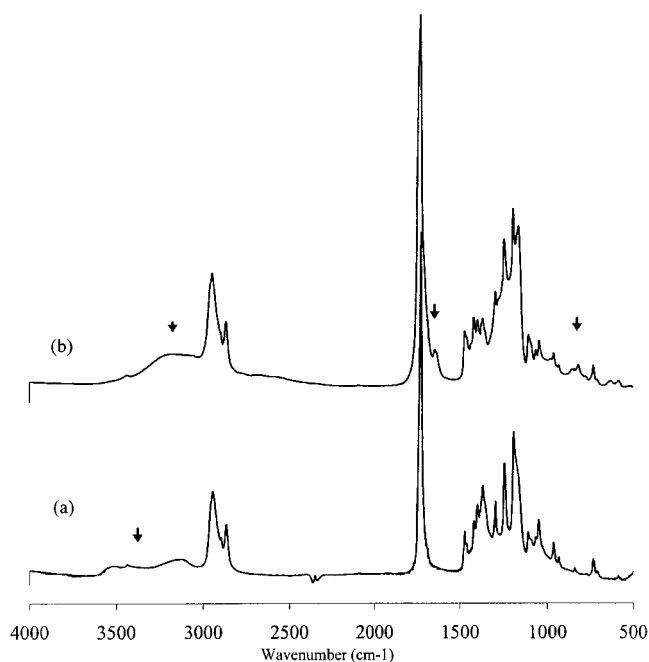


Figure 5 FTIR spectra of hydroxyl-terminated multiarm poly(ϵ -caprolactone) (PPCL-OH) and double-bond-functionalized multiarm poly(ϵ -caprolactone) (PPCL-Ma): (a) PPCL-OH-1; (b) PPCL-Ma-1.

spectrum of a linear hydroxyl-terminated poly(ϵ -caprolactone).²³ The strong peak at 63.96 ppm was assigned to the ϵ -carbon C_1 in the ϵ -oxycaproyl unit located in the middle of the PCL arm, whereas the peak at 62.18 ppm was assigned to the ϵ -carbon C_1' in the ϵ -oxycaproyl unit located at the end of the PCL arm.

It could be expected that ^{13}C -NMR signals of C_2 and C_7 of pentaerythritol in PPCL-OHs were closely related to the feed molar ratio of ϵ -caprolactone monomer to pentaerythritol. It is possible that one, two, or even three hydroxyl groups of pentaerythritol in PPCL-OH may remain unreacted over such a wide range of the feed molar ratio of the CL to OH. The C_2 ,

TABLE III
Range of Molecular Weight of Double Bond-functionalized Multiarm Poly(ϵ -caprolactone) (PPCL-Ma) Prepared from Hydroxyl-Terminated Multiarm poly(ϵ -caprolactone) (PPCL-OH) and Maleic Anhydride

Sample	PPCL-OH ^a		Sample	PPCL-Ma ^a	
	M_n^b ($\times 10^3$)	Polydispersity (M_w/M_n)		M_n^b ($\times 10^3$)	Polydispersity (M_w/M_n)
PPCL-OH-1	4.29	1.40	PPCL-Ma-1	3.52	2.27
PPCL-OH-2	7.23	1.45	PPCL-Ma-2	5.11	2.67
PPCL-OH-3	17.3	1.39	PPCL-Ma-3	9.51	2.86
PPCL-OH-4	28.9	1.43	PPCL-Ma-4	11.7	2.94

^a The left column is the original polymer PPCL-OH and the right column is the corresponding produced polymer PPCL-Ma (e.g., the polymerization of ϵ -caprolactone in the presence of PPCL-OH-1 and stannous octoate produced corresponding PPCL-Ma-1).

^b M_n and M_w are the number-average and weight-average molecular weights, respectively, and were determined by GPC with PS standards.

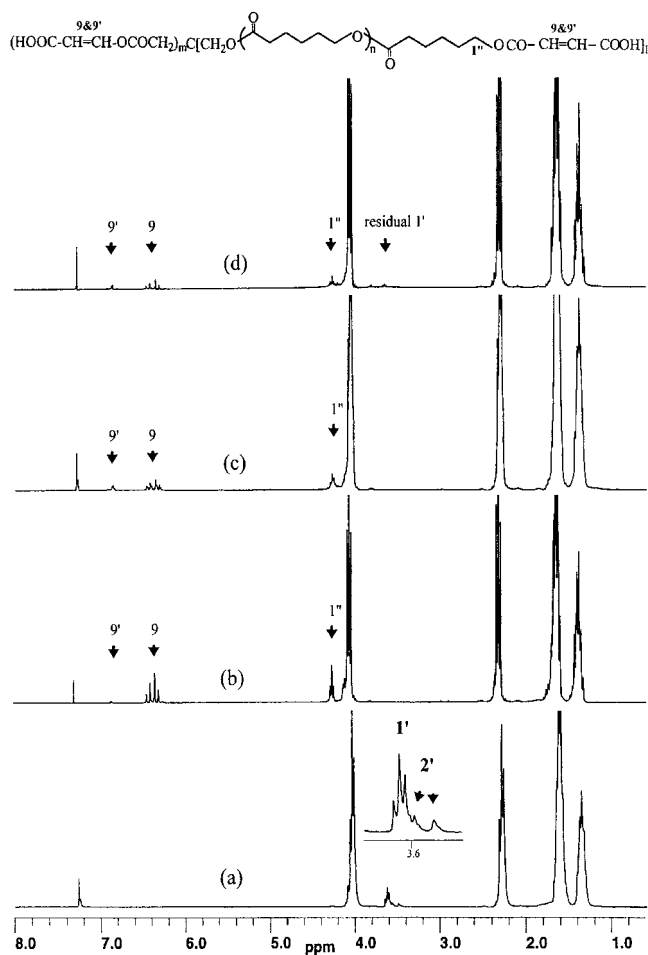


Figure 6 ^1H -NMR spectra (in CDCl_3) of hydroxyl-terminated multiarm poly(ϵ -caprolactone) (PPCL-OH) and double-bond-functionalized multiarm poly(ϵ -caprolactone) (PPCL-Ma): (a) PPCL-OH-2; (b) PPCL-Ma-2; (c) PPCL-Ma-3; (d) PPCL-Ma-4.

of these residual hydroxyl groups (Fig. 3) were detected at 60.45 ppm in all samples, but their intensity decreased consistently with increases in the feed molar ratio of CL to OH to reach a trace value at the 40 : 1 feed molar ratio.

The C_7 peak gave interesting information, as shown at the right appurtenance in Figure 3. The number of peaks of C_7 decreased with increases in the feed molar ratio of CL to OH; PPCL-OH-1 had four C_7 peaks, PPCL-OH-2 and PPCL-OH-3 had three peaks, and PPCL-OH-4 had only two peaks. Because one peak stands for one type of C_7 , PPCL-OH-1 had four types of C_7 (i.e., PPCL-OH-1 has all four possible structures of four-, three-, two-, and one-arm PPCL-OHs). The four peaks from high to low field represented these four types of PPCL-OH-1, respectively. The four-arm PPCL-OH-1 appeared to be the most abundant because its signal at 43.49 ppm was the strongest in the ^{13}C -NMR spectrum. When the feed molar ratio of CL/OH increased to 10 : 1, more than two hydroxyls

of the $-\text{CH}_2\text{OH}$ in pentaerythritol took part in the reaction, to produce two-, three-, and four-arm PPCL-OHs (Fig. 3, spectrum b). The four-arm PPCL-OH-2 had the highest fraction in PPCL-OH-2. When the feed molar ratio of CL/OH increased to 40 : 1, more than three hydroxyls in pentaerythritol took part in the reaction with ϵ -caprolactone to produce mainly three- and four-arm PPCL-OH-4 (Fig. 3, spectrum d).

Synthesis and characterization of PPCL-Ma

Double-bond-functionalized four-arm poly(ϵ -caprolactone)s were prepared by reacting hydroxyl-functionalized poly(ϵ -caprolactone)s (PPCL-OH) with maleic anhydride in the melt (Scheme 1, step two). The hydroxyl end groups (and possibly the free hydroxyls of the $-\text{CH}_2\text{OH}$ in pentaerythritol) were esterified and converted to maleic acid and monoesters.

The reaction of maleic anhydride with the hydroxyl end groups of the PCL arms appeared, on the basis of SEC data, to cause some chain breakages of PCL arms. An example of SEC data is shown in Figure 4, in which the SEC traces of both the original polymer PPCL-OH-4 and the corresponding product PPCL-Ma-4 clearly indicate some fragmentations of PCL chains. The elution time shifted from 18.7 min for PPCL-OH-4 to 19.5 min for PPCL-Ma-4, with a corresponding reduction in molecular weight from 28,900 to 11,700. The

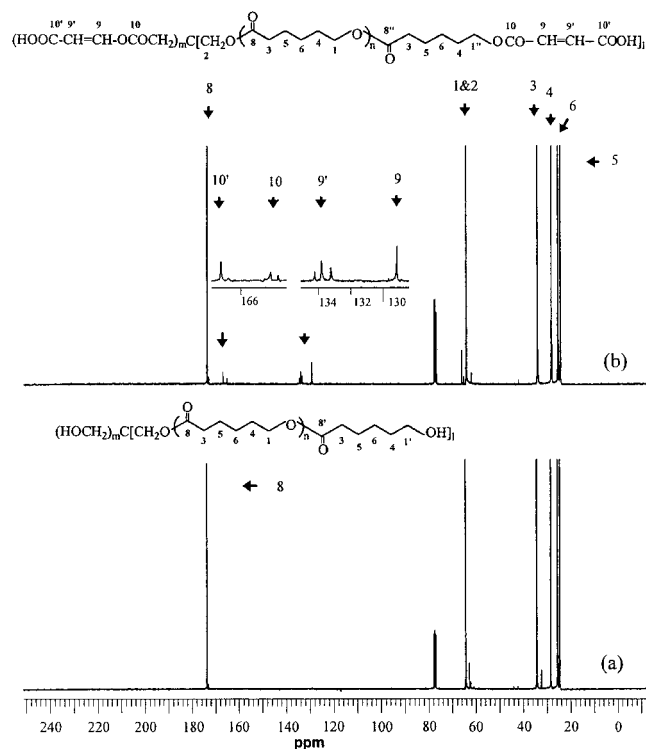


Figure 7 ^{13}C -NMR spectra of hydroxyl-terminated multiarm poly(ϵ -caprolactone) (PPCL-OH) and double-bond-functionalized multiarm poly(ϵ -caprolactone) (PPCL-Ma): (a) PPCL-OH-3; (b) PPCL-Ma-3.

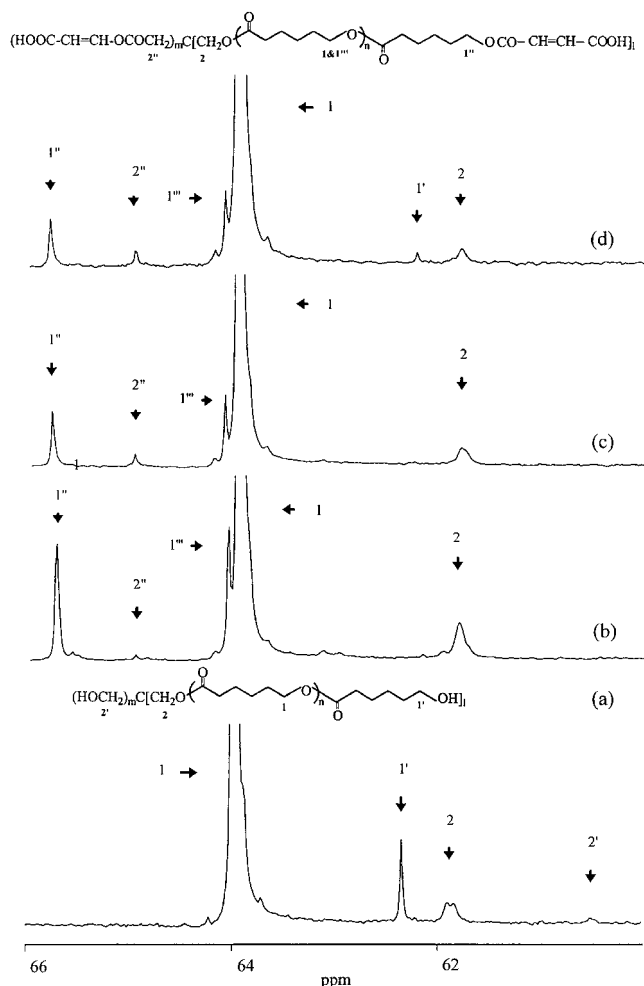


Figure 8 ^{13}C -NMR spectra at the C_1 and C_2 regions of hydroxyl-terminated multiarm poly(ϵ -caprolactone) (PPCL-OH) and double-bond-functionalized multiarm poly(ϵ -caprolactone) (PPCL-Ma): (a) PPCL-OH-3; (b) PPCL-Ma-2; (c) PPCL-Ma-3; (d) PPCL-Ma-4.

molecular weight distribution also became broader, from 1.43 for PPCL-OH-1 to 2.94 for PPCL-Ma-1 (see Table III).

In the FTIR spectra of PPCL-Ma-1 (Fig. 5), the original broad band for the hydroxyl absorption (3430 to 3570 cm^{-1}) in PPCL-OH disappeared because of the incorporation of a maleic monoester unit. Meanwhile, the new broad peak at 2830 – 3420 cm^{-1} for the carboxylic acid appeared. Double-bond stretches were also observed at 1645 and 821 cm^{-1} . Other double-bond absorption of PPCL-Ma at 3025 – 3085 cm^{-1} was masked by the absorption of CH_2 .

The ^1H -NMR spectra of PPCL-Ma are shown in Figure 6. A comparison of the spectra with Figure 2 (^1H -NMR spectra of PPCL-OHs) clearly indicates that the incorporation of a maleic acid segment into the PCL chain ends led to the disappearance of $\text{CH}_2\text{-OH}$ end group peaks at 3.64 – 3.69 ppm ($\text{H}_{1'}$) and the appearance of a new peak for the ϵ -hydrogen of the

terminal ϵ -oxycaproyl unit adjacent to the maleic monoester group ($\text{H}_{1''}$) at 4.22 – 4.34 ppm (Fig. 6, spectra b–d). Meanwhile, the signals for double-bond hydrogens (H_9) at 6.27 – 6.48 ppm further illustrated the incorporation of maleic acid segments onto the ends of the PCL arms in PPCL-OH. Another signal for double-bond hydrogens at 6.80 – 6.93 ppm was found. As discussed in our previous study,²³ this signal was assigned to the double-bond hydrogens, $\text{H}_{9'}$, in the fumaric acid monoester produced by the rearrangement reaction of the maleic acid group.

In Figure 6, spectra a and b, the $\text{H}_{2'}$ signals at 3.44 – 3.49 ppm (the residual hydroxyls of $\text{CH}_2\text{-OH}$ in pentaerythritol in PPCL-OH) completely disappeared, indicating that the residual hydroxyls of $\text{CH}_2\text{-OH}$ in pentaerythritol in PPCL-OH were also converted to maleic monoester acid.

Peaks at 3.64 – 3.69 ppm for $-\text{CH}_2\text{-OH}$ end groups of the PCL arms in PPCL-OH (Fig. 6, spectra b and c versus spectrum a) completely disappeared by conversion to the maleic monoester acid when the molecular weight of PPCL-OH was low, such as PPCL-OH-1 and PPCL-OH-2. Higher MW PPCL-OH (e.g., PPCL-OH-4), however, exhibited the residual $\text{H}_{1'}$ peaks at 3.64 – 3.69 ppm (Fig. 6, spectrum d; i.e., the presence of a free $-\text{CH}_2\text{-OH}$ end group in the PCL arms). This incomplete reaction is attributed to the very high viscous reaction mixture for higher molecular weight PPCL-OH at the reaction temperature of 130°C . For example, 18% of the hydroxyl groups of the PCL arms of PPCL-OH-4 remained unreacted.

In our previous study²³ the $-\text{CH}_2\text{-OH}$ end groups of PCL arms reacted with maleic anhydride considerably easier than did the polylactide end group $-\text{CH}(\text{CH}_3)\text{OH}$. Under the same reaction condition, 54% of the terminal $-\text{CH}(\text{CH}_3)\text{OH}$ end group of polylactide remained unreacted.

An example of the ^{13}C -NMR spectrum of PPCL-Ma (PCL-Ma-3) is shown in Figure 7. The double-bond signals for the maleic acid monoesters (carbons C_9 and $\text{C}_{9'}$, C_{10} and $\text{C}_{10'}$) appeared at 129.13 and 129.63 ppm for C_9 ; and at 133.22 , 133.79 , and 134.20 ppm for $\text{C}_{9'}$. The peaks at 164.77 and 165.00 ppm were assigned to the carbonyl carbon (C_{10}) and the peaks at 166.40 and 166.66 ppm to the carboxylic acid carbon ($\text{C}_{10'}$). The multiplex signals of C_9 and $\text{C}_{9'}$, C_{10} and $\text{C}_{10'}$ found in PPCL-Ma-3 were attributed to the many types of hydroxyl groups in PPCL-OH, such as the residual hydroxyls of pentaerythritol and the terminal hydroxyls of the PCL arms.

The incorporation of maleic anhydride onto the $-\text{CH}_2\text{-OH}$ chain ends of the PCL arms also altered this terminal-carbon signal by downshifting from 62.31 ppm for C_1 (Fig. 8, spectrum a, peak 1') to 66.07 ppm for $\text{C}_{1''}$ (Fig. 8, spectra b and c, peak 1''). The residual $-\text{CH}_2\text{-OH}$ groups of the pentaerythritol core in PPCL-OH was also downshifted from 60.49 ppm for C_2 (Fig.

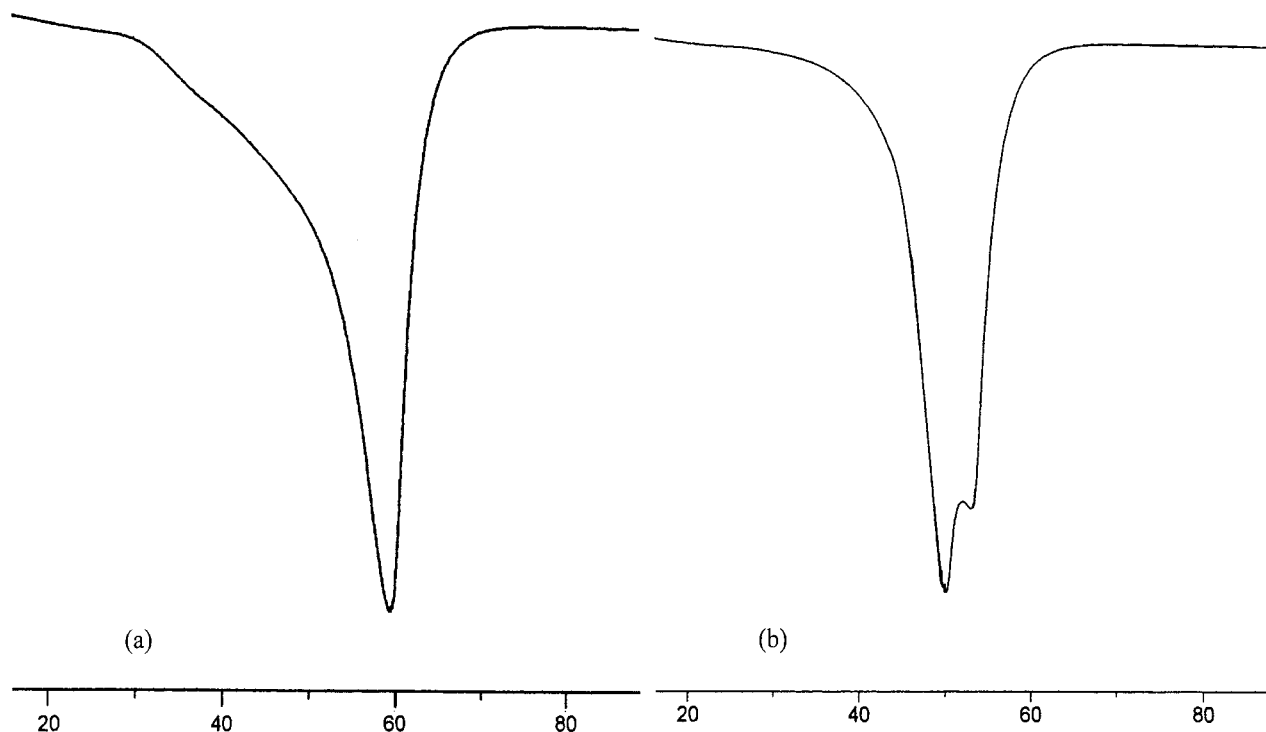


Figure 9 DSC thermograms of hydroxyl-terminated multiarm poly(ϵ -caprolactone) (PPCL-OH) and linear poly(ϵ -caprolactone): (a) linear poly(ϵ -caprolactone); (b) hydroxyl-terminated multiarm poly(ϵ -caprolactone) (PPCL-OH-2).

8, spectrum a, peak 2') to 64.98 ppm for $C_{2''}$ (Fig. 8, spectra b and c, peak 2''). This demonstrated once again that maleic anhydride groups had been attached to both PCL chain ends as well as hydroxyl groups of the pentaerythritol core. Some terminal hydroxyls ($-\text{CH}_2\text{OH}$ groups in the PCL arms) in high MW PPCL-OH remained unreacted ($C_{1'}$ peak at 62.31 ppm in Fig. 8, spectrum d) because of the high viscous nature of the molten high molecular weight PPCL-OH.

Thermal property

DSC data of a four-arm hydroxyl-functionalized poly(ϵ -caprolactone) (PPCL-OH-2) and linear poly(ϵ -caprolactone) control are shown in Figure 9. PPCL-OHs showed one strong melting peak, with a shoulder ranging from 40 to 60°C, depending on the molecular weight of PPCL-OH. The melting point increased with an increase in the molecular weight of the PPCL-OH (Table IV). The linear PCL control, which had a much higher molecular weight than that of PPCL-OH, always had one well-defined melting peak (near 60°C) without a shoulder (Fig. 9, curve a). The glass-transition temperature T_g of PPCL-OH was too low to be detected at the temperature range of our study (-50 to 120°C). Obviously, the incorporation of PCL multiarms into the pentaerythritol core did not increase the T_g of PPCL-OH enough to be detected in the temperature range.

The DSC curves of PPCL-Ma and its photocrosslinked NPPCL-Ma are shown in Figure 10. Every PPCL-Ma sample had two melting peaks of similar intensity, whereas the corresponding crosslinked PPCL-Ma had only one endothermic peak. The melting points of both the PPCL-Ma and its crosslinked products all shifted to higher temperatures as the molecular weight increased. Furthermore, the melting point of PPCL-Ma decreased after crosslinking (Table IV). The T_g values of PPCL-Ma and its crosslinked products were still not detected in the range from -50 to 120°C .

It was also noted that the heats of fusion (ΔH_f) of PPCL-OH, PPCL-Ma, and its crosslinked product in-

TABLE IV
Relationship Between the Thermal Properties and Molecular Weight of Hydroxyl-Terminated Multiarm Poly(ϵ -caprolactone) (PPCL-OH)

Sample	Molecular weight ^a ($\times 10^3$)	Melting point ($^\circ\text{C}$)	ΔH_m (J/g)	χ_c^b (%)
PPCL-OH-1	4.29	43.9, 48.4 (shoulder)	77.6	57.5
PPCL-OH-2	7.23	49.7, 53.4 (shoulder)	80.4	59.6
PPCL-OH-3	17.3	54.3, 57.0 (shoulder)	85.2	63.1
PPCL-OH-4	28.9	57.1, 58.1 (shoulder)	94.9	70.3

^a Number-average molecular weight and measured by GPC with PS standards.

^b Degree of crystallinity $\chi_c = (\Delta H_{m, \text{sample}} / \Delta H_{m, 100\% \text{ crystalline}}) \times 100\%$.

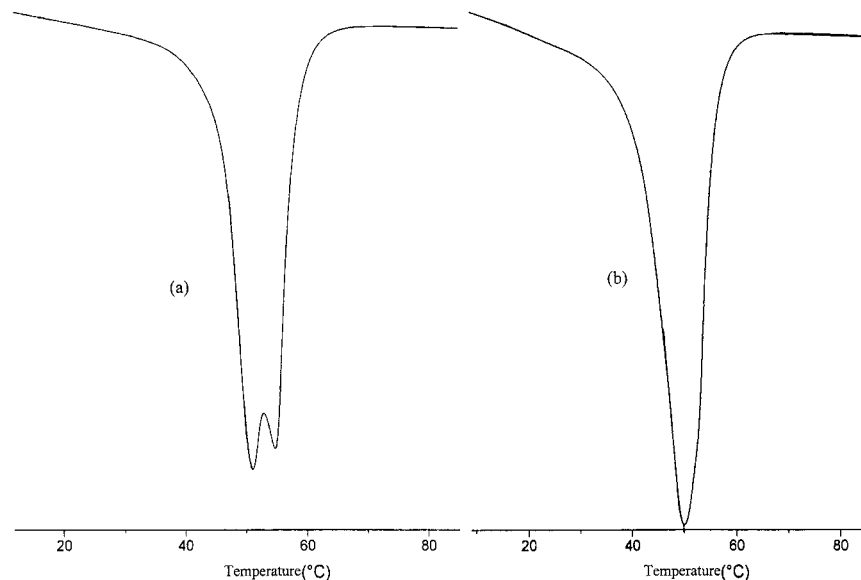


Figure 10 DSC thermograms of double-bond-functionalized multiarm poly(ϵ -caprolactone) (PPCL-Ma) and its network: (a) double-bond-functionalized multiarm poly(ϵ -caprolactone) (PPCL-Ma-2); (b) network from crosslinked PPCL-Ma-2.

creased with an increase in the molecular weight of the PCL arms (Tables IV and V). On the other hand, ΔH_f of PPCL-Ma decreased after crosslinking. The relative number of the PCL chain ends decreased with an increase in the molecular weight of the PCL arms, which led to a lower number of free chain ends that could make the chain crystallize much more easily. This increase in the level of crystallinity (χ_c) with an increase in the molecular weight of PPCL-Ma (Table IV) was reflected in an increase in both the melting points and the heats of fusion. When PPCL-Ma was converted to its network by photocrosslinking, the chain ends of PPCL-Ma were restricted that would disrupt the orderly formation of crystallites, resulting in a significant reduction in the level of crystallinity.

Solubility of crosslinked PPCL-Ma network

PPCL-Ma is a polymer in powder form that dissolves easily in most organic solvents (Table VI), whereas crosslinked PPCL-Ma (NPPCL-Ma) is an opaque film

that could not be dissolved in 13 common polar and nonpolar organic solvents. We expect that PPCL-Ma could also be used as the starting material for additional free-radical polymerization with any unsaturated monomers and/or polymers.

CONCLUSIONS

Hydroxyl-functionalized four-arm poly(ϵ -caprolactone)s (PPCL-OH) were synthesized by the ring-opening polymerization of ϵ -caprolactone in the presence of pentaerythritol and stannous octoate with high yields. The desired molecular weights of PPCL-OH can be obtained by adjusting the feed molar ratio of ϵ -caprolactone monomer to pentaerythritol. At a low feed molar ratio of ϵ -caprolactone monomer to pentaerythritol, residual hydroxyl groups in pentaerythritol were observed and could be used as the initiator to initiate the polymerization of ϵ -caprolactone. The double-bond-functionalized four-arm poly(ϵ -caprolactone)s (PPCL-Ma) were successfully synthesized by

TABLE V
Thermal Properties of Double-Bond-Functionalized Multiarm Poly(ϵ -caprolactone) (PPCL-Ma) and Its Photocrosslinking Network NPPCL-Ma

PPCL-Ma					NPPCL-Ma			
Sample	M_n^a ($\times 10^3$)	T_m ($^{\circ}\text{C}$)	ΔH_m (J/g)	χ_c^b (%)	Sample	T_m ($^{\circ}\text{C}$)	ΔH_m (J/g)	χ_c^b (%)
PPCL-Ma-1	3.52	22.8, 34.0	43.4	32.1	NPPCL-Ma-1	34.1	0.04	0
PPCL-Ma-2	5.11	44.9, 49.9	71.7	53.1	NPPCL-Ma-2	43.5	24.3	18.0
PPCL-Ma-3	9.51	50.7, 54.9	79.8	59.1	NPPCL-Ma-3	49.9	61.8	45.8
PPCL-Ma-4	11.7	53.9, 56.4	81.0	60.0	NPPCL-Ma-4	54.6	61.6	45.6

^a Number-average molecular weight and measured by GPC with PS standards.

^b Degree of crystallinity $\chi_c = (\Delta H_{m, \text{sample}} / \Delta H_{m, 100\% \text{ crystalline}}) \times 100\%$.

TABLE VI
Solubility of Double Bond-Functionalized Multiarm Poly(ϵ -caprolactone) (PPCL-Ma) and Its Photocrosslinking Network NPPCL-Ma^a

Solvent	PPCL-Ma	NPPCL-Ma
Water	–	–
Ethyl acetate	+	–
Dioxane	+	–
Chloroform	+	–
Tetrahydrofuran	+	–
Methyl sulfoxide	+	–
N,N-Dimethyl formamide	+	–
Dichloromethane	+	–
Toluene	+	–
Acetone	+	–
Ethanol	–	–
Ethyl ether	–	–
Hexane	–	–
Petroleum ether	–	–

^a –, does not dissolve at room temperature; +, dissolves at room temperature.

reacting PPCL-OH and maleic anhydride in the melt at 130°C. A quantitative conversion of hydroxyl functionality, including the residual hydroxyl of pentaerythritol and the end hydroxyl of poly(ϵ -caprolactone) arms, was achieved for low molecular weight PPCL-OH. However, the hydroxyl groups cannot be completely converted to double-bond functionality for high molecular weight PPCL-OH ($M_n > 1.7 \times 10^4$).

The photocrosslinking of PPCL-Ma produced the crosslinked PPCL-Ma (NPPCL-Ma). The solubility greatly decreased and the thermal properties, such as melting point, heat of fusion, and degree of crystallinity, decreased.

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