Synthesis and Characterization of Poly(ε-caprolactone)-b-Poly(ethylene glycol)-b-Poly(ε-caprolactone) Triblock Copolymers with Dibutylmagnesium as Catalyst

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ABSTRACT: Two series of poly(ε-caprolactone)-b-poly(ethylene glycol)-b-poly(ε-caprolactone) triblock copolymers were prepared by the ring opening polymerization of ε-caprolactone in the presence of poly(ethylene glycol) and dibutylmagnesium in 1,4-dioxane solution at 70°C. The triblock structure and molecular weight of the copolymers were analyzed and confirmed by ^{1}H NMR, ^{13}C NMR, FTIR, and gel permeation chromatography. The crystallization and thermal properties of the copolymers were investigated by wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). The results illustrated that the crystallization and melting behaviors of the copolymers were depended on the copolymer composition and the relative length of each block in copolymers. Crystallization exothermal peaks (T_c) and melting endothermic peaks (T_m) of PEG block were significantly influenced by the relative length of PCL blocks, due to the hindrance of the lateral PCL blocks. With increasing of the length of PCL blocks, the diffraction and the melting peak of PEG block disappeared gradually in the WAXD patterns and DSC curves, respectively. In contrast, the crystallization of PCL blocks was not suppressed by the middle PEG block. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 429–436, 2009

Key words: triblock polymers; poly(ε-caprolactone); dibutylmagnesium; crystallization; thermal properties

INTRODUCTION

Biodegradable aliphatic polyesters have received great research interest for their environmental, medical, and pharmaceutical applications.[1–3] Poly(ε-caprolactone) (PCL) is one of the most widely investigated aliphatic polyesters because of its unique properties such as biodegradability, biocompatibility, miscibility with other polymers, high permeability to a wide range of drugs, and so forth. However, its high crystallinity, hydrophobicity, and slow biodegradation rate have considerably limited its medical applications.[4–6]

Poly(ethylene glycol) (PEG) exhibits some outstanding properties, for example, hydrophilicity, solubility in water and in organic solvents, nontoxicity, and absence of antigenicity and immunogenicity, which allow PEG to be used for many clinical applications.[7] Recently, these kind of polyester–polyether amphiphilic block copolymers have been prepared by the ring opening polymerization of ε-caprolactone (ε-CL) using PEG as the macroinitiator.[8–15] Copolymerization offers the possibility to combine the hydrophilicity of PEG with the degradability of PCL to make a wide range of biomaterials, which can be promising for temporary therapeutic applications.[14,15]

Stannous octoate has been frequently used as one of the effective catalyst in this polymerization.[10–12,14,15] However, like many other catalysts, the cytotoxicity and difficulties in complete removal of the catalyst residue from the resulting polymer have limited its use in many cases.[1,2] For some medical and pharmaceutical applications, the synthetic polymers without containing any toxic heavy metal ions are reasonably desirable. Continuous efforts have been devoted to the new and nontoxic catalysts and initiators for the ring opening polymerization of lactones, thus, many Ca-, Fe-, and Zn-based compounds used as the nontoxic and restorable catalysts were reported in recent publications,[9,16–21] because these metals participate in the human metabolism. Although the metal residues were nontoxic, however, either the preparation of the catalysts was too

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much complex and fastidious or their catalytic activity was limited and the polymerization rate was slow.

A nontoxic alternative is magnesium compounds, because magnesium ion is an absolutely harmless ion, and its high catalytic activity was demonstrated in recent publications.[22–26] In our recent article,[26] magnesium octoate was used as a catalyst for the copolymerization of L-lactide and ε-CL to prepare biodegradable aliphatic copolyesters. Special attention has been paid to the influence of catalyst and copolymer composition on the microstructure and the crystallization and thermal properties of the obtained copolymers. The main aim of this article was to afford a facile method to prepare PCL-PEG-PCL amphiphilic triblock copolymers by the ring opening polymerization of ε-CL in the presence of PEG using Bu_2Mg as a catalyst. The copolymer composition and triblock structure were confirmed by ^1H NMR, ^{13}C NMR, gel permeation chromatography (GPC), and FTIR. Effects of the copolymer composition and the relative length of PEG and PCL blocks on crystallization and melting behaviors of triblock copolymers were investigated by wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

ε-CL (99%, purchased from Acros Organics) and 1,4-dioxane were dried over CaH_2 by stirring, distilled under reduced pressure, and stored under N_2 before use. PEG (M_n = 800, 2000, 6000, 20,000) were imported and subpackaged by Tiantai Fine Chemicals (Tianjin, China) and dried under vacuum before use. Di-n-butyl magnesium (Bu_2Mg) solution ($1M$ in heptane) was purchased from Aldrich Chemical. All other reagents were used as received.

Synthesis of the PCL-PEG-PCL triblock copolymer

All polymerization reactions were carried out in a previously flamed and nitrogen purged glass reactor equipped with magnetic stirrer. Designed amounts of 1,4-dioxane, PEG, and Bu_2Mg were sequentially added to the flask and aged for 30 min before the ε-CL monomer was injected by a syringe. The reaction vessel was then immersed into a thermo stated oil bath at 70°C under stirring for 24 h. The products were precipitated in hydrochloric acidic mixture of hexane and diethyl ether and dried in vacuum at room temperature for 24 h.

Characterization

Nuclear magnetic resonance (^1H- and ^{13}CNMR) spectra were recorded on a Bruker DRX 400 NMR

spectrometer (Bruker, Switzerland) at room temperature, with $CDCl_3$ as solvent, and TMS as internal reference.

FTIR spectra in the range of 4000–400 cm^{-1} were recorded on a Nicolet 5DX spectrometer, with a resolution of 2 cm^{-1} using film samples cast on a KBr plate from 5 wt % $CHCl_3$ solution.

GPC measurement was conducted with GPC-220 (Polymer Lab, UK) using THF as eluent at the flow rate of 1.0 mL/min at 40°C, and the polymer molecular weights were calibrated with the narrow molecular weight distribution polystyrene (PS) standards.

DSC was carried out on a Mettler Toledo DSC 822^e (Mettler Toledo, Switzerland) instrument using nitrogen as purge gas. The samples were heated from −60 to 100°C for the first run at 10°C/min, then cooled to −60°C at 10°C/min, and heated again to 100°C for the second run at 10°C/min. Before and after cooling, the temperature was kept constant for 5 min.

WAXD was performed using a Dmax-Ultima + X-ray diffractometer (Rigaku, Japan) with Ni-filtered Cu/K-α radiation (0.15418 nm). The operating target voltage was 40 kV and the tube current was 100 mA. The scanning rate was 0.02° θ/s from 5° to 50°.

RESULTS AND DISCUSSION

Two series of PCL-PEG-PCL triblock copolymers with various lengths of each block were obtained from copolymerization of ε-CL in the presence of PEG catalyzed with Bu_2Mg. As seen in Table I, Series A, Sample 1–4, being different lengths of the PCL block and a fixed PEG2000 as the prepolymer, while Series B, Sample 3 and 5–7, being the approximate same length of PCL block and various molecular weights of PEG segment (degree of polymerization, DP = 18–450). For the sake of clarity, the triblock copolymers were denoted PCL_x-PEG_y-PCL_x, x and y represented the number average degree of polymerization of PCL and PEG blocks (x = DP_{PCL} and y = DP_{PEG}).

All the polymeric products presented well-defined NMR spectra with similar characteristics reported in the literature for triblock copolymers synthesized with other catalyst/initiator systems.[9,12,13] Figures 1 and 2 showed the ^1H and ^{13}C NMR spectra of the pure PEG and Sample 3 (Table I), together with the assignments for characteristic peaks. In Figure 1, the hydroxyl end groups of PEG at 3.71 ppm almost disappeared after the reaction and a new peak appeared at 4.10 ppm. The hydroxyl end groups of PEG were consumed in the reaction, and then formed new ester bonds with the PCL block, resulting in its proton was deshielded to lower field. Hence, it was concluded that the reacted products

TABLE I
Molecular Weight and Composition of the PCL-PEG-PCL Triblock Copolymers Catalyzed with Bu₂Mg at 70°C for 24 h

Sample	Structure (PCL$_y$-PEG$_x$-PCL$_y$)	PEG content (wt %)	$n(CL)/n(EG)$ in feed[a]	$n(CL)/n(EG)$ in product[b]	CL conversion (%)	$M_{n(\text{HNMR})}$[c]	$M_{n(\text{GPC})}$[d]	$M_{w(\text{GPC})}$[d]	PDI[d]
1	4-45-4	68	0.2	0.2	99	2,900	4,100	5,500	1.34
2	13-45-13	40	0.4	0.5	97	5,000	6,100	9,900	1.62
3	32-45-32	21	1.2	1.4	98	9,300	12,000	22,400	1.87
4	57-45-57	13	2.3	2.5	96	15,000	16,600	32,500	1.96
5	35-18-35	9	3.0	3.5	96	8,800	13,800	25,300	1.83
6	36-136-36	42	0.4	0.5	95	14,200	17,700	30,400	1.72
7	32-450-32	73	0.1	0.1	94	27,300	30,000	50,600	1.68

[a] Molar ratio of the CL to EG in feed.
[b] Molar ratio of the CL to EG in the product measured by ^{1}H NMR.
[c] Calculated as eq. (1) from ^{1}H NMR spetra.
[d] Measured by GPC using polystyrene standard calibration, THF as eluent at 40°C.

were triblock copolymers consisting of a PEG central block and two PCL lateral blocks.

In Figure 2, the peak at 70.5 ppm was attributed to the methylene carbon of PEG block, and the peak at 173.4 ppm was attributed to the carbonyl carbon of the PCL block. The end groups of PEG methylene carbon was found at 72.6 ppm. Similar to the ^{1}H NMR spectra, they almost disappeared after reaction, and a new peak appeared at 69.2 ppm (Fig. 2 upper). This finding showed that PEG hydroxyl end groups were totally consumed and esterified in the reaction. Therefore, ^{13}C NMR spectra confirmed that the formation of triblock copolymers in the copolymerization of ε-CL in the presence of PEG and Bu₂Mg, which corroborated the results of the ^{1}H NMR analysis.

^{1}H NMR spectra of the triblock copolymers were used to determine CL/EG ratios from the integration ratio of resonances due to PCL blocks at 4.05 ppm and to PEG blocks at 3.65 ppm, as described in Figure 1. As shown in Table I, the compositions of the copolymers were rather close to those of the feed,

and the conversion of ε-CL monomer was high than 94%. The results suggested that the copolymerization almost completed and all monomers were engaged in polymer chains.

Considering that PEG was almost monodispersed ($M_w/M_n = 1.1$), the polymer molecular weight could be calculated from the molar ratio of CL/EG in the triblock copolymers, according to the following equations:

$$M_{n(\text{HNMR})} = M_{n\text{PEG}} + 2 \times 114 \times \text{DP}_{\text{PCL}} \qquad (1)$$

Where $\text{DP}_{\text{PEG}} = x = M_{n\text{PEG}}/44$, $\text{DP}_{\text{PCL}} = y = \text{DP}_{\text{PEG}} \times (\text{CL/EG})$; 44 and 114 were the molar masses of EG and CL repeat units, respectively.

The values of DP_{PCL} derived from ^{1}H NMR were in agreement with calculated data, assuming total conversion of CL. The molecular weight ($M_{n(\text{H NMR})}$) calculated by ^{1}H NMR also depended on feed compositions. The higher the CL/EG ratio in the feed, the higher the $M_{n(\text{H NMR})}$. Therefore, the compositions and M_n of the triblock copolymers can be
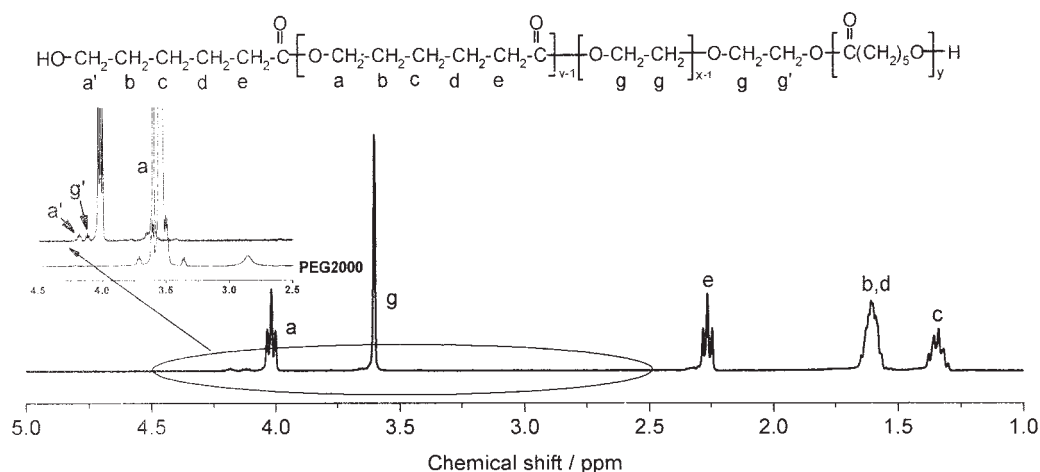

Figure 1 400 MHz ^{1}H NMR spectrum (below) of a PCL-PEG-PCL triblock copolymer (Sample 3 in Table I) and its expanded spectra (upper) including the pure PEG2000.
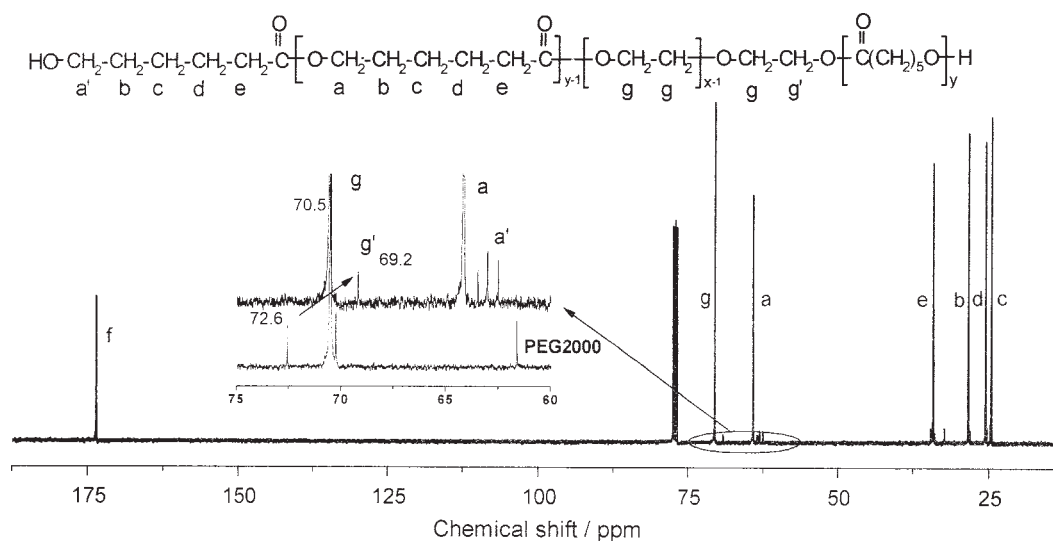
Figure 2 100 MHz ^{13}C NMR spectrum (below) of a PCL-PEG-PCL triblock copolymer (Sample 3 in Table I) and its expanded spectra (upper) including the pure PEG2000.

easily adjusted and controlled by changing the M_n of PEG and the ratio of monomer to PEG.

The GPC traces also confirmed the successful initiation of ε-CL copolymerization by PEG prepolymer in the presence of Bu$_2$Mg. The GPC curves of the block copolymers (Fig. 3) were unimodal and symmetric, confirming that there were few homopolymers in the final products. However, their distributions became tolerably broad, being from 1.3 to 1.8. These findings were in agreement with the literature data obtained for triblock copolymers using calcium ammoniate or stannous octoate as catalysts.[9,27] On the other hand, the molecular weight ($M_{n(GPC)}$) calibrated by PS calibration was slightly larger than the corresponding $M_{n(H\ NMR)}$. This result was in accordance to the pervious reports that GPC measurements calibrated with PS overestimated the real molecular weights of aliphatic polyesters, due to the increased difference in hydrodynamic volume of the polymers with higher molecular weight.[25,28–30]

The microstructure of the copolymers was further analyzed by FTIR spectra. FTIR spectra of the different reacted products were shown in Figure 4(A,B). When compared with the spectrum of the pure PEG, the band of the triblock copolymers in the hydroxyl region (about 3450 cm^{-1}) almost disappeared, suggesting that the hydroxyl end groups of PEG were consumed. The peak at 2945 cm^{-1} belongs to the absorption of C—H stretch of CH$_2$ from PCL blocks, whereas the peak at 2865 cm^{-1} corresponds to the C—H stretching band of PEG. A strong and sharp band at 1725 cm^{-1} was assigned to the stretching vibrations of PCL carbonyl groups. For Series A shown in Figure 4(A), its intensity increased with the increase in the length of PCL block, whereas the intensities of the crystalline-sensitive bands for the

PEG block at 1114 and 843 cm^{-1} [27,31] decreased generally. Some other bands at 1244 and 731 cm^{-1}, which were attributed to the bands of the PCL crystals,[11,27] were detected in the spectra of the triblock copolymers. For Series B, as expected, with increasing the molecular weights of the middle PEG blocks, a decrease in the relative intensity of the band at 1725 cm^{-1} to the band at 1114 cm^{-1} was observed in Figure 4(B). Therefore, it could be concluded that the crystallization of PEG block was hindered the introduction of PCL block, whereas PCL block was crystallizable and free from the influence of PEG block.

The above analyses of ^{1}H NMR, ^{13}C NMR, GPC, and FTIR confirmed that the triblock structure of the polymers was obtained by Bu$_2$Mg. The central PEG served as a macroinitiator for the copolymerization
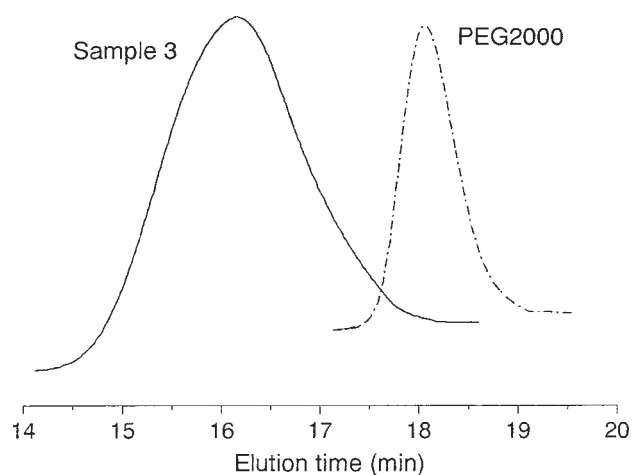

Figure 3 Typical GPC curves of the pure PEG2000 and the resulting PCL-PEG-PCL (Sample 3 in Table I).
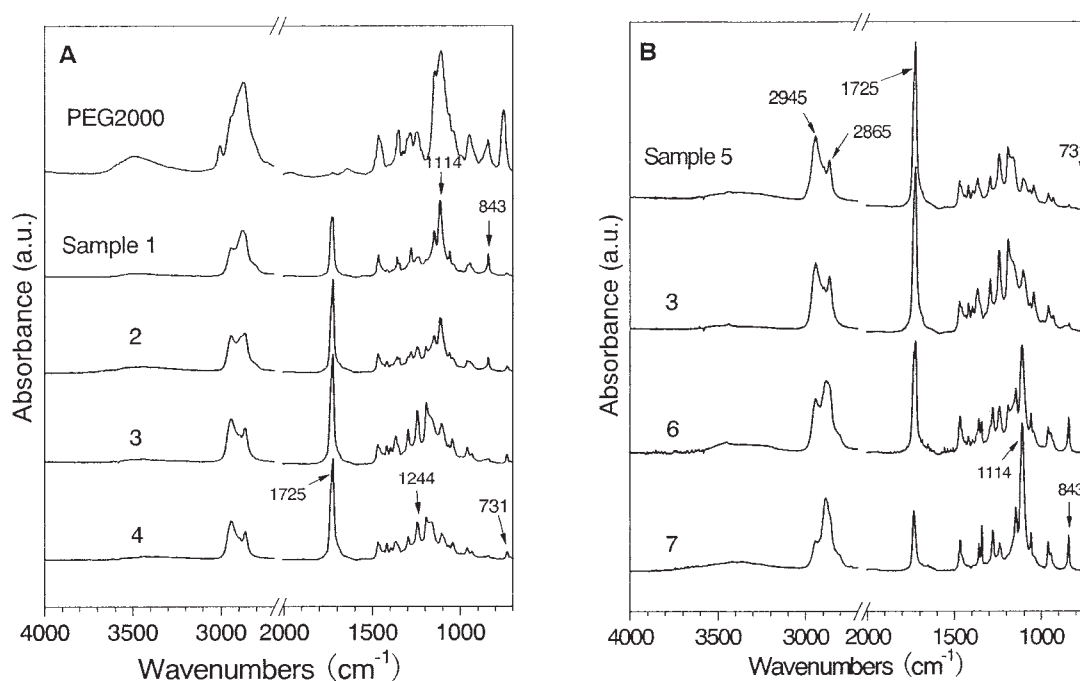
Figure 4 FTIR spectra of the pure PEG2000 and the PCL-PEG-PCL triblock copolymers (Series A and B).

of ε-CL. The neighboring PCL blocks were connected with the middle PEG through an ester linkage. It is well known that the ring opening polymerization of lactones initiated with metal alkoxides proceeded through the coordination-insertion mechanism by acyl-oxygen bond scission.[9,13,22] A similar mechanism can be considered operative in the case of the polymerization of ε-CL catalyzed with Bu₂Mg in the presence of PEG. Thus, the above polymerization procedure could be described in Scheme 1. Firstly, the PEG prepolymer was dissolved in 1,4-dioxane followed by the equimolar addition of Bu₂Mg under N₂ atmosphere with gaseous butane escaping. Formation of the macroinitiator was accomplished through conversion of the hydroxyl end groups of

PEG into magnesium alkoxide end groups. Then, the propagation proceeds through the insertion of the ε-CL monomers into the active centers BuMg—(OCH₂CH₂)$_x$—OMgBu by the acyl-oxygen bond scission to form the two PCL blocks. It was assumed that these two Mg—O active centers had the same chemical activity; consequently, the two PCL blocks should be identical. Finally, the propagation was terminated by hydrolysis of the active centers to form the dihydroxyl end groups, that is, the dihydroxyl-terminated PCL-PEG-PCL triblock copolymers were achieved.

It is well-known that the WAXD patterns of PEG and PCL are clearly distinguishable when compared with their crystallization and melting peaks in the
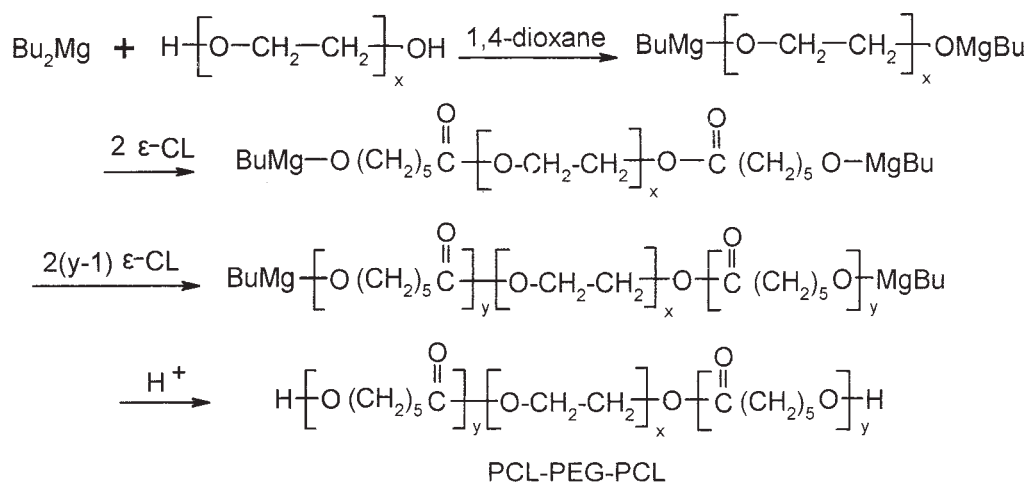
Scheme 1 Proposed mechanism for synthesis of the PCL-PEG-PCL triblock copolymer.
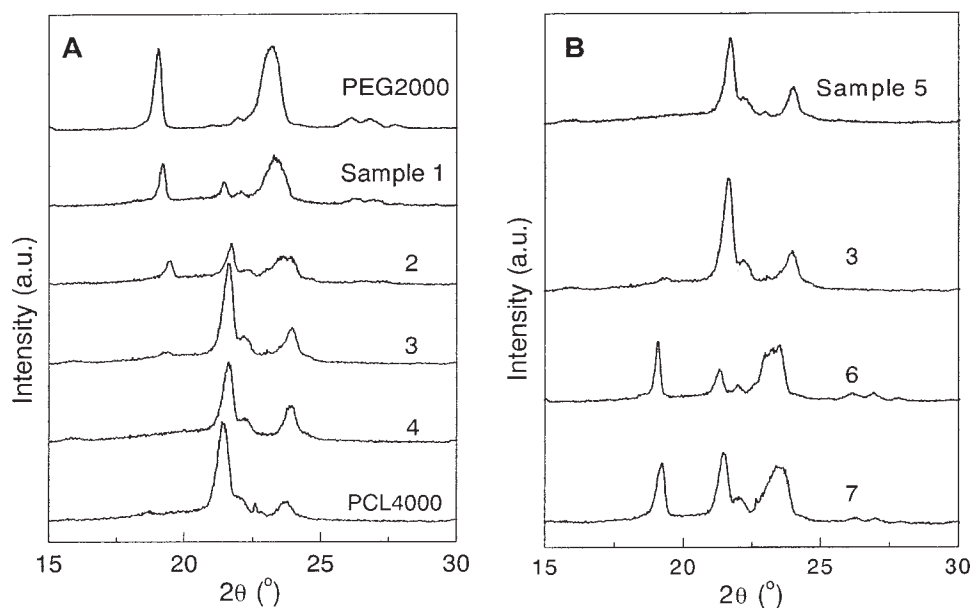
Figure 5 WAXD patterns of the pure PEG2000 and the PCL-PEG-PCL triblock copolymers (Series A and B).

DSC curves. Firstly, we used WAXD technique to examine the crystallization of the PCL-PEG-PCL triblock copolymers. Figure 5 showed the crystalline patterns of the PCL-PEG-PCL triblock copolymers in comparison with the starting PEG2000. PEG2000 exhibited the two main crystalline peaks at $2\theta = 19.2°$ and $23.4°$, whereas PCL showed an intense peak at $2\theta = 21.6°$, and two small ones at $22.0°$ and $23.8°$.

For Series A with a given PEG block length, a small but identifiable peak of PCL crystal could be detected for Sample 1, which the length of PCL block is about four repeating units and very short when compared with that of PEG block, indicating that the short PCL block is able to crystallize. With increasing the length of PCL blocks, the crystalline patterns of both PCL and PEG blocks were distinctly observed for Sample 2, indicating that they are able to crystallize and form two separate crystalline. When the length of PCL blocks were long enough to that of PEG block, the longer PCL blocks hindered the crystallization of PEG block; accordingly, the PEG peaks almost disappeared for Sample 4.

For Series B that the length of PCL block was fixed at around 32 monomer units, and the diffraction peaks of PCL crystal were observed regardless of the length of PEG blocks. No diffraction peaks of crystalline PEG were detected in the spectra of the copolymers with short PEG blocks (Sample 5). The PEG peaks were observed in Sample 6 and 7 with the starting PEG6000 and PEG20000. The results indicated that the PEG block can crystallize when the length of PEG block was comparably very long with respect to that of PCL block.

Based on the WAXD results, it was concluded that the relative length of PEG and PCL blocks, namely,

the copolymer composition, had a profound influence on their crystalline patterns. The intensity of their crystalline peaks increased as the relative proportions of their respective composition increased. On the other hand, the crystallization of PEG block was strongly restricted by the crystallization of the lateral PCL blocks, in contrast, the crystallization ability of PCL blocks was not suppressed by the middle PEG block.
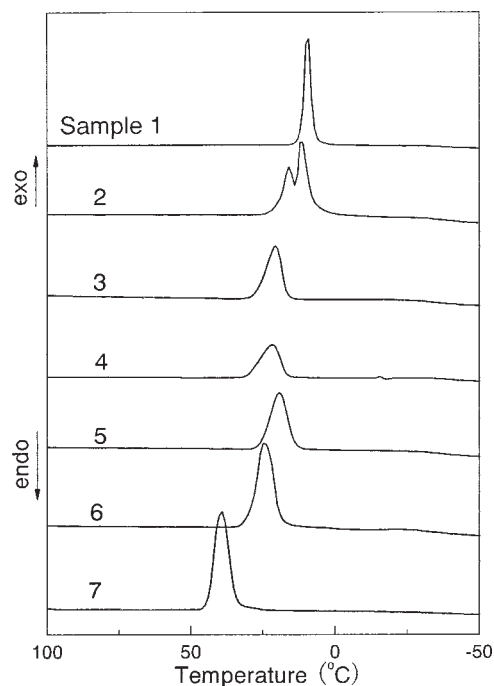

Figure 6 Cooling run of the DSC traces of the PCL-PEG-PCL triblock copolymers at 10°C/min.
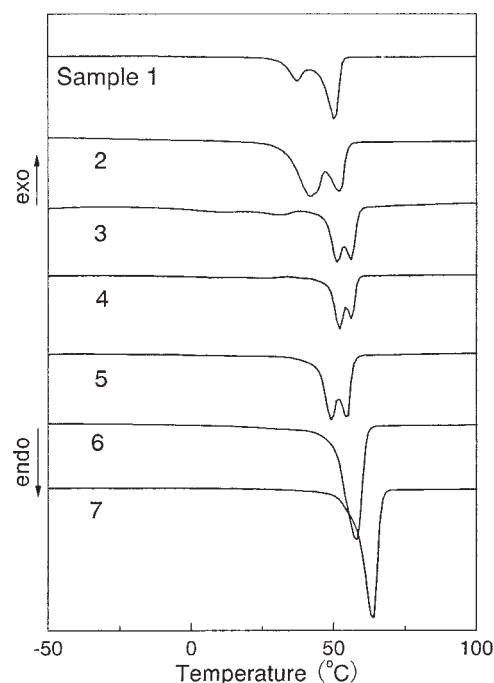
Figure 7 Second heating run of the DSC traces of the PCL-PEG-PCL triblock copolymers at 10°C/min.

The crystallization and melting behaviors by DSC for the PCL-PEG-PCL triblock copolymers were presented in Figures 6 and 7, respectively. All samples were melted at 100°C for 5 min to remove the thermal history, then cooled to −60°C at 10°C/min, and reheated to 100°C at 10°C/min. PEG and PCL homopolymers were also determined for comparison. It was suggested from the WAXD results that PEG and PCL had distinctly different cell unit and there was no eutectic or mixed crystals of the two components. From analysis of WAXD, T_cs of some samples could be directly assigned to the corresponding component. As shown in Figure 6, there was a single or

overlapping crystallization peak in all triblock copolymers except for Sample 2, which showed double exothermic peaks of two blocks.

In Figure 7, two melting peaks were observed in Sample 1, which the length of PCL blocks was very short with respect to that of PEG block. The higher temperature melting peak was attributed to the PEG domain, and the lower temperature one was attributed to the PCL domain. With increasing of the length of PCL block, two melting peaks were also observed in Sample 2; however, the order of assignment was reversed. When the PCL blocks were long enough with respect to the PEG block, for Sample 4 and 5, the crystallization and melting peaks of PEG block disappeared in the DSC curves, hence, the crystallization of PCL block was predominant. It was suggested from the WAXD results that no crystalline pattern of PEG domain was detected. Therefore, the double melting peaks were attributed to the PCL blocks in Sample 3, 4, and 5. The results indicated that the crystallizability of PEG block was destroyed by the crystallization of the longer lateral PCL blocks. That is, chain mobility of the middle PEG to fold, when large PCL end groups are attached may account for this.

Interestingly, for Samples 6 and 7, the PCL blocks were relatively short when compared with the PEG block, the crystallization and melting temperatures of PCL and PEG blocks were rather comparable, and consequently, a superposed crystallization peak and a superposed melting one were observed. The findings elucidated that, if the PCL block was long enough, its crystallization was not suppressed by the longer middle PEG block. In general, the phenomena of overlapping melting peaks were observed in case of diblock copolymers consisting of the comparable length of PCL and PEG blocks.[11,32] However, for triblock copolymers, it was required that the length of

TABLE II
Assignments of Crystallization and Melting Temperatures and Their Enthalpies of the Samples in Table I

Sample	T_c (°C)		ΔH_c (J/g)		T_m (°C)		ΔH_m (J/g)	
	PEG	PCL	PEG	PCL	PEG	PCL	PEG	PCL
1	10.2[a]		−85.0		49.9	36.8	76.0	19.8
2	12.2	16.5	−50.4	−31.7	41.2	51.7	49.7	32.5
3		21.1		−55.1	31.7	50.6, 59.6	53.8	
4		22.2		−61.5		51.6, 59.1	63.3	
5		19.7		−59.9		48.5, 54.1	64.7	
6	25.3[a]		−85.2		57.0[a]		90.6	
7	40.1[a]		−137.4		62.7[a]		143.9	
PEG800	16.2		−144.0		35.1		148.7	
PEG2000	25.8		−158.3		55.8		160.6	
PEG6000	38.5		−180.4		64.2		180.1	
PEG20000	43.3		−173.9		66.4		173.4	
PCL4000		25.1		−79.0		52		86.6

[a] Overlapping peaks.

the middle PEG block was considerably longer than those of the lateral PCL blocks (Samples 6 and 7). Otherwise, two separate crystallization and melting peaks were still observed (Sample 2).

From the DSC and WAXD analyses, the crystallization temperature (T_c), melting temperature (T_m), exothermic enthalpy (ΔH_c), and endothermic enthalpy (ΔH_m) for all triblock copolymers were assigned to the corresponding component, as shown in Table II. The T_c and T_m of each block in the triblock copolymer as well as their enthalpies (ΔH_c and ΔH_m) were lower than those of the starting homopolymers due to the hindered crystallization. For Series A with a given PEG block length, the T_c and T_m of PCL blocks slightly increased with increasing the length of PCL blocks, whereas those of PEG block decreased, because the crystallization of PEG block was strongly restricted by the crystallization of the lateral PCL blocks. Moreover, the melting and crystallization peaks of PEG block disappeared when PCL blocks were long enough. In contrast, for Series B with the comparably long PCL blocks, the T_c and T_m of both PEG and PCL blocks slightly increased with increasing the length of the starting PEG.

CONCLUSIONS

Two series of PCL-PEG-PCL triblock copolymers with different lengths of each block were synthesized successfully by using dibutylmagnesium as catalyst and PEG as macroinitiator. The triblock structure was confirmed by ^{1}H NMR, ^{13}C NMR, GPC, and FTIR. The results by DSC and WAXD demonstrated that the crystallization and melting behaviors of the PCL-PEG-PCL triblock copolymers were greatly influenced by the copolymer composition and the relative length of each block. The crystallization of PEG block was strongly restricted by the crystallization of the lateral PCL blocks, whereas the crystallization of PCL blocks was not suppressed by the middle PEG block.

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