Preparation of Novel Poly(ethylene oxide-co-glycidol)-
graft-Poly(ε-caprolactone) Copolymers and Inclusion
Complexation of the Grafted Chains with α-Cyclodextrin

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ABSTRACT: A well-defined comblike copolymer of poly(ethylene oxide-co-glycidol) [(poly
(EO-co-Gly))] as the main chain and poly(ε-caprolactone) (PCL) as the side chain was
successfully prepared by the combination of anionic polymerization and ring-opening
polymerization. The glycidol was protected by ethyl vinyl ether to form 2,3-epoxy-
propyl-1-ethoxyethyl ether (EPEE) first, and then ethylene oxide was copolymerized
with EPEE by an anionic mechanism. The EPEE segments of the copolymer were
deprotected by formic acid, and the glycidol segments of the copolymers were recovered
after saponification. Poly(EO-co-Gly) with multihydroxyls was used further to initiate
the ring-opening polymerization of ε-caprolactone in the presence of stannous octoate.
When the grafted copolymer was mixed with α-cyclodextrin, crystalline inclusion com-
plexes (ICs) were formed, and the intermediate and final products, poly(ethylene ox-
ide-co-glycidol)-graft-poly(ε-caprolactone) and ICs, were characterized with gel permea-
tion chromatography, NMR, differential scanning calorimetry, X-ray diffraction, and
thermogravimetric analysis in detail. The obtained ICs had a channel-type crystalline
structure, and the ratio of ε-caprolactone units to α-cyclodextrin for the ICs was higher
Keywords: α-cyclodextrin; anionic polymerization; ε-caprolactone; graft copolymers;
poly(ethylene oxide); ring-opening polymerization

INTRODUCTION

Graft copolymerization via the functional groups
of an exiting polymer main chain offers an easy
and effective approach for incorporating new
properties into the original polymers. Poly(ε-cap-
rolactone) (PCL) has been extensively used as an
important biomaterial for a wide variety of drug
delivery carriers and biomedical devices because
of its biodegradability, versatile mechanical prop-
erties, and proven biocompatibility. On other hand, poly(ethylene oxide) (PEO) presents some unique and outstanding proper-
ties, such as hydrophilicity, nontoxicity, and solu-
bility in water and organic solvents. To meet the
increasing demands for better performances and
satisfy the requirements of some specific applica-
tions, biodegradable PCL polymers modified by
PEO have attracted much attention. PEO/PCL
diblock, triblock, and star-shaped block copolymers
have been prepared, and the thermal properties
and morphology of the copolymers are affected
significantly by the chain length of PCL and poly
(ethylene glycol) (PEG) and by the types of co-
polymers. These copolymers can be employed in
biomedical and pharmacological fields as synthetic
biomaterials, injectable materials, and drug carriers in a controlled delivery system.\textsuperscript{7–9} However, graft copolymers of PEO as the backbone and PCL as the side chain have not been known up to now because of the difficulty of synthesis.

It is well known that supramolecular inclusion complexes (ICs) are formed by some polymers such as PCL and PEO with cyclodextrins, and these ICs can serve as models for understanding molecular recognition and precursors for designing novel materials for biomedical applications.\textsuperscript{10,11} It has been reported that linear PCLs with various molecular weights, star-shaped PCLs with four or six arms, and organic/inorganic hybrid star PCLs with eight arms can form ICs with \( \alpha \)-cyclodextrin (\( \alpha \)-CD) in high yields.\textsuperscript{12–16} However, when grafted polymers with more than 20 PCL arms are mixed with \( \alpha \)-CD, what will happen? This question has attracted our attention very much.

This presentation reports the preparation of the graft copolymer poly(ethylene oxide-co-glycidol)-graft-poly(\( \varepsilon \)-caprolactone) [poly(EO-co-Gly)-g-PCL] and the preliminary results for the graft copolymer threaded by \( \alpha \)-CDs and the properties of the complexes.

**EXPERIMENTAL**

**Materials**

Glycidol (Acros Organics) and \( \varepsilon \)-caprolactone (CL; Acros Organics) were dried over calcium hydride for 48 h and distilled under reduced pressure just before use. Ethyl vinyl ether (98%) and stannous octoate were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethylene oxide (EO; 98%; Sinopharm Chemical Reagent) was dried with calcium hydride for 48 h and then distilled under reduced pressure just before use. Triethylene glycol was distilled from CaH\(_2\) under reduced pressure, and the fraction at 134 °C and 90 Pa was collected. \( p \)-Toluene sulfonyl acid (Aldrich; >98%) and \( \alpha \)-CD (Aldrich) were used as received. All other reagents were commercially available chemicals and used as received.

**Measurements**

The monomer conversion was measured gravimetrically. Gel permeation chromatography (GPC) was performed on an Agilent 100 with a G1310A pump, a G1362A refractive-index detector, and a G1314A variable-wavelength detector with tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min at 35 °C. Polystyrene standards were used for calibration. For poly(ethylene oxide-co-glycidol) [poly(EO-co-Gly)], GPC was performed in distilled water at 40 °C with an elution rate of 0.5 mL/min with the same instruments, except that the G1314A variable-wavelength detector was substituted by a G1315A diode-array detector, and PEO standards were used for calibration. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed with a Bruker Reflex II MALDI-TOF mass spectrometer equipped with a nitrogen laser delivering 3-ns laser pulses at 337 nm; \( \varepsilon \)-cyano-4-hydroxycinnamic acid was used as the matrix. \(^1\)H NMR spectra were recorded with Bruker (500 MHz) spectrometers in CDCl\(_3\) or dimethyl sulfoxide-\( d_6\) (DMSO-\( d_6\)) with tetramethylsilane as the standard at room temperature. The solid-state \(^{13}\)C cross-polarization/magic-angle spinning (CP–MAS) NMR spectra were measured on a Varian Infinity Plus NMR spectrometer at 75 MHz with a sample spinning rate or at 5 kHz at room temperature; the spectra were acquired with a 4.00-\( \mu \)s proton 90 pulse and a 4-ms contact time. X-ray diffraction (XRD) patterns of the complexes were recorded on an XPert Pro X-ray powder diffractometer with Cu K\( \alpha \) (1.541 Å) radiation (40 kV, 40 mA), and the samples were exposed at a scanning rate of \( 2\theta = 0.0007 \text{s}^{-1} \) in the range of 3–50°. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris 1 thermogravimetric analyzer, and the samples were heated from room temperature to 500 °C at a heating rate of 20 °C/min under a nitrogen flow (10 mL/min). The differential scanning calorimetry (DSC) analysis was carried out with a PerkinElmer Pyris 1 DSC instrument under a nitrogen flow (10 mL/min); all samples were first heated from –20 to 100 °C at 10 °C/min, then cooled to –20 °C at 10 °C/min, and scanned two times to erase the thermal history. An ultrafiltration membrane separator was purchased from the Shanghai Institute of Nuclear Research (Chinese Academy of Science); a membrane of poly(ether sulfone) with a molecular weight cutoff of 20,000 was used.

**Synthesis of Glycidol with an Acetal Protecting Group [2,3-Epoxypropyl-1-ethoxyethyl Ether (EPEE)]**

EPEE\textsuperscript{17} was prepared according to the literature with a yield of 84%. It was a colorless liquid, and its boiling point was in the range of 152–154 °C.
Poly(EO-co-EPEE) was removed.

Anionic Copolymerization of EPEE with EO

Diphenylmethylpotassium (DPMK) was prepared with the following steps. Naphthalene (7.7 g, 0.06 mol) was added to a 150-mL three-necked flask with about 100 mL of dry THF, and then potassium (2.34 g, 0.06 mol) with a fresh surface was added under the bubbling of the dry nitrogen; after 4 h of stirring, diphenylmethane (11.1 g, 0.066 mol) was introduced by a syringe, the system was refluxed at 80 °C for 24 h and then filtered, and the filtrate was titrated with 0.1 mol/L HCl. The concentration of DPMK was 0.57 mol/L.

The copolymerization was carried out in a kettle; the typical procedure was as follows. A 150-mL kettle was vacuumed at 80 °C for 24 h and cooled to room temperature and then to −20 °C; to this, a given volume of an initiator solution composed of triethylene glycol (0.67 mL, 0.005 mol) and DPMK (3.5 mL, 0.002 mol) in 50 mL of THF, EPEE (16.0 g, 0.11 mmol), and EO (44.0 g, 1.0 mmol) were introduced successively under magnetic stirring. Subsequently, the mixture was heated to 60 °C under stirring for 48 h. The reaction was terminated by the addition of a few drops of acidified methanol. After all the solvents were removed by reduced distillation, the crude product was dissolved in CH2Cl2 and then filtered, and the filtrate was titrated with 0.1 mol/L HCl. The concentration of DPMK was 0.57 mol/L.

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Deprotection of the EPEE Segments of the Copolymers

Poly(EO-co-EPEE)A [number-average molecular weight (Mn) = 11,600, 10 g, 0.86 mmol] was mixed with 160 mL of formic acid (0.266 mol); the solution was stirred at 20 °C for 30 min and then evaporated in vacuo at 50 °C to remove the formic acid. The crude product was then dissolved in a mixture of dioxane (100 mL) and methanol (50 mL), hydrolyzed by a KOH solution (1 mol/L, 27 mL) under refluxing for 24 h, and then neutralized with 5% HCl. After the solvents were removed under reduced pressure, the polymer was dissolved in water and purified by an ultrafiltration membrane; then, the filtered aqueous solution was concentrated to dryness, dissolved in CH2Cl2, and dried over anhydrous MgSO4. The filtrate was distilled in vacuo to remove CH2Cl2 and dried in vacuo at 50 °C. The pale yellow product, poly(EO-co-Gly), was obtained in a yield of 93%.

Synthesis of Graft Copolymer Poly(EO-co-Gly)-g-PCL

A typical process was as follows. A dried ampule containing CL (0.6 g, 5.26 mmol), and poly(EO-co-Gly)500 (Mn = 9200, 0.46 g, 0.05 mmol) was bubbled with nitrogen for 1 h at room temperature, and then a given amount of the catalyst ([Sn(Oct)2]/[OH] = 0.5) was injected under nitrogen by a syringe. The reaction was allowed to proceed for 24 h at 100 °C. After cooling to room temperature, the products were dissolved in THF and precipitated in cold diethyl ether. The copolymers were purified twice by dissolution/precipitation with THF/ether.

Synthesis of ICs of poly(EO-co-Gly)-g-PCL with z-CD

Poly(EO-co-Gly)500-g-PCL500 (Mn of grafted copolymer = 20,600, Mn of grafted PCL chains = 500, 50 mg, 2.5 μmol) and z-CD (300 mg, 308.4 μmol) were dissolved in 5 mL of acetone at 50 °C and 3 mL of distilled water at 60 °C, respectively, and then the copolymer solution was added dropwise to the z-CD solution at 60 °C for 6 h with stirring; the mixture was then cooled to room temperature and stirred for 35 h. The solid IC was isolated by centrifugation, washed with a limited amount of water and acetone, and dried in vacuo at 40 °C for 1 day. The yield was calculated on the basis of the used amounts of the copolymers and z-CD.

The whole polymerization process is outlined in Scheme 1.

RESULTS AND DISCUSSION

Characterization of Copolymer Poly(EO-co-EPEE) and Its Hydrolyzed Product Poly(EO-co-Gly)

The anionic copolymerization of EPEE and EO was carried out with a mixture of triethylene glycol and DPMK as the initiator. Table 1 shows the
data for the parent poly(EO-co-EPEE) and poly
(EO-co-Gly) copolymers. The molecular weight
distributions for all the samples were narrow,
and the composition of the poly(EO-co-EPEE)
copolymer was approximate to the monomer
feed ratio. The samples poly(EO-co-EPEE)A
($M_n = 11,600$) and poly(EO-co-EPEE)B
($M_n = 6200$) were deprotected under an acidic condition, and
poly(EO-co-Gly) with multihydroxyls was re-
covered. The measurements of the molecular
weights of poly(EO-co-EPEE) and its hydrolyzed
product poly(EO-co-Gly) were conducted in dif-
f erent systems because the former was soluble in
THF and insoluble in water and the latter was
insoluble in THF and soluble in water. The mo-
lecular weight of hydrolyzed product poly(EO-co-

Table 1. Data for the Parent Poly(EO-co-EPEE) and Poly(EO-co-Gly) Copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_f^a$</th>
<th>$R_r^b$</th>
<th>$M_n^c$</th>
<th>$M_w/M_n^d$</th>
<th>$M_n^e$</th>
<th>$M_w/M_n^f$</th>
<th>$N_{EPEE}^g$</th>
<th>$N_{OH}^h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(EO-co-EPEE)_A</td>
<td>1/9</td>
<td>1/8</td>
<td>13,800</td>
<td>1.06</td>
<td>11,600</td>
<td>1.01</td>
<td>22</td>
<td>2</td>
</tr>
<tr>
<td>Poly(EO-co-Gly)_A</td>
<td>—</td>
<td>—</td>
<td>9,200</td>
<td>1.15</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>24</td>
</tr>
<tr>
<td>Poly(EO-co-EPEE)_B</td>
<td>1/10</td>
<td>1/11</td>
<td>6,400</td>
<td>1.08</td>
<td>6,200</td>
<td>1.05</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Poly(EO-co-Gly)_B</td>
<td>—</td>
<td>—</td>
<td>4,300</td>
<td>1.18</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>12</td>
</tr>
</tbody>
</table>

$^a$ Feed ratio of EPEE to EO.

$^b$ Molar ratio of EPEE to EO in copolymer poly(EO-co-EPEE) measured by $^1$H NMR.

$^c$ Determined by GPC. Poly(EO-co-EPEE) was calibrated against polystyrene standards in THF, and poly(EO-co-Gly) was cali-
brated against PEO in water.

$^d$ Determined by MALDI-TOF MS.

$^e$ Determined by MALDI-TOF MS.

$^f$ Number of EPEE units in poly(EO-co-EPEE): $N_{EPEE} = M_n/(146 + 44R_r^b)$.

$^g$ Number of OH units in poly(EO-co-Gly): $N_{OH} = N_{EPEE} + 2$. $N_{EPEE}$ was calibrated by $M_n$ with $R_r$.
Gly) could be compared with the MALDI-TOF value of poly(EO-co-EPEE) by the consideration of the mass change from EPEE to glycidol in the copolymers. The molecular weight distribution before and after deprotection (shown in Table 1) did not change obviously, and this meant that the main chain of the copolymers was not cleaved under our experimental conditions.

The 1H NMR spectra of poly(EO-co-EPEE) and its hydrolyzed product poly(EO-co-Gly) are shown in Figure 1. The quadrilets at \(\delta = 4.63–4.75\) ppm were assigned to the methine protons \((a)\) of the EPEE moiety, the doublets at \(\delta = 1.29\) and \(1.30\) ppm and the triplet at \(\delta = 1.18–1.21\) ppm were assigned to the methyl protons of the EPEE moiety \((b\) and \(d)\), and the chemical shift at \(\delta = 3.53–3.80\) ppm were assigned to the protons of the main chain \((\gamma)\) and the methene protons of the lateral chains \((c\) and \(h)\). The ratio of EPEE to EO \((R_r)\) in the copolymers was calculated from Figure 1(a) with the following equation:

\[
R_r = \frac{I_b}{\left(\frac{I_{\gamma} - I_{c+h}}{4}\right)}
\]

where \(I_b\) and \(I_{\gamma} - I_{c+h}\) are the integrated areas of the methyl \((b)\) of ethyl vinyl ether and the protons of the main chain \((\gamma)\) and lateral chains \((c\) and \(h)\), respectively. The \(R_r\) values of copolymers A and B were 1/8 and 1/11, respectively, which were close to the feed ratio.

The protected group acetal of the EPEE segments in poly(EO-co-EPEE) could be cleaved by formic acid, and hydroxymethyl was recovered after saponification. The peaks at \(\delta = 4.63–4.75\) ppm \([-\text{O-CH(CH}_3\text{)}-\text{O-}; a]\), at \(\delta = 1.30\) and \(1.29\) ppm \([-\text{OCH(CH}_3\text{)}-\text{O-}; b]\), and at \(\delta = 1.18–1.21\) ppm \((-\text{O-CH}_3\); \(d)\), assigned to EPEE units of poly(EO-co-EPEE), disappeared completely in the spectra of poly(EO-co-Gly) [Fig. 1(b)]; this indicated that the efficiency of deprotection was very high, nearly 100%.

**Characterization of the Poly(EO-co-Gly)-g-PCL Copolymer**

Poly(EO-co-Gly) with hydroxyl groups could be used as the macroinitiator in the presence of Sn(Oct)$_2$ to initiate the polymerization of CL. Table 2 summarizes the data of the graft copolymerization of CL; the single peak in all the GPC traces

![Figure 1. 1H NMR spectra (CDCl$_3$) of (a) poly(EO-co-EPEE) and (b) poly(EO-co-Gly).](image-url)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Monomer Conversion (%)</th>
<th>(M_n^c)</th>
<th>(M_w^c/M_n^c)</th>
<th>(M_{n,NMR}^d)</th>
<th>(M_{n,\text{IC}}^e)</th>
<th>(M_{n,g}^f)</th>
<th>IC Yield (%)</th>
<th>CL/(\alpha)-CD g</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_1$</td>
<td>98</td>
<td>20,600</td>
<td>1.33</td>
<td>22,200</td>
<td>500</td>
<td>540</td>
<td>30</td>
<td>2.1</td>
</tr>
<tr>
<td>A$_2$</td>
<td>97</td>
<td>37,000</td>
<td>1.28</td>
<td>35,600</td>
<td>1,000</td>
<td>1,100</td>
<td>42</td>
<td>1.8</td>
</tr>
<tr>
<td>B$_1$</td>
<td>98</td>
<td>10,800</td>
<td>1.19</td>
<td>11,900</td>
<td>600</td>
<td>630</td>
<td>26</td>
<td>1.9</td>
</tr>
<tr>
<td>B$_2$</td>
<td>96</td>
<td>21,100</td>
<td>1.16</td>
<td>18,500</td>
<td>1,200</td>
<td>1,184</td>
<td>41</td>
<td>1.5</td>
</tr>
</tbody>
</table>

For A$_1$ and A$_2$ and B$_1$ and B$_2$, poly(EO-co-Gly)$_{9200}$ and poly(EO-co-Gly)$_{4300}$ were used. The polymerization conditions were as follows: for A$_1$, [poly(EO-co-Gly)]/[CL] = 1/100 mol/mol; for A$_2$, [poly(EO-co-Gly)]/[CL] = 1/200 mol/mol; for B$_1$, [poly(EO-co-Gly)]/[CL] = 1/120 mol/mol; polymerization temperature = 100 °C; and polymerization time = 24 h.

b Determined by gravimetry.
c Determined by GPC with polystyrene standards.
d Calculated as follows: \(M_{n,NMR} = M_{n,\text{poly(EG-co-Gly)}} + N_{\text{OH}} \times M_{n,g}^f\). \(M_{n,\text{poly(EG-co-Gly)}}\) is the molecular weight of poly(EG-co-Gly) derived by GPC; \(N_{\text{OH}}\) is the hydroxyl number.
e Theoretical number-average molecular weight of grafted PCL.
f Obtained by 1H NMR for grafted PCL.
g Measured by 1H NMR.

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confirmed that there was no macroinitiator \([\text{poly(EO-co-Gly)}]\) remaining. Table 2 also shows that the molecular weight distribution of the graft copolymer initiated by \([\text{poly(EO-co-Gly)9200}]\) was wider than that of \([\text{poly(EO-co-Gly)4300}]\); this may be attributed to the more difficult diffusion of \([\text{poly(EO-co-Gly)9200}]\) with a higher molecular weight than that of \([\text{poly(EO-co-Gly)4300}]\) with a low molecular weight in CL polymerization.

Figure 2 shows the \(^1\text{H NMR spectrum (CDCl}_3\) of poly(EO-co-Gly)-g-PCL.\]

Characterization of the Inclusion of the Graft Copolymers with \(\alpha\)-CD

ICs of PCL graft copolymers with \(\alpha\)-CD were successfully prepared. An aqueous solution of \(\alpha\)-CD became turbid immediately after the addition of the copolymers, and this indicated the rapid formation of the ICs. Figure 3 shows the \(^1\text{H NMR spectrum of the poly(EO-co-Gly)-g-PCL/\alpha\-CD IC.}\) The IC composition of poly(EO-co-Gly)\(\_\_\_\_\_\text{g-PCL/\alpha\-CD could be given by a comparison of the integral areas of the proton peaks of the graft copolymer with respect to the linear PCL; this is listed in Table 2. It has been reported that the PCL/\(\alpha\)-CD composition is stoichiometrically one to one (CL unit = cyclodextrin). However, in our system, as Table 2 shows, the amount of \(\alpha\)-CD threaded by grafted PCL chains was less than that of the linear PCL; the yield was in the range of 70–94%.

The chain length of PCL can be controlled by the variation of the molar ratio of the CL monomer to poly(EO-co-Gly), and the molecular weight of grafted PCLs and graft copolymer poly(EO-co-Gly)-g-PCL can also be obtained from the \(^1\text{H NMR spectrum as the following formula shows:}\]

\[
M_{n\_\_\_\_\text{g}} = 114 \times \frac{I_c}{I_h}
\]

where \(M_{n\_\_\_\text{g}}\) is the number-average molecular weight of the grafted PCL side chains and \(I_h\) and \(I_c\) are the integral areas of the methylene of glycidol segments of poly(EO-co-Gly) and of the methylene in the repeating unit of PCL, respectively. As Table 2 shows, the molecular weight of grafted PCL derived from NMR was near the theoretical values but was different from the value from GPC because of the different hydrodynamic volume of the graft copolymer with respect to the linear polystyrene standard.
26–42%. It was demonstrated that some CL units near the main chain could be difficult to thread by 2-CDs because of the repulsion of side chains and the steric hindrance between the backbone and side chains. The yield of ICs increased with the length of the PCL side chain, and this demonstrated that the short side chains were more difficult to thread than the long side chains because of the steric hindrance from the backbones.

The XRD patterns of 2-CD, the pure copolymers, and the corresponding ICs are shown in Figure 4. For the pure copolymers, only prominent peaks at 21.4 and 23.8° belonging to PCL appeared, but no PEG crystalline peaks with a strong reflection at 2θ = 19.3 and 23.5° were found. This indicated that the poly(EO-co-Gly) main chain of poly(EO-co-Gly)-g-PCL might not be crystallized because of the existence of PCL side chains. The characteristic peak at 2θ = 20° in the curve of the complex demonstrated that 2-CD rings were stacked along the PCL side-chain axis to form the necklace structure. Therefore, the XRD results confirmed that poly(EO-co-Gly)9200-g-PCL1000/2-CD and poly(EO-co-Gly)4300-g-PCL1200/2-CD possessed a channel structure, the free 2-CD had a cage structure, and the PCL side chains were included in the hydrophobic cavities of 2-CD. Solid-state 13C CP–MAS spectroscopy provided more evidence for the IC formation, and the spectra of ICs composed of poly(EO-co-Gly)9200-g-PCL1000/2-CD and free 2-CD are shown in Figure 5. It has been reported that free 2-CD of C-1 and C-4 associated with the six 2,1,4-linked glucose residues assume a less symmetrical conformation in the crystalline state. The peaks at δ = 80.5 and 98 ppm, assigned to the C-1 and C-4, respectively, adjacent to the conformally strained glucose linkage disappeared in the spectrum of the complex. Each carbon of glucose could be observed in a single peak. It could be concluded that 2-CD including the grafted PCL guest adopted a symmetrical cyclic conformation and that each glucose unit of 2-CD was in a similar environment; this confirmed that 2-CD was threaded onto the PCL side chains in the complexes.

The melting behavior and cold-crystallization behavior of the pure copolymer and the ICs are shown in Figure 6. The melting peak and the crystallization peak were observed in the curve.
of the pure copolymer poly(EO-co-Gly)$_{9200}$-g-PCL$_{1000}$, but no melting peak was detected for z-CD and the ICs. This fact confirmed further that no free copolymers existed, the crystallization of PCL was remarkably suppressed in the z-CD cavity, and the original crystalline properties of the copolymers were lost.

The thermal properties of copolymer/z-CD complexes were investigated with TGA, as shown in Figure 7. The curve of poly(EO-co-Gly)$_{4300}$-g-PCL$_{1200}$ presents a two-step thermal degradation: the first step can be attributed mainly to the decomposition of the poly(EO-co-Gly) main chain, whereas the second step is mainly that of grafted PCL. After complexation, the initial decomposition of poly(EO-co-Gly)$_{4300}$-g-PCL$_{1200}$/z-CD and the decomposition of the second step were higher than those of pure poly(EO-co-Gly)$_{4300}$-g-PCL$_{1200}$, and this indicated that complexation with z-CD enhanced the thermal stability of the grafted PCL.

**CONCLUSIONS**

A series of grafted poly(EO-co-Gly)-g-PCL copolymers were synthesized by the combination of anionic polymerization and ring-opening polymerization. GPC and $^1$H NMR data demonstrated that the polymerization courses were under control. The crystalline ICs formed by the grafted copolymers with z-CD were characterized with $^1$H NMR, DSC, XRD, TGA, and $^{13}$C CP–MAS NMR in detail. XRD indicated that all ICs with z-CD had a channel-type crystalline structure. The stoichiometry of the CL unit to the z-CD ring for the ICs, given by $^1$H NMR spectra, indicated that the PCL branches were not completely covered by CDs. This could be explained as follows: the steric hindrance between the backbone and side chains prevented z-CDs from being fully covered.

**REFERENCES AND NOTES**