

# Starch-*g*-Polycaprolactone Copolymerization Using Diisocyanate Intermediates and Thermal Characteristics of the Copolymers

DONG-KEON KWEON, DONG-SOO CHA, HYUN-JIN PARK, SEUNG-TAIK LIM

Graduate School of Biotechnology, Korea University, 5-1, Anam-dong, Sungbuk-ku, Seoul 136-701, South Korea

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**ABSTRACT:** Starch-*g*-polycaprolactone copolymers were prepared by two-step reactions. The diisocyanate-terminated polycaprolactone (NCO-PCL) was prepared by introducing NCO on both hydroxyl ends of PCL using diisocyanates (DI) at a molar ratio between PCL and DI of 2:3. Then, the NCO-PCL was grafted onto corn starch at a weight ratio between starch and NCO-PCL of 2:1. The chemical structure of NCO-PCL and the starch-*g*-PCL copolymers were confirmed by using FTIR and  $^{13}\text{C}$ -NMR spectrometers, and then the thermal characteristics of the copolymers were investigated by DSC and TGA. By introducing NCO to PCL ( $M_n$ : 1250), the melting temperature ( $T_m$ ) was reduced from 58 to 45°C. In addition, by grafting the NCO-PCL (35–38%) prepared with 2,4-tolylene diisocyanate (TDI) or 4,4-diphenylmethane diisocyanate (MDI) onto starch, the glass transition temperatures ( $T_g$ 's) of the copolymers were both 238°C. With hexamethylene diisocyanate (HDI), however,  $T_g$  was found to be 195°C. The initial thermal degradation temperature of the starch-*g*-PCL copolymers were higher than that of unreacted starch (320 versus 290°C) when MDI was used, whereas the copolymers prepared with TDI or HDI underwent little change. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 986–993, 2000

**Key words:** starch-*g*-polycaprolactone copolymer; diisocyanate-terminated polycaprolactone; thermal properties

## INTRODUCTION

In recent years, much attention has been given to the environmental pollution from nondegradable plastic wastes. However, the production and consumption of petroleum-based plastics increases by 5–10% every year. Countries worldwide have put much effort and emphasis on legislation and the mandating of recycling and, at the same time, on the development of alternative degradable materials.<sup>1,2</sup>

As a biopolymer from agricultural resources, starch is an attractive and economically feasible alternative material in developing degradable plastics. Different approaches have been made to utilize starch for thermoplastic production.<sup>3</sup> Native starch itself can be processed under controlled pressure and temperature into thermoplastic products by extrusion, injection, or blow molding.<sup>4</sup> Starch-based thermoplastics which have already been introduced into the market include agricultural foils, garbage or composting bags, injection-molded golf tees and picnic wares, and variously shaped starch foams for short-time usage in the packaging and fast-food industry.<sup>5</sup>

Starch by itself, however, cannot satisfactorily replace the functional and physical properties of nondegradable plastics, as starch-based plastics

Correspondence to: S.-T. Lim (limst@mail.korea.ac.kr).  
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are predominantly water-soluble and mechanically weak. To overcome these drawbacks, blending or grafting with hydrophobic polymers is commonly exercised. Much literature has reported the improvement in physical properties by blending or grafting with synthetic polymers, such as polyethylene, poly(vinyl alcohol), poly(vinyl chloride), and the poly(ethylene-co-acrylic acid) copolymer.<sup>6–12</sup>

Most of the synthetic polymers, however, are immiscible with starch. Consequently, the thermodynamic incompatibility usually leads to poor performance of the blended materials. Even though there are improvements in performance, the incorporated polymers often cause incomplete degradability of the blend.

Polycaprolactone (PCL), usually prepared by polymerization of caprolactone with glycol as an initiator, is recognized as one of the few synthetic polymers which are biodegradable.<sup>13</sup> PCL has been developed, also, as a carrier in drug-delivery systems owing to its biocompatibility and nontoxicity.<sup>14,15</sup> Moreover, because of its high compatibility and hydrophobicity, PCL is of interest for use in modifying material in blends with starch or other polymers.<sup>16,17</sup> The preparation method for grafting PCL onto starch and the effects from PCL incorporation as a modifier on the thermal characteristics, the phase morphology, the interfacial adhesion, and the ultimate mechanical properties of the starch, however, have not been adequately reported.<sup>18,19</sup>

In this study, starch-g-PCL copolymers were prepared by using diisocyanated intermediates of PCL, and the conformation and thermal properties of the copolymers were investigated.

## EXPERIMENTAL

### Materials and Reagents

Corn starch and two PCLs ( $M_n$  1250 and 2000) terminated with hydroxyl groups were purchased from the Aldrich Chemical Co. (Milwaukee, WI). Three diisocyanates (DIs) including 2,4-tolylene diisocyanate (TDI), 4,4-diphenylmethane diisocyanate (MDI), and hexamethylene diisocyanate (HDI) were purchased from the Tokyo Kasei Co. (Tokyo, Japan). Dimethyl sulfoxide (DMSO) and dibutylamine (DBA) were purchased from the Junsei Chemical Co. Ltd. (Tokyo, Japan). The starch and PCLs were dried in a vacuum oven at 50°C for 24 h prior to use. All other commercially

available chemicals were reagent grade and used without further purification.

### Measurement of Hydroxyl Value

The hydroxyl value in PCL was measured by alkaline titration after acetylation.<sup>20</sup> A PCL (3 g) and an acetic anhydride/pyridine solution (5% w/w, 200 mL) were mixed and reacted at 100°C for 3 h under N<sub>2</sub>. After being cooled to room temperature, it was titrated with 0.5N NaOH solution until neutralization. The hydroxyl value of PCL was calculated by the following equation:

$$\text{Hydroxyl value} = [(A - B) \times N]/W \quad (1)$$

where  $A$  is the titration volume (mL) of the NaOH solution for blank;  $B$ , the titration volume (mL) of the NaOH solution for PCL;  $N$ , the normality of the NaOH solution; and  $W$ , the dry weight (g) of PCL.

### Preparation of DI-terminated PCL (NCO-PCL)

NCO-PCL was prepared by reacting PCL with DI (TDI, MDI, or HDI) in bulk. PCL (20 g) and an appropriate amount of DI (5.27–20.4 g) were charged in a four-necked flask equipped with a mechanical stirrer, reflux condenser, and N<sub>2</sub> inlet. The reaction was then carried out at 100°C for 3 h. The unreacted DI was removed by a rotary vacuum evaporator.

### Measurement of NCO Content

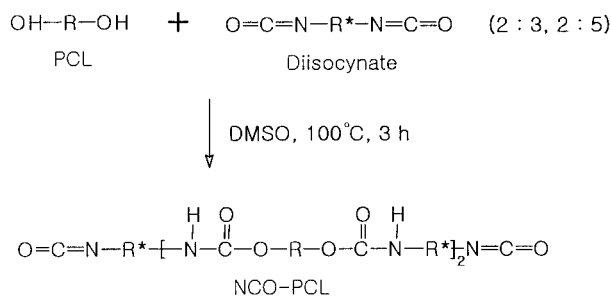
Accurately weighed NCO-PCL (1 g) was mixed with DBA (10 mL) and toluene (10 mL). The mixture was then mechanically stirred for an additional 10 min and titrated with 1.0N HCl solution. The isocyanate content in the NCO-PCL was calculated according to the following equation:

$$\begin{aligned} \text{NCO content (\%)} \\ = [0.042 \times 100 \times N \times (A - B)]/W \quad (2) \end{aligned}$$

where  $A$  is the titration volume (mL) of the HCl solution for blank;  $B$ , the titration volume (mL) of the HCl solution for NCO-PCL;  $N$ , the normality of the HCl solution; and  $W$ , the dry weight (g) of NCO-PCL.

### Preparation of Starch-g-PCL Copolymers

Vacuum-dried starch (10 g) was dissolved in anhydrous DMSO (200 mL) and, separately, NCO-



**Scheme 1** Preparation of NCO-PCLs.

PCL (5 g) was dissolved in anhydrous DMSO (100 mL). The starch solution was slowly added to the NCO-PCL solution while stirring for 30 min. The mixture was then stirred at 100°C for 3 h. The reaction mixture was cooled to room temperature, and then excess methanol was added to the mixture. The precipitate was recovered by filtration and the unreacted NCO-PCL was removed by Soxhlet extraction with toluene for 24 h.

### Structural and Thermal Characterization

Fourier transform infrared (FTIR) spectra were obtained from KBr pellets of the diisocyanated PCLs and grafted copolymers with an FTIR spectrometer (Perkin-Elmer Spectrum GX, Beaconsfield, UK).<sup>13</sup> Carbon nuclear magnetic resonance (<sup>13</sup>C-NMR) spectra were obtained from DMSO-*d*<sub>6</sub> solutions containing the diisocyanated PCLs and grafted copolymers with an NMR spectrometer (Varian EM-360A, San Fernando, CA).

Glass transition and melting characteristics of the NCO-PCLs and grafted copolymers were measured using a differential scanning calorimeter (DSC; Seiko 6100, Chiba, Japan) in a temperature range of -150–250°C at a heating rate of 10°C/min. Thermal degradation of the NCO-PCLs and grafted copolymers was measured using a thermal gravimetric analyzer (TGA; Mettler TG 50, Greifensee, Switzerland) in a temperature range of 20–500°C, at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Measurement of Hydroxyl Value

The hydroxyl values of PCL-1250 and 2000 were 0.00163 and 0.00105 mol/g, respectively. On the basis of these hydroxyl values, the reaction ratio between PCL and DI (TDI, MDI, or HDI) was determined.

### Preparation of NCO-PCL

NCO-PCLs were prepared by the bulk reaction between hydroxyl-terminated PCL and DI (TDI, MDI, or HDI) at 100°C for 3 h. The reaction is briefly shown in Scheme 1. Additionally, the NCO content and the reaction product yield for the NCO-PCL under various conditions are shown in Table I.

The determined NCO content of NCO-PCL was similar to the theoretical values. Therefore, the reaction appeared complete within 3 h at 100°C. When the molar ratio between PCL and DI was 2:3, the product yield of the NCO-PCL based on the initial amount of PCL and DI was 85–93%, indicating that most of the reagents participated in the isocyanate reaction. Furthermore, there was no significant difference in the reaction yield between the two PCLs differing in molecular weight (PCL-1250 and PCL-2000). With more DI (PCL:DI, 2:5), however, the yield decreased prominently to 60–65%. It was inferred that, at this ratio, monomeric isocyanate was formed as a side reaction.

Comparing the three DIs, the yield of NCO-PCL was slightly higher when MDI was used rather than TDI or HDI. This result indicates that MDI has a superior reactivity to PCL than to TDI and HDI.

In general, the reaction between diol and DI follows a second-order kinetics, and the rate de-

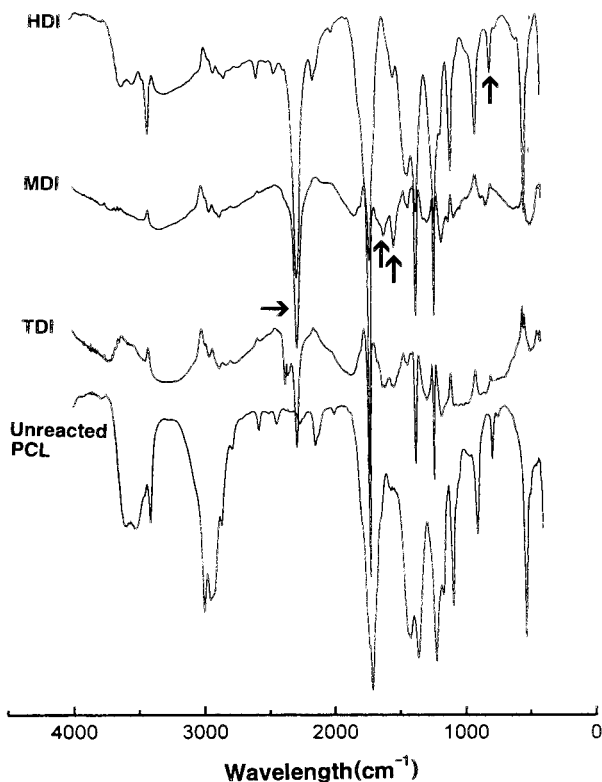
**Table I** Isocyanate (NCO) Content and Yield of NCO-PCL in Various Reaction Conditions

Reactants	Molar Ratio of PCL : DI	NCO Content (%) <sup>a</sup>		Yield <sup>b</sup> (%)
		The	Exp	
PCL-1250 + TDI	2:5	2.67	2.62	60
PCL-1250 + MDI		2.49	2.40	65
PCL-1250 + HDI		2.69	2.50	63
PCL-1250 + TDI	2:3	2.67	2.62	90
PCL-1250 + MDI		2.49	2.42	95
PCL-1250 + HDI		2.69	2.51	90
PCL-2000 + TDI		1.81	1.83	88
PCL-2000 + MDI		1.72	1.50	93
PCL-2000 + HDI		1.81	1.62	87

Reaction was carried out in DMSO at 100°C for 3 h.

<sup>a</sup> The and Exp represent the theoretical and experimental values, respectively.

<sup>b</sup> Wt. of NCO-PCL/(wt. of PCL + wt. of DI).



**Figure 1** FTIR spectra of the NCO-PCLs prepared with PCL-1250 and different DIIs (TDI, MDI, and HDI).

depends on the molar ratio of both components.<sup>21</sup> Changing the molar ratio makes it possible to control the end group and molecular weight of the isocyanate products.

In the experimental conditions used, NCO-PCL, having isocyanate terminals at both ends, could be prepared by the reaction of PCL and DI at the molar ratio of 2:3 for PCL:DI. Therefore, the NCO-PCL prepared under this molar ratio was used as the intermediate for the starch-g-PCL copolymerization.

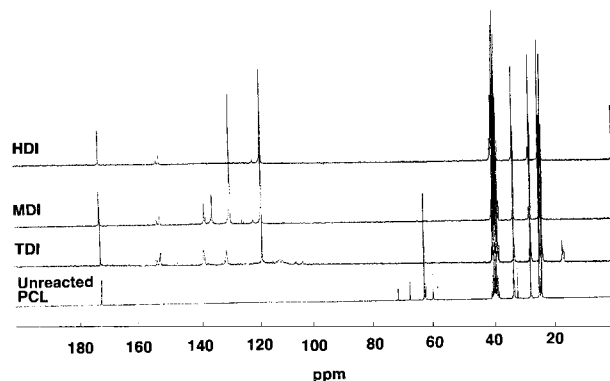
The FTIR and <sup>13</sup>C-NMR of the NCO-PCL prepared with PCL-1250 and different DIIs at a 2:3 molar ratio are given in Figures 1 and 2. The FTIR spectra of unreacted PCL-1250 showed a strong hydroxyl peak around 3400 cm<sup>-1</sup> and a sharp peak at 1710 cm<sup>-1</sup> for the internal ester groups. By introducing NCO groups onto the PCL terminals, a new sharp peak at 2270 cm<sup>-1</sup> (marked by an arrow) representing the NCO groups and 1520 cm<sup>-1</sup> for the newly formed amide —NH groups (marked by an arrow) were shown. At the same time, the hydroxyl peak around 3400 cm<sup>-1</sup> almost disappeared in the NCO-PCL spectra.

For the NCO-PCL prepared with TDI and MDI, the FTIR spectra showed a new peak around 1600 cm<sup>-1</sup> (marked by an arrow), indicating the presence of the aromatic group originated from TDI and MDI. The FTIR spectra of the NCO-PCL prepared with HDI showed a slightly increased peak, around 780 cm<sup>-1</sup> (marked by an arrow), indicating the presence of the methylene group originated from HDI.

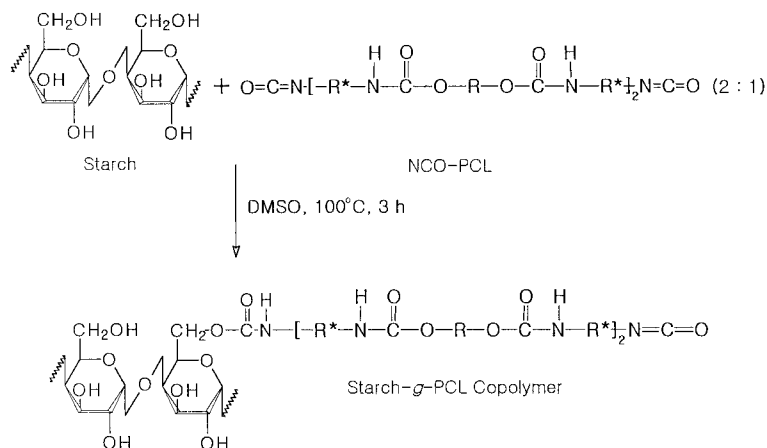
As shown in Figure 2, the <sup>13</sup>C-NMR spectrum of the unreacted PCL showed a characteristic peak around 64 ppm, indicating the terminated alcohol groups. The internal ester linkages and hydrocarbons could be confirmed around 172 and 24–34 ppm, respectively. By the NCO incorporation, the NMR spectra showed a new intense signal around 120 ppm, representing the isocyanate carbon. The hydroxyl terminal carbon signal completely disappeared with the NCO-PCLs, indicating that the isocyanation on the terminals of PCL was almost complete. The NMR spectra of the NCO-PCLs prepared with TDI or MDI showed new peaks around 130–137 ppm due to the presence of aromatic groups. When PCL-2000 was used, the FTIR and NMR spectra of the NCO-PCLs were similar to those prepared with PCL-1250 (data not shown).

### Preparation of Starch-g-PCL Copolymers

The starch-g-PCL copolymer was prepared by reacting NCO-PCL with starch at 100°C for 3 h. The reaction for the starch-g-PCL copolymerization is briefly shown in Scheme 2, and the % grafting and product yield of the starch-g-PCL copolymers are shown in Table II. The percent grafting and yield were relatively constant, 32–



**Figure 2** <sup>13</sup>C-NMR spectra of the NCO-PCLs prepared with PCL-1250 and different DIIs (TDI, MDI, and HDI).



**Scheme 2** Preparation of starch-g-PCL copolymers.

38% and 88–92%, respectively, regardless of DI type. But the grafting was slightly more efficient when PCL-1250 was used. The yield over 88% indicates that NCO-PCL added to the mixture was effectively incorporated into the starch.

The FTIR and  $^{13}\text{C}$ -NMR spectra of the starch-g-PCL copolymers are shown in Figures 3 and 4, respectively. In Figure 3, the native starch showed a typical broad hydroxyl peak at approximately  $3400\text{ cm}^{-1}$  on the FTIR spectrum. By grafting NCO-PCL onto starch, the FTIR spectra showed new peaks around  $1730\text{ cm}^{-1}$ , indicating the amide ester linkage, around  $2270\text{ cm}^{-1}$  for the NCO group, and around  $1540\text{ cm}^{-1}$  for the amide  $-\text{NH}$  group (marked by arrows). The substitu-

tion by NCO-PCL also reduced the peak intensity of the hydroxyl groups in starch ( $3400\text{ cm}^{-1}$ ). With the grafted copolymers, the aromatic ring from TDI and MDI were also shown by a new peak around  $1640\text{ cm}^{-1}$ .

**Table II** Percent Grafting and Yield for Starch-g-PCL Copolymerization with Various NCO-PCL Intermediates

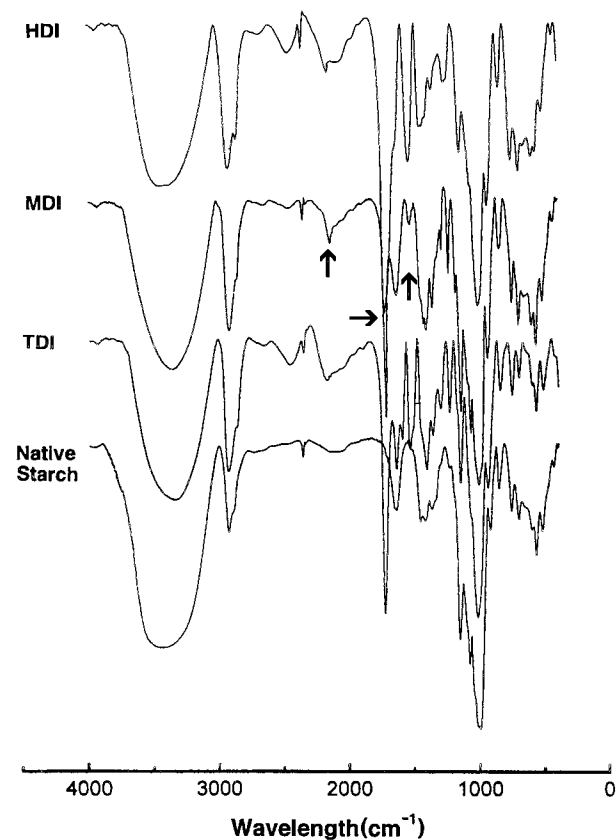
Intermediates (NCO-PCL) <sup>a</sup>	Grafting <sup>b</sup> (%)	Yield <sup>c</sup> (%)
TDI-PCL-1250	38	92
MDI-PCL-1250	35	90
HDI-PCL-1250	35	90
TDI-PCL-2000	32	88
MDI-PCL-2000	32	88
HDI-PCL-2000	35	90

Grafting was carried out in DMSO at  $100^\circ\text{C}$  for 3 h at a starch : NCO-PCL weight ratio of 2 : 1.

<sup>a</sup> The molar ratios of PCL and DI for isocyanation were both 2 : 3.

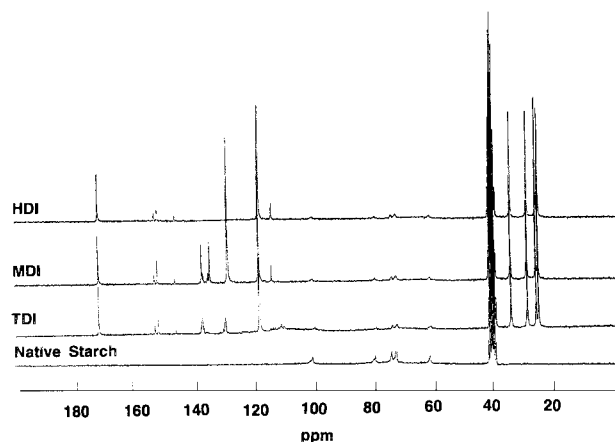
<sup>b</sup> (Wt of starch-g-PCL copolymer - wt of starch)/wt of starch.

<sup>c</sup> Wt of starch-g-PCL copolymer/(wt of starch + wt of NCO-PCL).



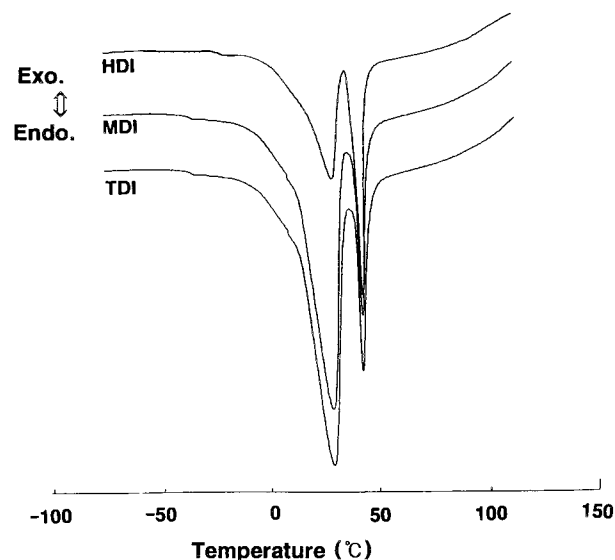
**Figure 3** FTIR spectra of starch-g-PCL copolymers prepared with PCL-1250 and different DI (TDI, MDI, and HDI).



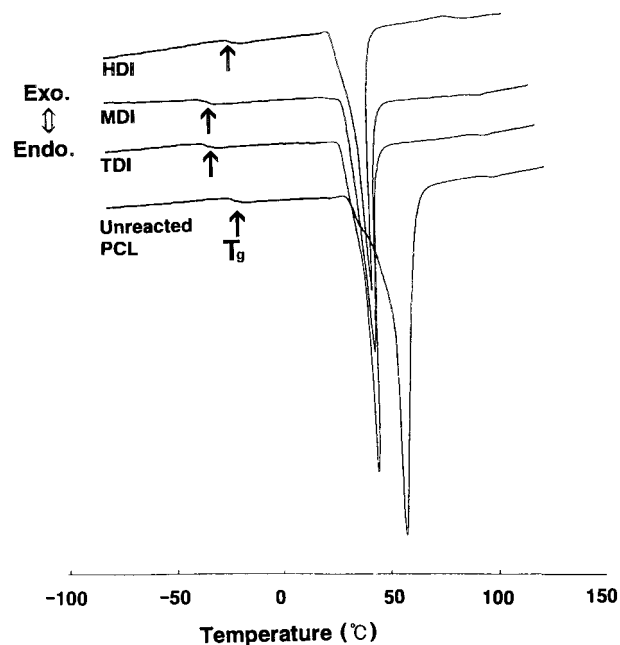


**Figure 4**  $^{13}\text{C}$ -NMR spectra of starch-g-PCL copolymers prepared with PCL-1250 and different DI's (TDI, MDI, and HDI).

The NMR spectra also confirmed the grafting of NCO-PCL onto starch (Fig. 4). The grafted copolymers showed that several peaks newly appeared around 24–34 ppm, indicating the presence of the hydrocarbon chains of PCL, at 172 ppm from the ester linkages, and around 120 ppm from the NCO groups. The NMR spectra also showed aromatic groups with peaks around 130–137 ppm with the copolymers prepared with TDI or MDI. In the case of starch-g-PCL copolymers prepared with PCL-2000, the FTIR and NMR spectra were similar to those prepared with PCL-1250 (data not shown).



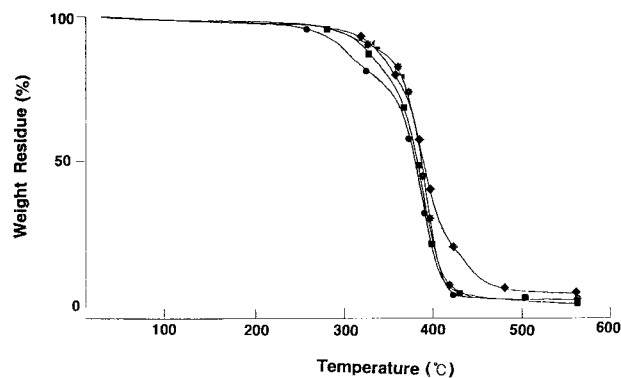
**Figure 5** DSC thermograms of resulting products prepared with PCL-1250 and different DI's (TDI, MDI, and HDI) at a molar ratio of 2:5 for PCL:DI.



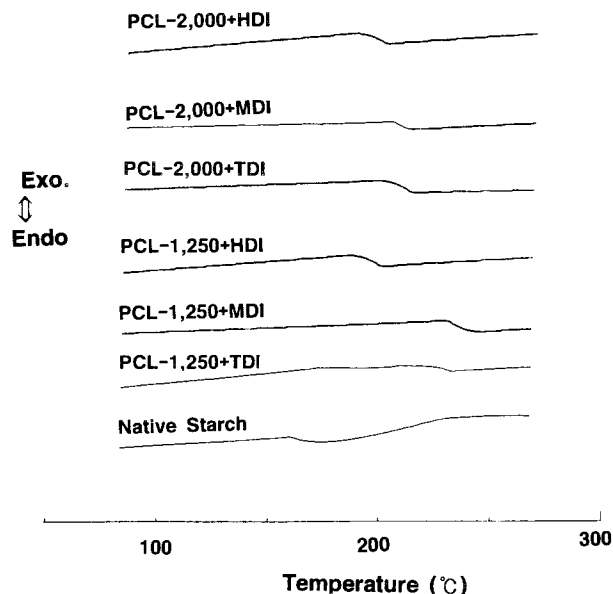
**Figure 6** DSC thermograms of NCO-PCLs prepared with PCL-1250 and different DI's (TDI, MDI, and HDI) at a molar ratio of 2:3 for PCL:DI.

#### Thermal Properties of NCO-PCL

The thermal characteristics for the NCO-PCL prepared with PCL-1250 and various DI's are given in Figures 5–7. As shown in Figure 5, the NCO-PCL at a molar ratio of 2:5 for PCL:DI without additional purification showed a DSC thermogram having two major peaks at the peak temperatures of 30 and 45°C, respectively. But the NCO-PCL prepared at a molar ratio of 2:3 showed that the  $T_m$  of the NCO-PCL appeared at



**Figure 7** TGA thermograms of NCO-PCLs prepared with PCL-1250 and different DI's (TDI, MDI, and HDI) at a molar ratio of 2:3 for PCL:DI. (\*) Unreacted PCL; (●) TDI-PCL; (◆) MDI-PCL; (■) HDI-PCL.



**Figure 8** DSC thermograms of starch-*g*-PCL copolymers prepared with different PCLs and DIs (TDI, MDI, and HDI).

45°C regardless of the type of DI (Fig. 6). As indicated previously, monomeric isocyanate was formed at the molar ratio of 2:5, and this decreased the overall yield of the NCO-PCL (Table I). The low-temperature endotherm might represent the melting of the monomeric isocyanate and that the high temperature endotherm at 45°C resulted from the melting of NCO-PCL. The  $T_m$  was found to be 13°C lower than that of unreacted PCL (Fig. 6). By introducing NCO groups onto PCL terminals by TDI and MDI, the  $T_g$  also decreased to a lower temperature (about -30°C), whereas the unreacted PCL-1250 showed a  $T_g$  at approximately -20°C. But the  $T_g$  of the NCO-PCL prepared with HDI underwent little change with the unreacted PCL (Fig. 6). The thermograms of the NCO-PCL prepared with PCL-2000 were similar to those with PCL-1250, but melting appeared at a slightly higher temperature (approximately 48°C) (data not shown).

In Figure 7, the thermal degradation of PCL-1250 started at approximately 360°C ( $T_d$ ) on the TGA curve. The NCO incorporation shifted the  $T_d$  to a lower temperature which ranged from 292 to 315°C. Also, the degradation of the NCO-PCLs occurred in broader ranges compared to that of the unreacted PCL. Among the DIs, the NCO-PCL prepared with MDI appeared more thermally stable than did those prepared with either TDI or HDI. In addition, the NCO-PCLs pre-

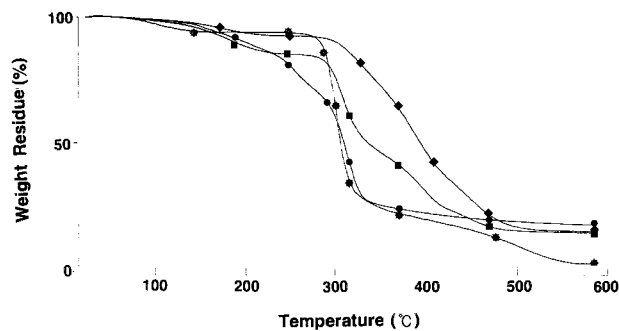
pared with PCL-2000 showed similar TGA trends, but the  $T_d$  values were 10–20°C higher than those of the NCO-PCLs with PCL-1250 (data not shown).

### Thermal Properties of the Starch-*g*-PCL Copolymer

The thermal transition behavior for the starch-*g*-PCL copolymers measured by DSC and TGA are shown in Figures 8 and 9. As shown in Figure 8, the DSC curve of the native starch showed a broad transition peak from 163 to 230°C. The starch measured was in the form of dry powder and contained approximately 10% moisture. We assumed that the transition which appeared on the thermogram was from both the melting of the starch crystals and the thermal decomposition.

By grafting NCO-PCL prepared with PCL-1250 onto starch, the glass transition of the copolymers could be clearly shown on the thermograms. However, no melting transition occurred while being heated to 250°C. Because the starch was fully melted during the copolymerization and recovered as amorphous state copolymers, no melting peak for the starch was detected. The  $T_g$  appeared at 233°C for the starch-*g*-PCL copolymer prepared with either TDI or MDI and at 195°C for the starch-*g*-PCL copolymer with HDI. In addition, the thermograms of the starch-*g*-PCL copolymer prepared with PCL-2000 were similar to those with PCL-1250, but the  $T_g$  for PCL-2000 was lower than that of PCL-1250.

As shown in Figure 9, the degradation temperature ( $T_d$ ) was found around 290°C for starch, and the degradation progressed at a narrow temperature range (290–310°C). The degradation of the copolymers, however, continued in broader temperature ranges. By grafting NCO-PCL (PCL-



**Figure 9** TGA thermograms of starch-*g*-PCL copolymers prepared with PCL-1250 and different DIs (TDI, MDI, and HDI). (\* Native starch; (●) TDI-PCL; (◆) MDI-PCL; (■) HDI-PCL.

1250), the  $T_d$  changed, depending on the type of DIIs. The  $T_d$  at the point where the degradation started was shifted to a lower temperature at approximately 245°C when TDI was used, but it was significantly higher (305°C) when MDI was used. With HDI, the  $T_d$  was similar to that of unreacted starch. Among the starch-*g*-PCL copolymers, those prepared with the MDI intermediate were most stable, to the point of thermal degradation.

TGA curves of the starch-*g*-PCL copolymers prepared with PCL-2000 were similar to those with PCL-1250 (data not shown). From these results, it was found that by grafting PCL onto starch the thermal stability was increased largely when MDI was used for the NCO-PCL intermediate.

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