

# Syntheses and Thermal Properties of Poly(hydroxy)urethanes by Polyaddition Reaction of Bis(cyclic carbonate) and Diamines

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Received 31 August 2000; accepted 26 December 2000

**ABSTRACT:** In this study, we synthesized poly(hydroxy)urethanes by the polyaddition reaction of bis(cyclic carbonate) and diamine. Bis(cyclic carbonate) was prepared from diglycidyl ether based on bisphenol S and carbon dioxide. Thermal properties and solubilities of the poly(hydroxy)urethanes of five different diamines were compared. The thermal properties of the poly(hydroxy)urethanes depended on the structure of the diamine as well as the structure of the monomer. These poly(hydroxy)urethanes were soluble only in aprotic solvents because of the hydrophilic character of the hydroxy group. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2735–2743, 2001

**Key words:** poly(hydroxy)urethane; bis(cyclic carbonate); carbon dioxide; phase transfer catalyst

## INTRODUCTION

Recently, synthetic materials prepared from carbon dioxide have received much attention from the viewpoint of environment preservation.<sup>1–6</sup> Due to their high polarities, coordination abilities, and reactivities, cyclic carbonates containing carbon dioxide, for example, have been widely investigated for optical, magnetic, and electronic applications.<sup>7,8</sup> Generally, syntheses of bis(cyclic carbonate)s from the reaction of diglycidyl ether with carbon dioxide have been performed in the presence of Lewis acids, transition–metal

complexes, or alkali metallic compounds as catalysts under high carbon dioxide pressures (>20 atm).<sup>2,5,10–12</sup> However, we have performed syntheses of bis(cyclic carbonate)s by the reaction of diglycidyl ether based on bisphenol S (DGEBS) with carbon dioxide using a phase transfer catalyst (PTC) under atmospheric pressure.<sup>13</sup> This reaction gave bis(cyclic carbonate)s in high yield at a relatively mild reaction temperature.

On the other hand, polyurethane (PU) products are generally used in the automobile, paint, furniture, medical, and textile industries. In this study, we have synthesized poly(hydroxy)urethanes using carbon dioxide, as a new polymer-bearing hydroxy groups. The poly(hydroxy)urethane is usually difficult to synthesize by the conventional polyaddition of polyol and diisocyanate.

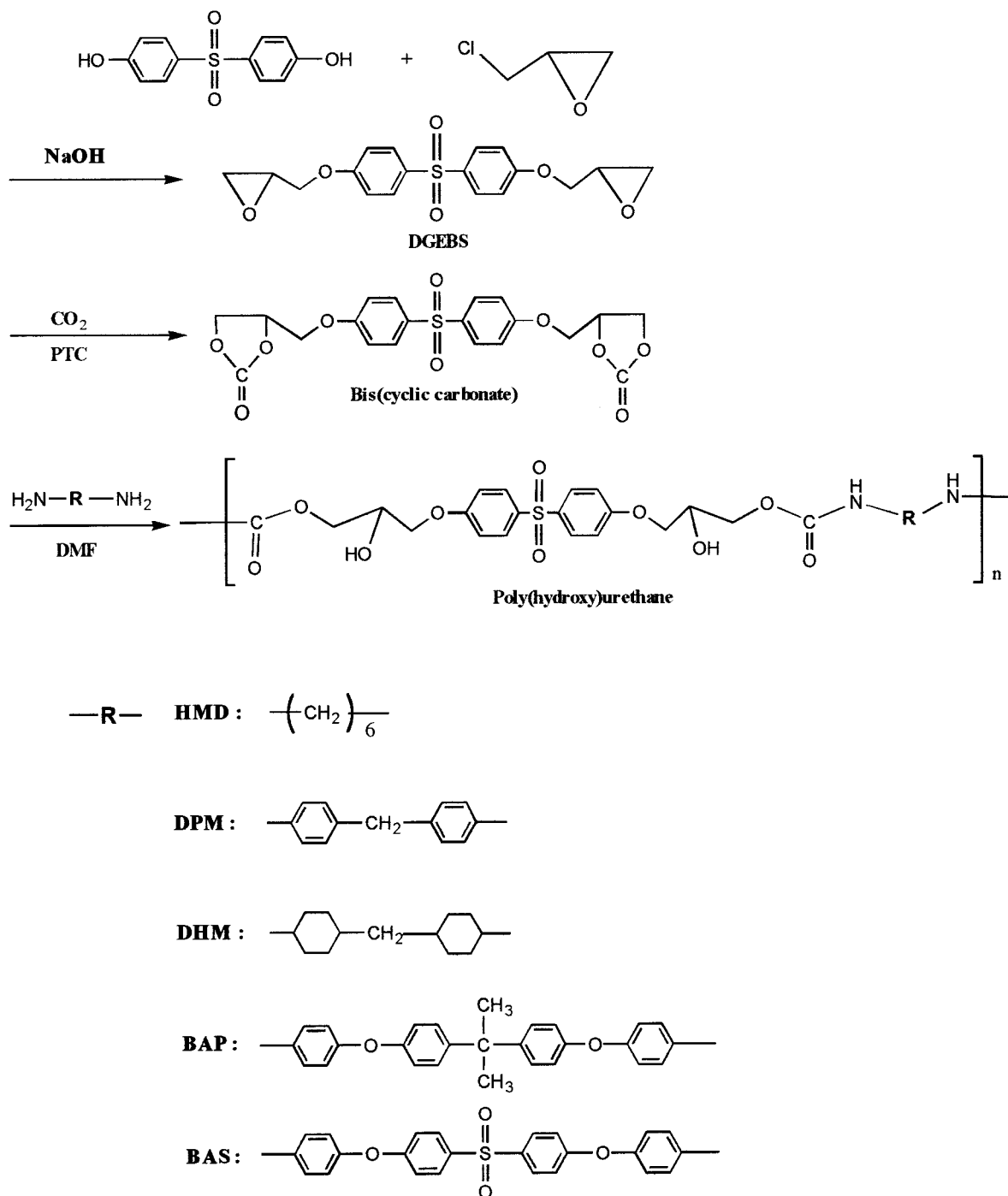
In this article, therefore, we report on the syntheses of bis(cyclic carbonate)s by the reaction of carbon dioxide with DGEBS in the presence of a PTC, and the polyaddition reactions of bis(cyclic

Correspondence to: J.-K. Lee.

Contract grant sponsor: Korea Science & Engineering Foundation; contract grant number: 8609509209509103.

Contract grant sponsor: Brain Korea 21 Project.

*Journal of Applied Polymer Science*, Vol. 81, 2735–2743 (2001)  
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**Figure 1** The synthetic routes and the structures of poly(hydroxy)urethanes.

carbonate)s and diamines. Poly(hydroxy)urethanes were synthesized by the polyaddition reaction of bis(cyclic carbonate)s and aliphatic or aromatic diamines. We have synthesized five different poly(hydroxy)urethanes using various diamines and investigated their thermal properties and solubilities.

## EXPERIMENTAL

### Materials

Bisphenol S (Tokyo Kasei Kogyo Co.) and epichlorohydrin (Aldrich Co.) were used without further purification. Carbon dioxide was supplied from Acetylene Gas Co. and used as re-

ceived. Benzyltrimethylammonium chloride (BTMACl) used as a PTC was purchased from Fluka Co. Hexamethylenediamine (HMD), 4,4'-diamino-dicyclohexylmethane (DHM), 4,4'-diamino-diphenylhexylmethane (DPM), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAP), and 2,2-bis[4-(4-aminophenoxy)phenyl] sulfone (BAS), obtained from Fluka Co., were used as received or distilled from KOH prior to use. Other chemicals were reagent grade and were used without further purification.

### Characterization

FTIR spectra were recorded on a Bruker IFS 66/FRA 106 spectrophotometer. Gas chromatography (GC) analyses were performed with a HP5890A equipped with a 1-m column packed with silicon SE-30.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a Varian 300 UNITY plus 300 (300 MHz) spectrophotometer using tetramethylsilane (TMS) as an internal standard. The melting point (m.p.) was determined on an Electrothermal IA9100 Operation digital melting point apparatus. Molecular weights were measured using gel permeation chromatography (GPC) with a Tosoh Co. HLC-8020 equipped with TSKgel G5000HXL, TSKgel G4000HXL, and TSKgel G2500HXL detected with UV-8011 at 270 nm. A 10 mL/L solution of chloroform was used as the eluent. Differential scanning calorimeter (DSC) analyses were carried out on a General V4.1C equipped with a sealed cell at a heating rate of  $10^\circ\text{C}/\text{min}$ . The glass transition temperature was reported based on a midpoint value from the second scan of DSC thermograms. Thermogravimetric analyses (TGA) were carried out on a Shimadzu TGA-50 in a nitrogen stream at a heating rate of  $10^\circ\text{C}/\text{min}$ .

### Synthesis of Diglycidyl Ether of Bisphenol S (DGEBS)<sup>13</sup>

Into a reactor equipped with a thermometer, a mechanical stirrer, and a reflux condenser were charged 25.0 g (0.1 mol) of bisphenol S and 92.5 g (1 mol) of epichlorohydrin. The mixture was maintained at  $100\text{--}110^\circ\text{C}$  for 3 h while adding 20 g of 40% aqueous NaOH solution. After the reaction was completed, the hot solution was filtered to remove sodium chloride. The resulting mass was washed with methanol. The solution was evaporated to remove unreacted epichlorohydrin and dried in a vacuum oven at  $60^\circ\text{C}$  for 24 h. The product was dissolved in chloroform and re-

**Table I** Characterization Data for DGEBS and Bis(cyclic carbonate)

Monomers	FTIR ( $\text{cm}^{-1}$ )	NMR <sup>a</sup>		Mass Spec. (rel. intensity)	Elemental Analysis	
		$^1\text{H}$ ( $\delta$ )	$^{13}\text{C}$ ( $\delta$ )		Calcd.	Found
DGEBS	3008(CH stretching)	2.8–2.4(t, 4H, $(\text{OCH}_2\text{CHCH}_2)_2$ )	43.6( $\text{OCH}_2\text{CHCH}_2$ )	362( $\text{M}^+$ , 95),	C; 59.66	C; 59.95
	1591(aromatic C=C)	3.4(quintet, 2H, $\text{OCH}_2\text{CHCH}_2$ )	49.3( $\text{OCH}_2\text{CHCH}_2$ )	319(5), 305(15),	H; 5.01	H; 4.85
	1280(O=S=O stretching)	4.4–3.8(d, 4H, $(\text{OCH}_2\text{CHCH}_2)_2$ )	69.3( $\text{OCH}_2\text{CH}$ )	276(7), 248(8),	S; 8.85	S; 8.69
	1150(C–O stretching)	7.8–7.1(8H, aromatic)	115.3, 129.2(CH aromatic)	140(40), 64(30),		
Bis(cyclic carbonate)	910(epoxide C–O–C)		133.7, 151.4(C aromatic)	57(100).		
	2931(CH stretching)	2.9–2.6(t, 4H, $(\text{OCH}_2\text{CHCH}_2)_2$ )	65.8 ( $\text{OCH}_2\text{CHCH}_2$ )	450( $\text{M}^+$ , 3),	C; 53.33	C; 52.79
	1795(cyclic carbonate C=O)	3.3(quintet, 2H, $(\text{OCH}_2\text{CHCH}_2)_2$ )	67.8( $\text{OCH}_2\text{CHCH}_2$ )	406(5), 362(55),	H; 4.03	H; 4.05
	1593(aromatic C=C)	4.4–3.65(d, 4H, $(\text{OCH}_2\text{CHCH}_2)_2$ )	74.4( $\text{OCH}_2\text{CH}$ )	248(10), 7(100),	O; 35.52	O; 34.87
	1259(O=S=O stretching)	7.8–7.1(8H, aromatic)	115.4, 129.3(CH aromatic)	64(85), 44(20).	S; 7.12	S; 7.17
	1151(C–O stretching)		134.0, 154.6(C aromatic)			
			161.4(cyclic carbonate C=O)			

<sup>a</sup> DMSO- $d_6$  solution.

**Table II** Characterization Data for Poly(hydroxy)urethanes

Polymer	FTIR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR (δ) <sup>a</sup>
HPU-HMD	3455(N—H stretching)	2.30–2.20(t, 4H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
	3345(O—H stretching)	3.71(quintet, 2H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
	1704(C=O stretching)	3.98(s, 2H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
	1535(N—H bending)	4.24–3.73(d, 4H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
	1209(C—O stretching)	6.85(2H, (OCONH) <sub>2</sub> )
HPU-DPM	3441(N—H stretching)	7.21–6.93(8H, aromatic)
	3380(O—H stretching)	2.50–2.27(t, 4H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
	1700(C=O stretching)	3.76(quintet, 2H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
	1536(N—H bending)	4.82(s, 2H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
	1251(C—O stretching)	4.00–3.83(d, 4H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
HPU-DHM	3401(N—H stretching)	7.07(2H, (OCONH) <sub>2</sub> )
	3367(O—H stretching)	7.62–7.05(8H, aromatic)
	1716(C=O stretching)	2.08–1.71(t, 4H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
	1538(N—H bending)	3.55–3.14(quintet, 2H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
	1257(C—O stretching)	4.07(s, 2H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
HPU-BAP	3450(N—H stretching)	3.98–3.93(d, 4H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
	3325(O—H stretching)	7.09(2H, (OCONH) <sub>2</sub> )
	1701(C=O stretching)	7.79–7.04(8H, aromatic)
	1538(N—H bending)	2.47–2.39(t, 4H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
	1257(C—O stretching)	3.64(quintet, 2H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
HPU-BAS	3448(N—H stretching)	4.11(s, 2H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
	3320(O—H stretching)	4.04–3.99(d, 4H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
	1703(C=O stretching)	7.04(2H, (OCONH) <sub>2</sub> )
	1533(N—H bending)	7.80–7.05(8H, aromatic)
	1255(C—O stretching)	2.49–2.06(t, 4H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
		3.25(quintet, 2H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
		3.97(s, 2H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
		3.88(d, 4H, (OCH <sub>2</sub> CH(OH)CH <sub>2</sub> ) <sub>2</sub> )
		6.85(2H, (OCONH) <sub>2</sub> )
		7.06–7.01(8H, aromatic)

<sup>a</sup> DMSO-d<sub>6</sub> solution.

crystallized from *n*-hexane. The structure of DGEBS is shown in Figure 1. Table I summarizes the characterization data for DGEBS; yield = 18.3 g (50%), m.p. = 158–160°C.

#### Synthesis of Bis(cyclic carbonate) of DGEBS from Carbon Dioxide<sup>13</sup>

A solution of 16.6 g of DGEBS (0.05 mol) and 0.925 g of 10 mol % BTMCl in 25 mL of *n*-methyl pyrrolidone (NMP) was heated to 100°C with vigorous stirring under a slow stream (20 mL/h) of carbon dioxide for 24 h. The reaction mixture was poured into acetone, to remove impurities and the catalyst, and then insoluble materials were filtered off. After the filtrate was precipitated in H<sub>2</sub>O, the precipitate was collected and recrystallized from toluene. The product was dried in a vacuum oven for 24 h. The reaction path of the formation of bis(cyclic carbonate) using carbon

dioxide is illustrated in Figure 1. The bis(cyclic carbonate) was obtained as a white powder. Table I summarizes the characterization data for bis(cyclic carbonate); yield = 16.63 g (74%), m.p. = 200–210°C.

#### Synthesis of Poly(hydroxy)urethane of Bis(cyclic carbonate) and Diamine

For a typical poly(hydroxy)urethane, HPU-HMD was synthesized as follows; a solution of 4.5 g of bis(cyclic carbonate) (0.01 mol) and 1.16 g of HMD (0.01 mol) in 10 mL of dimethylsulfoxide (DMSO) was sealed and heated at 100°C for 24 h. A small portion of the reaction mixture was separated out to analyze by GPC, and the remaining reaction mixture was poured into 30 mL of water. The precipitate was collected, washed thoroughly with water, and dried under vacuum to obtain a poly(hydroxy)urethane. The poly(hydroxy)urethanes,

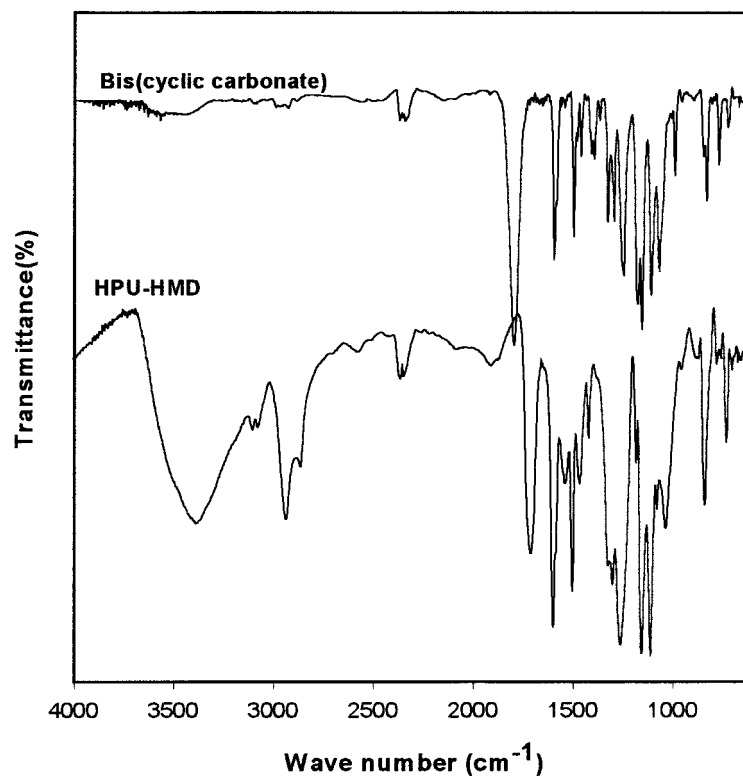


Figure 2 FTIR spectra of bis(cyclic carbonate) and HPU-HMD.

containing different amines, were designated as HPU-x, where x is the abbreviation of an amine used. For the syntheses of HPU-DPM, HPU-DHM, HPU-BAP, and HPU-BAS, the same pro-

cedures were followed as described above except that DPM, DHM, BAP, and BAS were adopted as diamines, respectively. The reaction path of the formation of the poly(hydroxy)urethane is

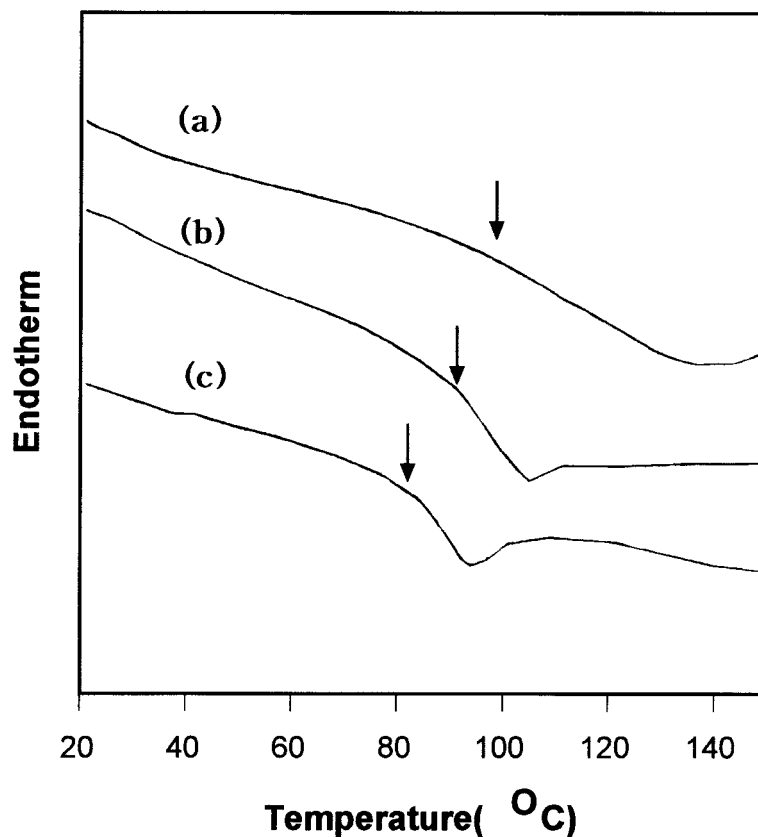
Table III GPC Data of Poly(hydroxy)urethanes with Different Mol Ratio of Bis(cyclic carbonate) to Diamine

Run	Polymer	Mol Ratio		GPC Data <sup>a</sup>		PDI <sup>b</sup>
		Bis(cyclic carbonate): Diamine		$M_n$	$M_w$	$(M_w/M_n)$
1	HPU-HMD	1:1		12,900	19,800	1.29
2		1:3		9100	13,400	1.47
3		1:5		9000	11,600	1.31
4		1:7		7500	8900	1.18
5	HPU-DHM	1:1		7000	9800	1.41
6		1:5		9500	14,700	1.55
7		1:1		4300	8500	1.99
8	HPU-DPM	1:5		5000	8600	1.74
9		1:1		4900	8500	1.73
10	HPU-BAP	1:5		6100	8700	1.43
11		1:1		4900	9000	1.83
12		1:5		6300	9600	1.52

<sup>a</sup> Solvent: chloroform, 10 mL/h.

<sup>b</sup> Polydispersity index.

Reaction condition: DMF, 100°C, 24 h.



**Figure 3** Effect of diamine structure on the  $T_g$ s of poly(hydroxy)urethanes (indicated by arrows); (a) HPU-DPM; (b) HPU-DHM; (c) HPU-HMD.

shown also in Figure 1. Table II summarizes the characterization data for poly(hydroxy)urethanes.

## RESULTS AND DISCUSSION

The syntheses of poly(hydroxy)urethanes were performed by the polyaddition of bis(cyclic car-

**Table IV** Glass Transition Temperatures ( $T_g$ s) and Initial Thermal Decomposition ( $T_d$ s) Temperatures of Poly(hydroxy)urethanes with Different Structures of Diamines

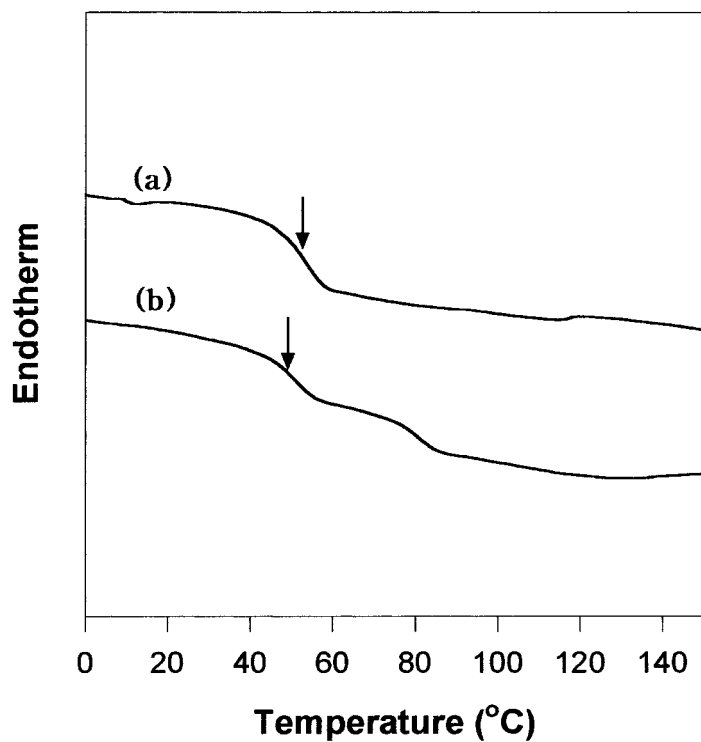
Polymer	$T_g$ (°C) <sup>a</sup>	$T_d$ (°C) <sup>b</sup>
HPU-HMD	83	339
HPU-DHM	91	356
HPU-DPM	102	375
HPU-BAP	50	385
HPU-BAS	55	388

<sup>a</sup> DSC thermogram data on the second heating, at a heating rate of 10°C/min.

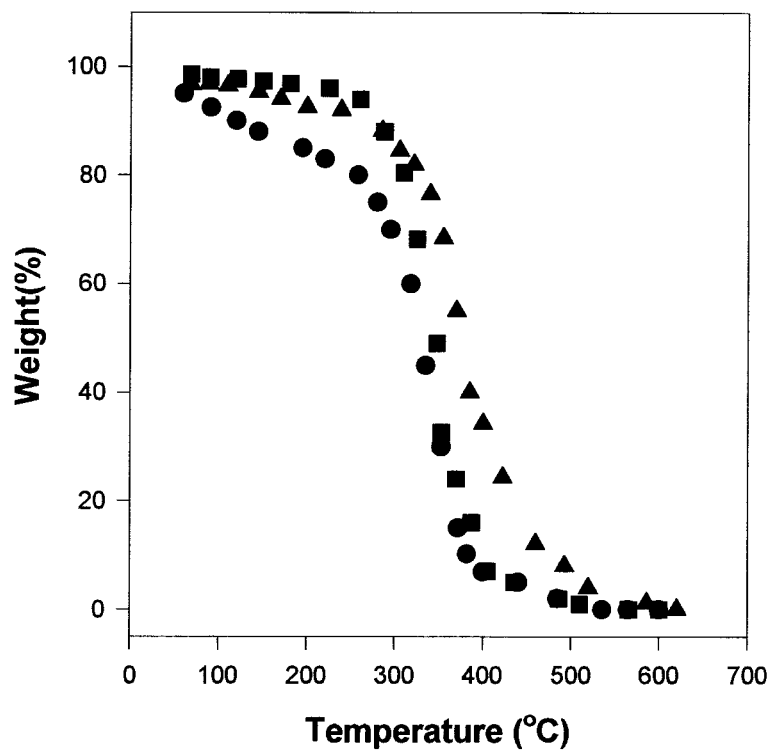
<sup>b</sup> TGA measurements at a heating rate of 10°C/min (nitrogen atmosphere).

bonate)s obtained from carbon dioxide and HMD, DPM, DHM, BAS, and BAP as diamines. In Figure 2, the FTIR spectra of the poly(hydroxy)urethanes showed characteristic absorption peaks at 3350  $\text{cm}^{-1}$  due to the OH stretching of the hydroxyl group, 1710  $\text{cm}^{-1}$  due to C=O stretching of the urethane group, and 1535  $\text{cm}^{-1}$  due to the NH deformation of the urethane group.

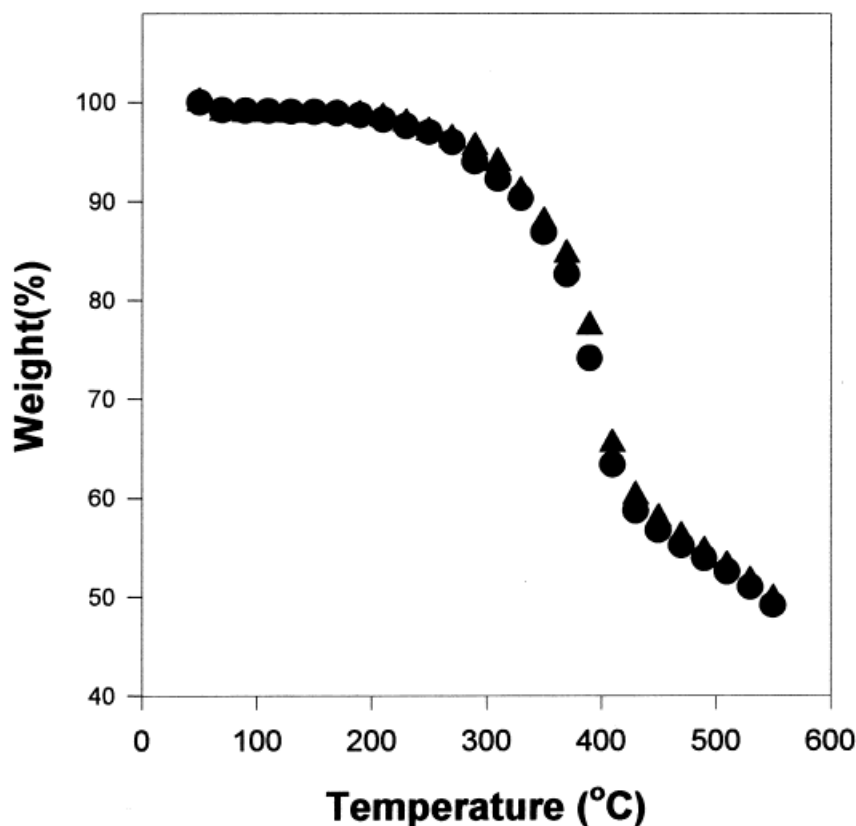
To estimate the molecular weight of the poly(hydroxy)urethanes, GPC analyses were carried out. The polyaddition reaction of bis(cyclic carbonate) and various diamines were investigated. The average molecular weights of the obtained poly(hydroxy)urethanes are listed in Table III. The  $M_w$  of HPU-HMD was higher than that of HPU-DPM under the same reaction conditions, probably because of the low structural flexibility of an aromatic diamine. Table III shows that the maximum molecular weight of the HPU-HMD was observed when bis(cyclic carbonate) and diamine was used in a stoichiometric ratio. The reaction of bis(cyclic carbonate) with diamine in a mol ratio of 1 : 1 resulted in the increase of the average molecular weight. Over a mol ratio of 1 : 7, the average molecular weight of the polymer



**Figure 4** Effect of diamine structure on the  $T_g$ s of poly(hydroxy)urethanes(indicated by arrows ); (a) HPU-BAS; (b) HPU-BAP.



**Figure 5** Effect of diamine structure on the  $T_d$ s of poly(hydroxy)urethanes; ● HPU-HMD; ■ HPU-DHM; ▲ HPU-DPM.



**Figure 6** Effect of diamine structure on the  $T_d$ s of poly(hydroxy)urethanes; ● HPU-BAP; ▲ HPU-BAS.

decreased because the excess diamine led to steric hindrance in the polyaddition reaction. For other HPU-x series, no significant effect was observed in their molecular weights, depending on the mole ratio of bis(cyclic carbonate) to diamine.

Figure 3 illustrates the effect of the diamine structure on the glass transition temperature ( $T_g$ ) of poly(hydroxy)urethanes. The  $T_g$ s indicated by arrows are summarized in Table IV. For HPU-x series, the  $T_g$ s of HPU-HMD, HPU-DHM, and HPU-DPM were observed to be at 83, 91, and 102°C, respectively. The different structures of diamine may account for this observation. Simi-

larly, the  $T_g$  of HPU-BAS (55°C) was higher than that of HPU-BAP (50°C). Although an aromatic diamine gave a lower molecular weight polymer, compared to that of the aliphatic amine because of low structural flexibility, the poly(hydroxy)urethane from aromatic diamine showed higher  $T_g$ , due to the stiffness of the aromatic chain. Similarly, as shown in Figure 4, the  $T_g$  of BAS, having an O=S=O group, was higher than that of BAP having a  $-\text{C}(\text{CH}_3)_2-$  group. The initial decomposition temperature ( $T_d$ ) results are shown in Figures 5 and 6. The thermal data are also summarized in Table IV. This  $T_d$  behavior indicates

**Table V** The Solubilities of Poly(hydroxy)urethanes with Different Diamines

Polymer	Hexane	Benzene	Methanol	Chloroform	Acetone	THF	DMF	DMSO
HPU-HMD	×	×	×	×	×	▲	●	●
HPU-DPM	×	×	×	×	×	▲	●	●
HPU-DHM	×	×	×	×	×	×	●	●
HPU-BAS	×	×	×	×	×	×	●	●
HPU-BAP	×	×	×	×	×	×	●	●

×: insoluble, ▲: swollen, ●: soluble.



that the thermal properties of the poly(hydroxy)urethane depend on the structure of diamine, as for  $T_g$ .

The solubilities of different poly(hydroxy)urethanes are summarized in Table V. The poly(hydroxy)urethanes were insoluble or swollen in common organic solvents due to the presence of hydroxyl groups, and were soluble only in aprotic solvents such as *N*-dimethyl formamide(DMF) and dimethyl sulfoxide(DMSO).

## CONCLUSIONS

In this study, poly(hydroxy)urethanes were synthesized by the polyaddition of a bis(cyclic carbonate) and five different diamines. Syntheses of bis(cyclic carbonate)s, from the reaction of carbon dioxide with DGEBS, were performed in the presence of a PTC, benzyltrimethylammonium chloride (BTMACl). This reaction using the PTC gave bis(cyclic carbonate)s in high yield under atmospheric pressure at relatively mild reaction temperature.

The thermal properties of poly(hydroxy)urethane depended on the structure of the diamine and the monomer. Poly(hydroxy)urethanes, synthesized from aromatic diamines, showed higher thermal stability than those from aliphatic amines because of the stiffness of the aromatic chain. However, the aromatic diamine yielded lower molecular weight polymers compared to

that from aliphatic amine because of low structural flexibility. Poly(hydroxy)urethanes were insoluble in organic solvents, probably because of the hydrophilic character of the hydroxy group.

This work was financially supported by the Korea Science & Engineering Foundation (Grant No. 97-05-02-05-01-3) and the Brain Korea 21 Project.

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