

# Shape-Memory Polyurethanes Minimally Crosslinked with Hydroxyl-Terminated AB<sub>2</sub>-Type Hyperbranched Polyurethanes

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**ABSTRACT:** A series of shape-memory polyurethanes based on poly( $\epsilon$ -caprolactone) diol were prepared with novel hydroxyl-terminated hyperbranched polyurethanes as crosslinkers and were characterized by Fourier transform infrared spectroscopy, <sup>1</sup>H-NMR, gel permeation chromatography, differential scanning calorimetry, scanning electron microscopy, wide-angle X-ray diffraction, dynamic mechanical analysis, tensile testing, and shape-memory testing. The molecular weight of the soluble polymers ranged from  $5.1 \times 10^4$  to  $29.0 \times 10^4$  g/mol. The differential scanning calorimetry and wide-angle X-ray diffraction data indicated that when the crystallinities of the crosslinked polymers were compared to that of linear

polyurethane, this parameter was improved when the crosslinker was in low quantity. The storage modulus ratios obtained from the dynamic mechanical analyses data of the crosslinked polymers were also high compared to that of the linear polyurethane. As a result, crosslinked polymers showed better shape-memory properties compared to the linear polyurethanes. Also, the incorporation of the hyperbranched polymer as a crosslinker into the polyurethane chain improved the thermal and mechanical properties of the polymer. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 725–734, 2011

**Key words:** branched; crosslinking; thermal properties

## INTRODUCTION

*Shape memory* refers to the ability of certain materials to remember their original shape even after rather severe deformations. In recent years, shape-memory polymers (SMPs), especially thermally stimulated SMPs, have received increasing attention because of their wide availability and broad possible applications in various areas of everyday life. Such applications include medical devices for treating stroke<sup>1</sup> and vascular and coronary diseases,<sup>2,3</sup> orthodontics,<sup>4</sup> catheters and smart stents,<sup>5</sup> implants for minimally invasive surgery,<sup>6</sup> information storage that can allow thermally reversible recording,<sup>7</sup> and smart fabrics.<sup>8</sup> One of the main approaches for the preparation of SMPs is to polymerize two different monomers; that process should result in a copolymer consisting of a soft-segment phase that is able to store the deformed temporary shape and a hard-segment phase. In most SMPs, the hard-segment phase is a physical network that is responsible for storing the permanent shape and mechanical properties of the polymer. Many

chemically crosslinked SMPs have been reported.<sup>9–19</sup> Among these reports, some have dealt with shape-memory polyurethanes.<sup>15–19</sup> In polyurethane, the polar urethane groups, in which strong secondary molecular forces are present, act as a physical network. In addition to this, chemical crosslinks can be introduced by the deliberate addition of crosslinker during polyurethane synthesis. A wide range of crosslinked SMPs were reviewed lightly by Behl and Lendlein<sup>20</sup> in their review.

Hyperbranched polymers (HBPs) are a new class of emerging materials. They have a large number of terminal functional groups, as they grow in dendritic fashion; for this reason, these materials show unusual properties compared to their linear analogues. Their applications span different technological areas.<sup>21</sup> The crosslinking process is an important application area for HBPs, provided the molecular weight of the polymer is substantially low and narrowly distributed. The reason to recommend low-molecular-weight HBPs as crosslinkers is that they have a lower number of terminal functional groups, which is essential to the control of gelation. The narrow molecular weight distribution is a useful parameter for stoichiometric calculations. Recently, we reported the use of amine-terminated hyperbranched polyamides with weight-average molecular weight ( $M_w$ ) values of 2337–13,063 as crosslinkers in the preparation of polyurethane elastomers and

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**TABLE I**  
**Molecular Weight Data for the Linear and Crosslinked Shape-Memory Polyurethanes**

Polymer code	MDIPP/BDO/HBPU (10 <sup>-2</sup> equiv)	Hard-segment content (wt %) <sup>a</sup>	$M_w$ (×10 <sup>4</sup> g/mol)	Polydispersity index
LPU <sup>b</sup>	1/1/0	18.8	5.1	1.47
CPU-1	1/0.99/0.01	19.0	5.5	1.59
CPU-2	1/0.94/0.06	19.4	6.3	2.03
CPU-3	1/0.90/0.10	19.8	8.7	2.50
CPU-4	1/0.85/0.15	20.0	29.0	4.84
CPU-5	1/0.83/0.17	20.5	–	–
CPU-6	1/0.80/0.20	20.8	–	–
CPU-7	1/0.85/0.15	19.8	5.9	1.62

The HBPU  $M_w$  values were 3500 g/mol for CPU-1 to CPU-6 and 4500 g/mol for CPU-7. MDIPP = MDI based Polyurethane Prepolymer.

<sup>a</sup> The hard-segment content was calculated according to the feed weight ratio:

$$\text{Hard-segment content (wt\%)} = (W_{\text{MDI}} + W_{\text{BDO/HBPU}}) / (W_{\text{MDI}} + W_{\text{BDO/HBPU}} + W_{\text{PCL-4000}}) \times 100$$

where  $W_{\text{MDI}}$  is the weight of MDI,  $W_{\text{BDO/HBPU}}$  is the weight ratio of BDO and HBPU, and  $W_{\text{PCL-4000}}$  is the weight of PCL-4000.

<sup>b</sup> LPU was prepared from PCL diol, MDI, and BDO.

found that a very low amount (0.01 equiv vs 1.0 equiv of the polyurethane prepolymer) of HBPs with a degree of polymerization (DP) approximately equal to 11 was sufficient for improving the tensile strength to a great extent.<sup>22</sup>

In the light of the observation made in our previous study, we intended to extend the use of HBP as a crosslinker in the synthesis of shape-memory polyurethanes based on poly( $\epsilon$ -caprolactone) (PCL) diol, which is a soft-switching segment. Thus, in this article, we describe the synthesis of shape-memory polyurethanes with novel hydroxyl-terminated hyperbranched polyurethanes (HBPU) as crosslinkers, a feat not attempted yet. We believed that because the crosslinker (i.e., HBPU) used here was in polymeric form and was fully hard segmented, it would enhance the hard-segment/soft-segment microphase separation in the polyurethane. Because of this enhancement in the phase separation, the crystallizability of PCL chain and associated stimuli responsive effect should be improved. We also envisaged that because of HBP as was used as a crosslinker, the resulting thermoresponsive polymer would show improved mechanical properties at the temperature at which the temporary shape was fixed or the permanent shape was recovered ( $T_{\text{trans}}$ ); this is desirable for polymer materials being considered for end uses.

## EXPERIMENTAL

### Materials

4,4'-Methylene bis(phenylisocyanate) (MDI; Lancaster), 1,4-butanediol (BDO; Alfa Aesar, Heysham, Lancs, UK), and dibutyl tin dilaurate (DBTDL; Lan-

caster) were used as received. Poly( $\epsilon$ -caprolactone) diol with a number-average molecular weight ( $M_n$ ) of 4000 g/mol (PCL-4000) was obtained from Daicel Chemical Industries, Ltd. (Japan) and was dried at 100°C *in vacuo* for 6 h before use. Hydroxyl-terminated HBPU ( $M_w$ 's = 3500 and 4500) were prepared according to our previous report.<sup>23</sup> Dimethylformamide (DMF; Merck, Mumbai, India) and methyl ethyl ketone (MEK; Merck) were purified according to standard procedures.

### Synthesis of the HBPU-crosslinked shape-memory polyurethanes

HBPU-crosslinked shape-memory polyurethanes were prepared by a two-step method. In the first step, 1.87 g ( $15 \times 10^{-3}$  equiv) of MDI was placed in a reaction vessel. To this, we added 10 g ( $5 \times 10^{-3}$  equiv) of PCL-4000 melt dropwise with stirring under a nitrogen atmosphere; the dropping rate was such that it took 1 h for complete transfer. The reaction time was 8 h; the first 2 h were maintained at 60°C, and the next 6 h were maintained at 75°C. After 8 h, the temperature was reduced to 40°C, and the –NCO content was determined by the dibutyl amine method;<sup>24</sup> the results were close to the expected theoretical value (observed value = 3.65%; theoretical value = 3.53%). On the basis of the –NCO content, this amount of polyurethane prepolymer was found to be 0.01 equiv. In the second step, 0.45 g (0.01 equiv) of BDO or a mixture of BDO and HBP (see Table I; the equivalents given were functionality based) and 0.04 g of DBTDL were dissolved in 15 mL of 4 : 1 MEK/DMF mixed solvent, and this

solution was added to the reaction vessel with an additional funnel for 15 min under strong agitation. The polymerization reaction was followed by the disappearance of the absorption peak due to  $\text{-NCO}$  groups in the IR region  $2250\text{--}2270\text{ cm}^{-1}$ . The time required for the completion of the reaction was 90 min. After the completion of the reaction, the high viscous reaction mass was diluted with 10 mL of the 4 : 1 MEK/DMF mixed solvent and was cast on a Teflon plate with a thickness of 5 mm. Initially, the film was dried at room temperature for 3 h and then maintained in a vacuum oven at  $70^\circ\text{C}$  for 6 h.

### Characterization

Fourier transform infrared (FTIR) and  $^1\text{H-NMR}$  analyses

The FTIR spectra of the polymers were recorded on a Thermo Matson (Madison, USA) Satellite model FTIR spectrometer by a neat method. The  $^1\text{H-NMR}$  spectrum of the HBPU-crosslinked polymer was recorded on a Bruker 300 MHz NMR instrument in hexadeuterated dimethyl sulfoxide with tetramethylsilane ( $\text{Me}_4\text{Si}$ ) as an internal standard.

Gel permeation chromatography (GPC) analyses

$M_w$ , polydispersity ( $M_w/M_n$ ), and molecular weight distribution of the polymers were estimated with a PL-GPC 50 (Polymer Laboratory, UK) gel permeation chromatograph equipped with a refractive-index detector and  $5\text{-}\mu\text{L}$  mixed columns. DMF was used as an eluent, and the instrument was calibrated with narrow molecular weight polystyrene standards.

Thermal characterization

Thermal properties, such as the glass-transition temperature ( $T_g$ ), crystalline melting temperature ( $T_m$ ), and crystallization temperature ( $T_c$ ) of the HBPU-crosslinked polyurethanes were measured with a Netzsch (Selb/Bavaria, Germany) DSC-200PC differential scanning calorimeter: a first heating rate of  $10^\circ\text{C}/\text{min}$  from  $-100$  to  $100^\circ\text{C}$ , a cooling rate of  $10^\circ\text{C}/\text{min}$  from  $100$  to  $-100^\circ\text{C}$ , and a second heating rate of  $10^\circ\text{C}/\text{min}$  from  $-100$  to  $100^\circ\text{C}$  were applied under a nitrogen atmosphere. Thermogravimetric analysis (TGA) were carried out in a Zetzsch-STA 409C/CD thermal analyzer (Selb/Bavaria, Germany) from  $30$  to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen atmosphere with a gas flow rate of  $90\text{ mL}/\text{min}$ .

Wide-angle X-ray diffraction (WAXD) and scanning electron microscopy (SEM) analyses

WAXD analyses were performed with a Rigaku Miniflex desktop X-ray diffractometer with a Cu source of radiation ( $\lambda = 1.541\text{ \AA}$ ) operating in transmission mode. The voltage and current used were

$30\text{ kV}$  and  $15\text{ mA}$ , respectively, and the exposure time was 30 min. Diffraction spectra were scanned at  $2\theta = 10\text{--}45^\circ$ . SEM measurements were carried out on a JEOL JSM 6362 instrument at  $10\text{ kV}$ .

Dynamic mechanical analysis (DMA)

The sample films were prepared for DMA measurements through film casting. The film dimensions were  $0.4\text{ mm}$  (thickness)  $\times$   $3.5\text{ mm}$  (width)  $\times$   $25\text{ mm}$  (length). DMA measurements were carried out with a Netzsch (Selb/Bavaria, Germany) DMA 242 instrument under tensile mode at a fixed frequency of  $1\text{ Hz}$ , a maximum dynamic force of  $4.0\text{ N}$ , and an oscillation amplitude of  $120\text{ }\mu\text{m}$  under a nitrogen atmosphere. The measurements were carried out from  $-100$  to  $150^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ .

Shape-memory behavior

The polymer samples were cut into rectangular strips with dimension of  $0.4 \times 5 \times 50\text{ mm}^3$ . The shape-memory behavior was examined by a bending test as follows. In a typical experiment, the specimen was deformed to angle  $\theta_i$  ( $\theta_i$  = initial deformation angle =  $90^\circ$ ) at  $60^\circ\text{C}$  and then cooled quickly to  $0^\circ\text{C}$  to fix the temporary bent shape by crystallization. The deformed specimen was placed in an oven (fabricated with an additional glass door) and maintained at testing temperature ( $50^\circ\text{C}$  or  $60^\circ\text{C}$  or  $70^\circ\text{C}$ ). Immediately, the changes in the angle (recovery of original shape) were recorded through the glass door with a digital video camera (Canon Powershot) at a rate of  $12\text{ frames}/\text{s}$ . We selected 25 frames from the video picture, and their deformed angle with respect to time were calculated. With these data, the ratio of recovery was defined as  $(\theta_i - \theta_f)/\theta_i$ . ( $\theta_f$  = final deformation angle =  $0^\circ$  to  $90^\circ$ ).

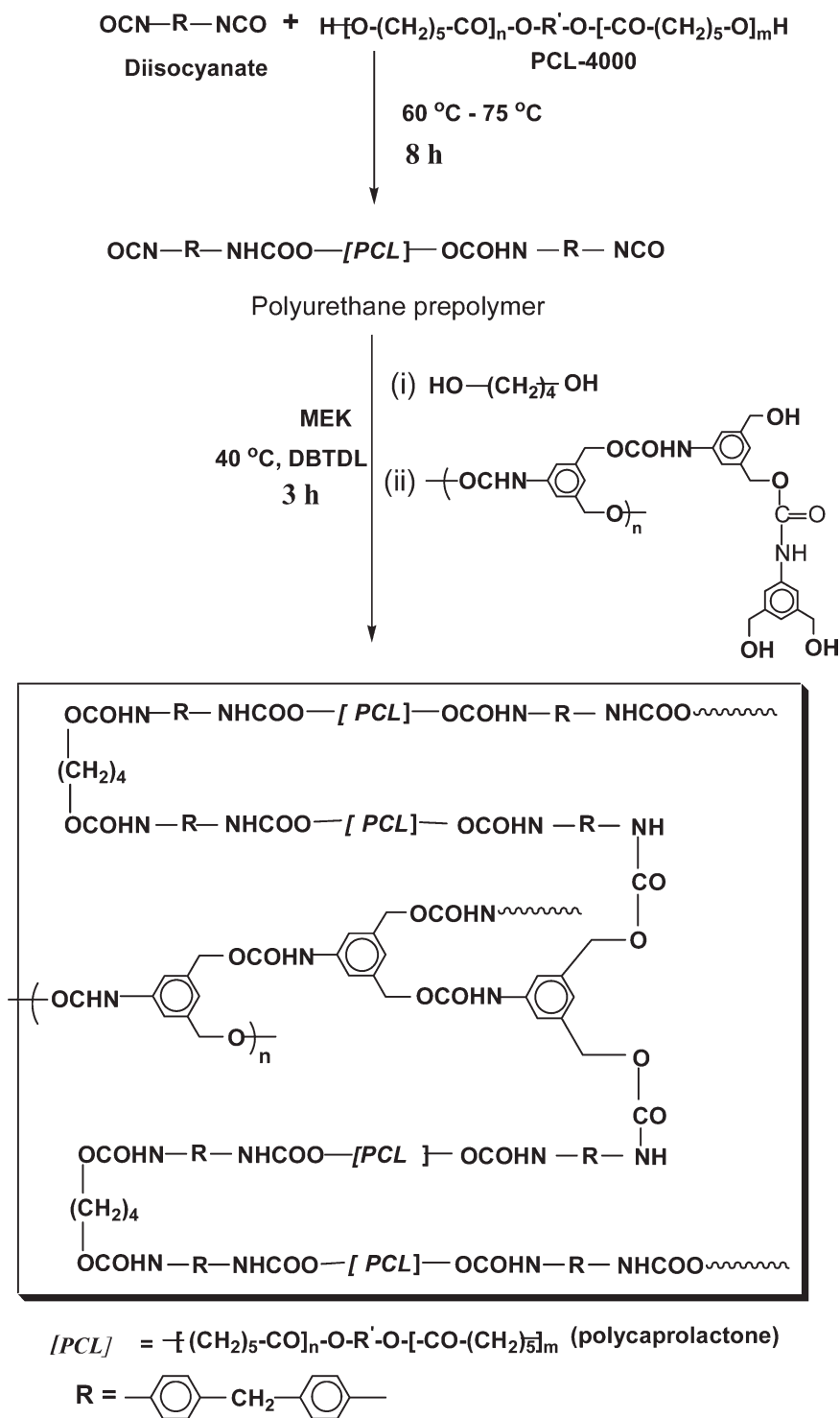
Mechanical properties

Tensile measurements were carried out on specimens with dimensions of  $5\text{ mm}$  (width)  $\times$   $40\text{ mm}$  (length) with a TKG-E-C-500N tensile testing machine (Hi-Tech India Equipments, Ltd.). The thickness of each specimen was measured (Fine Spavy Associates & Engineers Pvt. Ltd., Miraj, India) and recorded as the average of four measurements. The grip separation rate was  $100\text{ mm}/\text{min}$ . For each polymer, two tests were carried out, and the average values are reported.

## RESULTS AND DISCUSSION

### Synthesis of the HBPU-crosslinked shape-memory polyurethanes

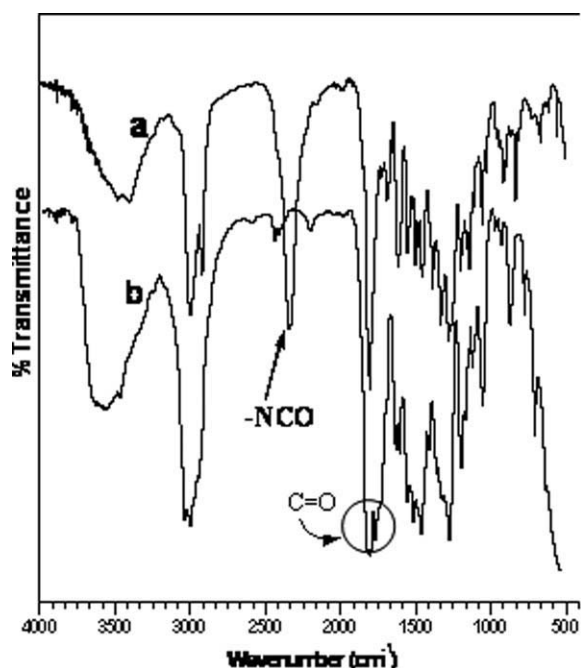
Generally, polyurethanes are prepared with a polyurethane prepolymer in combination with a short-chain glycol (chain extender) and/or a crosslinking



**Scheme 1** Synthesis of HBP-crosslinked shape-memory polyurethanes with hydroxyl-terminated HBPU as the crosslinkers.

agent with a functionality of three or more. Isocyanurates of different diisocyanates and polyols of higher functionality are used as crosslinking agents. In this study, the polyurethane prepolymer was prepared from MDI and PCL-4000. Here, PCL-4000 was chosen as a switching segment, and its  $T_m$  was

$60^\circ\text{C}$ . The hydroxyl-terminated HBPU ( $M_w = 3500$  g/mol, dispersity = 1.34) and polymer ( $M_w = 4500$  g/mol, dispersity = 1.54) were used as crosslinkers (Scheme 1). The approximate number of terminal hydroxyl groups (B) was calculated with the following equation:



**Figure 1** FTIR spectra of (a) the polyurethane prepolymer and (b) an HBPU-crosslinked polyurethane (CPU-1).

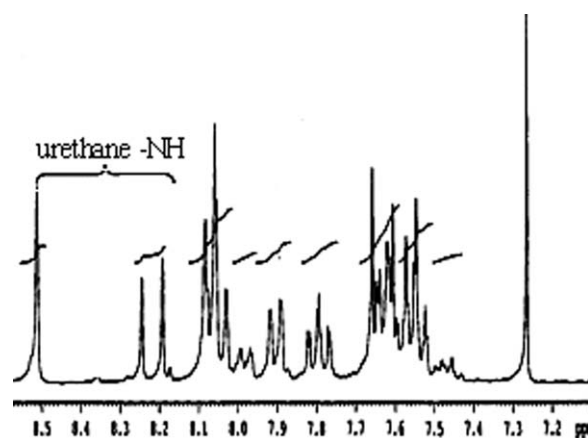
$$\text{Number of unreacted B} = (\text{Functionality} - 1) \times \text{DP} + 1$$

In this equation, the term *functionality* equals 2 because the monomer used for the preparation of the hydroxyl-terminated HBPU was AB<sub>2</sub> type. The calculated functionalities were used for the stoichiometric calculation in terms of equivalents. The amount of HBPU was varied from 0.01 to 0.2 equiv relative to 1.0 equiv of the polyurethane prepolymer.

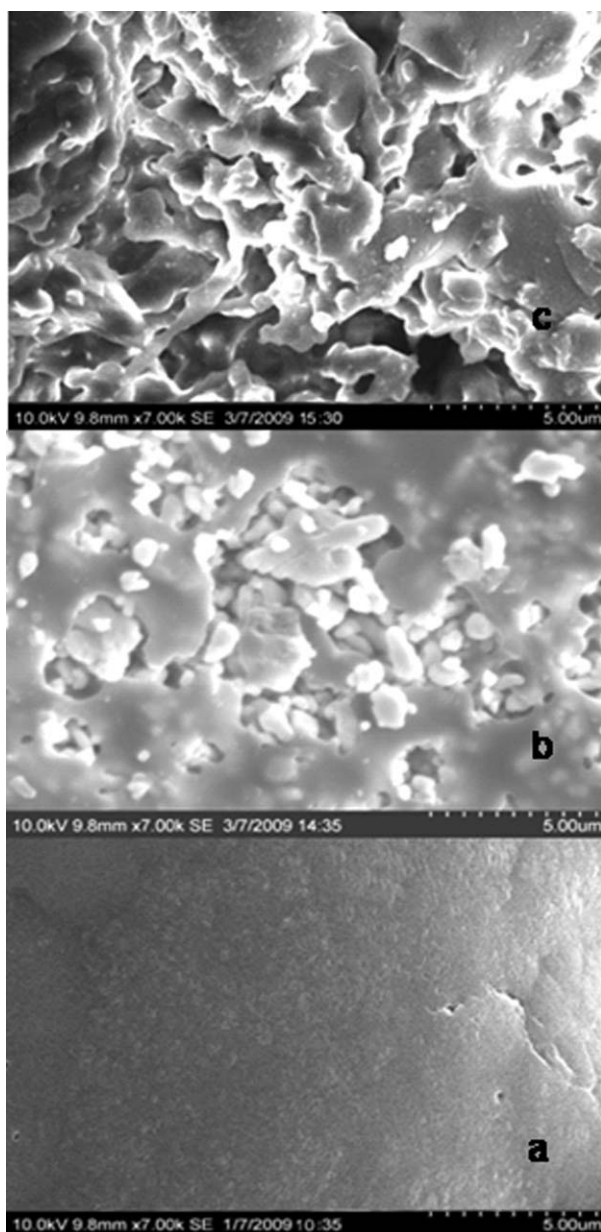
Seven polyurethanes were prepared with variation in the amount of chain extender and crosslinker (Table I). The FTIR spectra of the crosslinked polyurethanes (CPUs) were identical, and they did not show absorption for free  $\text{-NCO}$  groups at  $2270 \text{ cm}^{-1}$ , whereas the prepolymer showed a strong absorption band in the  $2270\text{--}2275\text{-cm}^{-1}$  range. Except CPU-6, all other polymers showed only one strong absorption in the carbonyl region ( $1675\text{--}1720 \text{ cm}^{-1}$ ). This was because of the amount of crosslinker used, which was relatively low (up to 0.17 equiv); hence, the carbonyl groups present in HBPU were not distinguished. However, when the amount of the crosslinker was increased up to 0.2 equiv, the two different carbonyl groups in the polymer chain, one from the polyurethane prepolymer and another from HBPU, absorbed separately at  $1720$  and  $1676 \text{ cm}^{-1}$ , respectively (Fig. 1). The  $^1\text{H-NMR}$  spectrum (Fig. 2) of CPU-2 clearly showed three distinct singlets between 8.19 and 8.5 ppm due to the presence of three different urethane  $\text{-NH}$  protons, one from polyurethane prepolymer, one from HBPU, and the

third one formed during the chain extension reaction with BDO. Thus, the IR and  $^1\text{H-NMR}$  spectral data confirmed the incorporation of HBPU into the polyurethane chain.

The hard-segment content and molecular weight data are summarized in Table I. Because the crosslinker was fully hard segmented, the hard-segment content of the polymers increased proportionally with increasing amount of HBPU. The hard-segment contents of the polymers ranged from 18.8 to 20.8 wt % and were substantially above the minimum value required to show a shape-memory effect.<sup>25</sup> As expected, the use of fully hard-segmented HBPU enhanced the microphase separation in the polymers. Such morphological changes were clear in the SEM pictures. Figure 3(a) confirms the phase-separated morphology of linear polyurethane (LPU), but the phases were uniformly distributed in one another, whereas Figure 3(b,c) reveals that the hard and soft phases were separated distinctly when the amount of crosslinker was increased. Except CPU-5 and CPU-6, which were prepared with 0.17 and 0.2 equiv of crosslinker, respectively, all of the other polymers were found to have adequate solubility in DMF to smoothly carry out GPC measurements, and the GPC curves obtained are given in Figure 4. There was a very significant difference in the  $M_w$  values of the polyurethanes prepared.  $M_w$  varied from  $5.1 \times 10^4 \text{ g/mol}$  for polymers containing no HBPU (LPU) to  $29.0 \times 10^4 \text{ g/mol}$  for CPU-4, for which the amount of HBPU used was 0.15 equiv. Such a significant increment in the molecular weight was due to the crosslinker used, which itself was a polymer. Because the polymers prepared with crosslinker of more than 0.15 equiv were found to be completely insoluble in DMF, the molecular weight data for CPU-5 and CPU-6 are not given. The polydispersity values were found to increase with increasing molecular weight.



**Figure 2**  $^1\text{H-NMR}$  spectrum (300 MHz) of an HBPU-crosslinked polyurethane (CPU-1).



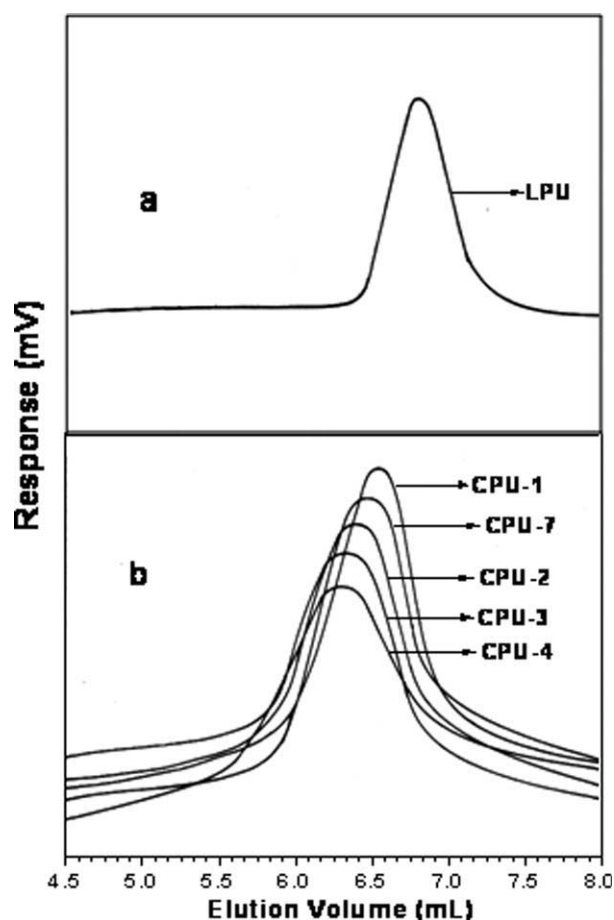
**Figure 3** SEM micrographs of (a) an uncrosslinked polyurethane (LPU), (b) a CPU with 0.1 equiv of HBPU as the crosslinker (CPU-3), and (c) a CPU with 0.2 equiv of HBPU as the crosslinker (CPU-6).

#### Differential scanning calorimetry (DSC) and WAXD

Thermal properties, such as  $T_g$ ,  $T_c$ , and  $T_m$ , and enthalpy data for the LPU and CPUs were determined with DSC, and the values are presented in Table II. Both the first and second heating curves showed  $T_g$  and  $T_m$  transitions. However, for some cases, the  $T_g$  transition was very clear in the first heating curves compared to the second heating curves. The soft-segment crystallization was observed only in the cooling curves. Thus, the first heating and cooling curves were considered for analysis, and typical examples

of DSC traces are given in Figure 5. The incorporation of HBPU crosslinker up to 0.1 equiv was found to increase  $T_g$  of the polymers by 44°C, and the polymers crosslinked with more than 0.1 equiv of crosslinker did not show  $T_g$ . For CPUs, the crystallization of the soft segment was observed between 5 and 8°C; this was comparable to LPU. The  $T_m$  values of the CPUs were between 55 and 60°C, and these values were a little high compared to that of LPU, which underwent melting at 54°C.

The crystallinities of the polymers were calculated from the enthalpy data of the crystalline melting peak with a 140 J/g enthalpy value for the fusion of 100% crystalline PCL,<sup>26</sup> and the values are summarized in Table II along with the corresponding enthalpy values. Within the series of CPU-1 to CPU-6, except for CPU-6, all of the CPUs showed high enthalpy and crystallinity compared to LPU. This was because crystallization occurred effectively in these cases as a result of enhanced phase separation between the soft crystalline phase and the hard amorphous phase. Generally, crosslinking is known to lower the overall crystallization of the soft segment. However, the observation here was the



**Figure 4** SEC traces of linear and HBPU-crosslinked polyurethanes.

TABLE II  
DSC Results for the Linear and Crosslinked Shape-Memory Polyurethanes

Polymer code	$T_g$ (°C)	$T_c$ (°C)	$T_m$ (°C)	Enthalpy (J/g)	Crystallinity (%)	
					DSC <sup>a</sup>	WAXD <sup>b</sup>
LPU	-46	11.0	54	62.5	36.6	33.5
CPU-1	-10	7.0	57	69.8	40.3	36.2
CPU-2	-10	8.0	58	67.0	38.5	35.2
CPU-3	-2	6.0	57	67.4	38.6	34.5
CPU-4	NO	7.0	57	63.0	37.0	34.0
CPU-5	NO	5.0	60	64.5	36.6	33.5
CPU-6	NO	7.0	55	61.3	34.6	32.7
CPU-7	NO	8.0	58	70.9	40.5	39.0

NO = not observed.

<sup>a</sup> The crystallinity was calculated as follows:<sup>26</sup>

$$\text{Crystallinity} = \text{Enthalpy}/140 \times \text{wt \% of PCL} - 4000 \text{ in LPU or CPU}$$

<sup>b</sup> The crystallinity was calculated as follows:

$$\text{Crystallinity} = (A_{100} + A_{101})/(A_{100} + A_{101} + A_a)$$

where  $A_{100}$  and  $A_{101}$  are the areas under the PCL (100) and PCL (101) diffraction peaks, respectively, and  $A_a$  is the area under the amorphous halo.

reverse. The reason could have been that generally crosslinkers used for polyurethanes are soft-segment-type, low-molecular-weight polyols, but here, the crosslinker was a hydrogen-bonded HBPU, which was a hard segment. Compared to LPU, the low enthalpy and associated crystallinity of CPU-6 revealed that there was a threshold limit for the addition of crosslinker; beyond that limit (0.2 equiv), the crosslinker's own contribution to the amorphous phase determined the crystallinity of the polymer.

The molecular weight of the HBPU crosslinker had a pronounced effect on the crystallinity of polymer, and this was observed in the crystallinity and enthalpy data of CPU-4 and CPU-7. The patterns of the X-ray diffraction profiles of the crosslinked and uncrosslinked polymers were identical, and representative X-ray spectra are given in Figure 6. All of the profiles showed two prominent peaks at Bragg angles of 22.5° (100) and 23.8° (101); these indicated

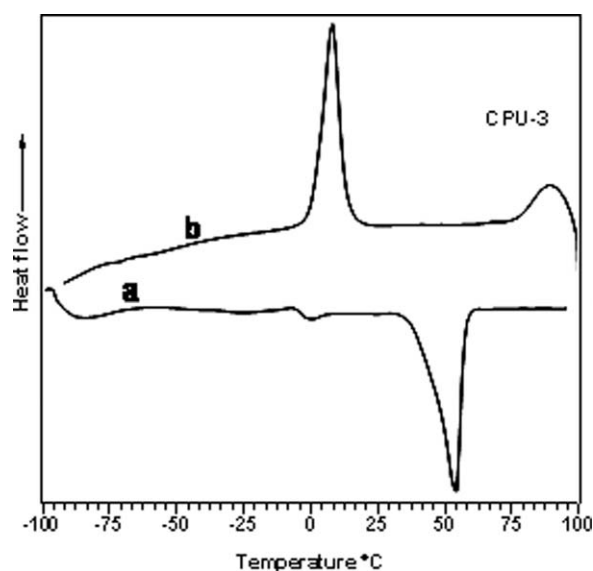


Figure 5 (a) Heating and (b) cooling DSC traces of an HBPU-crosslinked shape-memory polyurethane (CPU-3).

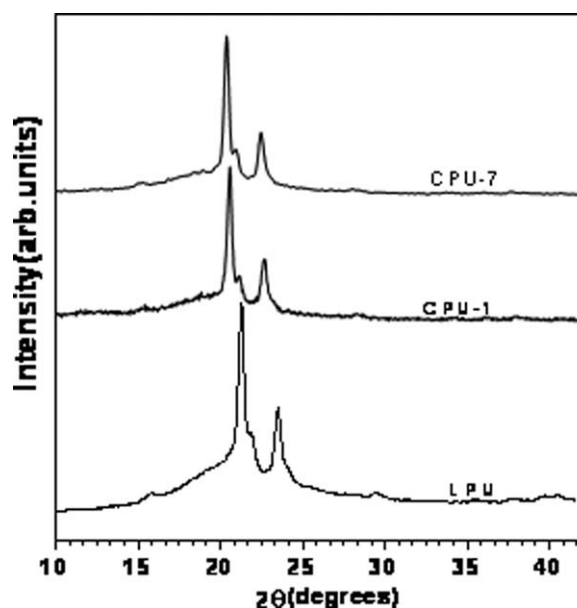


Figure 6 WAXD profile of linear and HBPU-crosslinked polyurethanes.

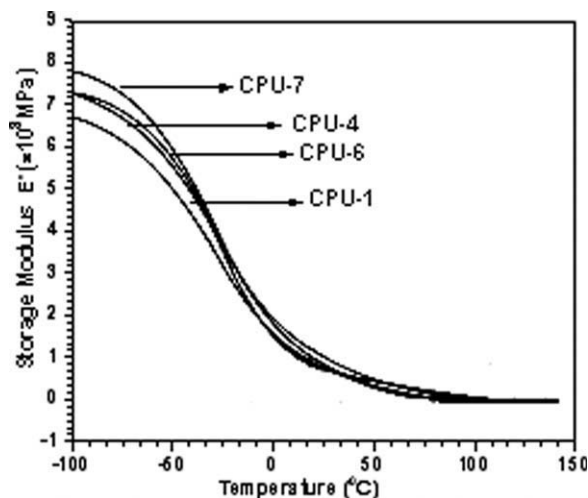
**TABLE III**  
DMA Results for the Linear and Crosslinked  
Shape-Memory Polyurethanes

Polymer code	$E'$ ratio	$\tan_{\max} \delta$	Temperature at $\tan_{\max} \delta$ ( $^{\circ}\text{C}$ )
LPU	6.4	0.06	40
CPU-1	9.25	1.93	77
CPU-2	–	1.84	94
CPU-3	9.6	4.85	78
CPU-4	13.6	3.10	84
CPU-5	–	6.7	85
CPU-6	13.75	–	–
CPU-7	12.5	–	–

that the hard- and soft-segment phases were sufficiently separated to result in no disturbance to the soft-segment crystallization. The pattern also featured a plateau from 15.5 to 21.5 $^{\circ}$ ; this suggested the presence of an amorphous region. The  $d$  values of (100) and (101) were found to be almost constant for all of the polymers. In addition to the DSC method, the percentage crystallinity of the polymer was also determined from X-ray profiles with a simple calculation,<sup>27</sup> and the values are given in Table II. The values and the trend present in the values were comparable to that determined from the DSC curves. The DSC and X-ray results showed that the crystallinity of the CPUs was not affected by the incorporation of HBPU crosslinker up to 0.2 equiv relative to 1.0 equiv of prepolymer.

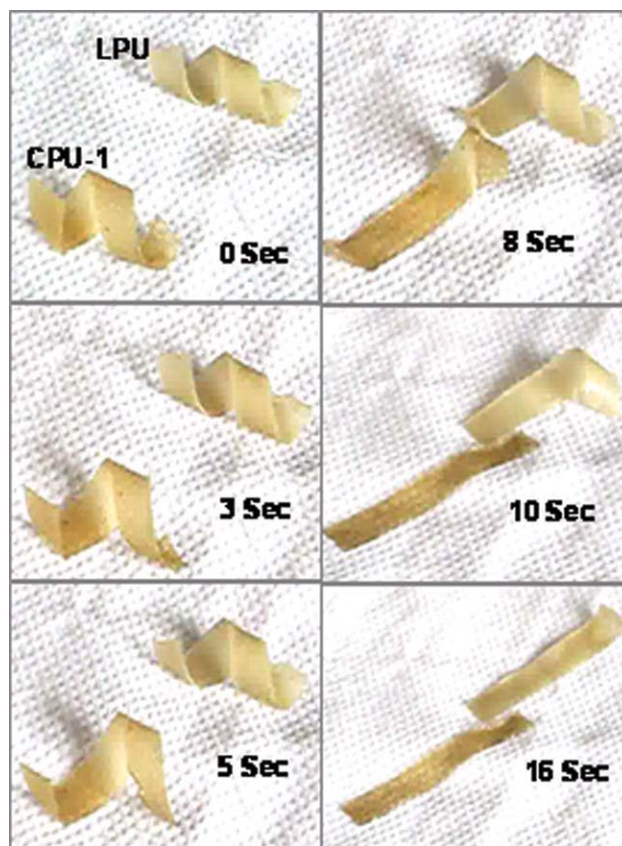
#### Dynamic mechanical properties and shape-memory effect

The tensile storage modulus ( $E'$ ) ratios ( $E'_g/E'_r$ , where  $E'_g$  is the modulus in the glassy region and  $E'_r$  is the modulus in the rubbery region),  $\tan \delta$  val-



**Figure 7** Curves of  $E'$  versus the temperature for HBPU-crosslinked shape-memory polyurethanes.

ues, and  $\tan \delta$  peak temperatures of the LPU and CPUs were obtained from the DMA traces and are presented in Table III. The  $E'$  curves of the CPUs are given in Figure 7. In addition to a sharp  $T_g$  or  $T_m$  transition, a large difference in the modulus above and below the transition temperature was also a most required property to render the materials capable of shape-memory functions, and this property is clearly shown in Figure 7. Compared to LPU, all of the CPUs showed a high  $E'$  ratio. These values increased with increasing amount of crosslinker used, and this result suggested that the shape recovery would be easily triggered at  $T_{\text{trans}}$ . Compared to LPU, the CPUs showed a high  $\tan \delta$  value, and this value increased proportionally with the amount of crosslinker used. Because  $\tan \delta$  value corresponded to the strain energy dissipated by viscous friction, we concluded that the HBPU-crosslinked polyurethanes were more likely viscous than elastic and possessed good damping properties compared to LPU. For all of the polymers, the glass-rubber



**Figure 8** Transition from the temporary shape (spiral) to the permanent shape (strip) for LPU and an HBPU-crosslinked shape-memory polyurethane (CPU-1). The switching temperature of the polymers was 55 $^{\circ}\text{C}$ . The recovery process took 10.0 and 16.0 s after heating to 60 $^{\circ}\text{C}$  for the crosslinked and linear polymers, respectively. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

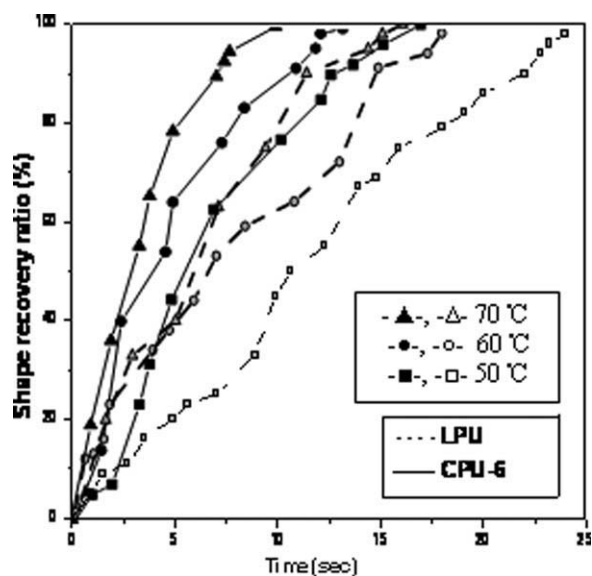


**TABLE IV**  
Shape-Recovery Data Obtained from Bending Tests of the Linear and Crosslinked Shape-Memory Polyurethanes

Polymer code	Time required for 100% shape recovery (s)		
	50°C	60°C	70°C
LPU	24.0	17.5	15.5
CPU-1	18.0	12.0	8.0
CPU-2	17.0	11.0	8.0
CPU-3	16.0	10.0	8.0
CPU-4	15.0	10.0	8.0
CPU-5	14.0	9.0	7.0
CPU-6	14.0	9.0	8.0
CPU-7	16.0	11.0	9.0

transition was found to start around  $-50^{\circ}\text{C}$  and end around  $0^{\circ}\text{C}$ , whereas the  $\tan_{\max} \delta$  temperature of LPU was  $40^{\circ}\text{C}$ , which was close to the melting temperature of LPU. This value was significantly higher for the CPUs. This observation indicated that the polymers responded separately for the glass transition and melting transitions.

A typical example of the shape-memory effect of CPU is shown in Figure 8. Although the DSC curve showed a peak for  $T_m$  of the LPU or CPU at above  $54^{\circ}\text{C}$ , the thermograms clearly indicated that the actual melting started well below  $50^{\circ}\text{C}$  for all of the cases. Hence, the polymers were expected to show a shape-memory effect at  $50^{\circ}\text{C}$  and above. The quantitatively evaluated shape-recovery ratio for the linear and crosslinked polymers at 50, 60, and  $70^{\circ}\text{C}$  are summarized in Table IV, and typical examples of the graphical representations are given in Figure 9.



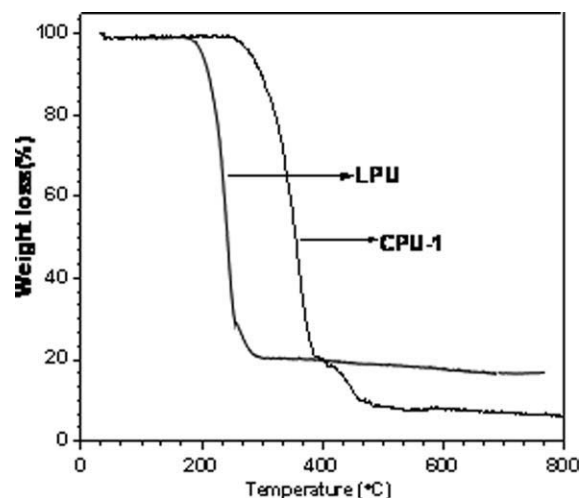
**Figure 9** Shape-memory behavior of linear and crosslinked shape-memory polyurethanes in the time series study.

On the basis of the  $E'$  values determined from the DMA results, SEM micrographs, and the percentage crystallinity calculated from the DSC and WAXD techniques, we envisaged that all of the CPUs prepared should show shape-memory behavior and that this effect should be better than that of the LPU. This anticipation is well reflected in Figures 8 and 9 and the results given in Table IV. The CPU-6 took less time compared to LPU for the transition from temporary shape to permanent shape. Such a performance was observed even in the third cycle of deformation. Within the series of CPU-1 to CPU-6, the shape-recovery rate was found to increase with increasing amount of HBPU crosslinker used.

### Thermal, mechanical, and solubility properties

TGA was performed for all of the polymers, and we found that both linear and crosslinked polymers underwent single-stage decompositions. A typical example of the TGA traces is given in Figure 10, and the initial decomposition temperatures obtained from the TGA traces are given in Table V. The initial decomposition temperature revealed that the thermal stability of the CPUs improved significantly compared to that of the LPUs. The mechanical properties, including tensile strength and elongation of polymers, are also summarized in Table V. Generally, the tensile properties are very sensitive to the amount of crosslinks present in the polymer. In this study, the tensile strength of the polymers was found to increase gradually from LPU, which had no added crosslinkers to CPU-6, which had the maximum amount of added crosslinker.

The LPU and CPUs prepared with up to 0.06 equiv of HBPU crosslinker were found to be highly soluble in polar solvents, including tetrahydrofuran and MEK. The CPUs prepared with 0.10 and 0.15



**Figure 10** TGA thermograms of LPU and an HBPU-crosslinked polyurethane (CPU-1).

TABLE V  
Thermal, Mechanical, and Solubility Properties of the Crosslinked Shape-Memory Polyurethanes

Polymer code	Initial decomposition temperature (°C) <sup>a</sup>	Mechanical properties		Solubility <sup>a</sup>	
		Tensile strength (MPa)	Elongation (%)	DMF, DMAc, NMP, DMSO, THF, and MEK	MeOH and EtOAc
LPU	236	13.6 ± 0.1	46	+	±
CPU-1	263	13.8 ± 0.2	80	+	–
CPU-2	275	13.8 ± 0.2	83	+	–
CPU-3	266	14.6 ± 0.1	50	±	–
CPU-4	252	14.9 ± 0.2	70	±	–
CPU-5	265	15.2 ± 0.2	105	–	–
CPU-6	272	17.3 ± 0.2	124	–	–
CPU-7	273	15.1 ± 0.1	83	±	–

DMAc = dimethylacetamide; DMSO = dimethyl sulfoxide; EtOAc = ethyl acetate; MeOH = methanol; NMP = *N*-methylpyrrolidone; THF = tetrahydrofuran.

<sup>a</sup> + = soluble; – = insoluble; ± = partially soluble.

equiv of crosslinker were found to be only partially soluble in DMF, dimethylacetamide, *N*-methylpyrrolidone, dimethyl sulfoxide, tetrahydrofuran, and MEK. The polymer became insoluble in these solvents with increasing amount of crosslinker beyond 0.15 equiv. Also, none of the CPUs were soluble in methanol or ethyl acetate.

## CONCLUSIONS

A series of shape-memory polyurethanes were prepared with PCL diol as a switching segment and novel hydroxyl-terminated HBPU as crosslinkers. The properties of the CPUs were compared with LPU. The microphase separation was more pronounced in the CPUs. The solubility of the polymers was not affected when the crosslinker was used in an amount up to 0.06 equiv relative to 1.0 equiv of the polyurethane prepolymer, and at the same time, the crystallinity of the polymers was improved. The *E'* ratios of the polymers increased with increasing amount of crosslinker. The morphological feature, crystallinity, and storage modulus ratio cumulatively contributed to improvement in the shape-memory properties of the CPUs over LPU. Obviously, the incorporation of crosslinker into the polymer chain improved the tensile properties of the polymer.

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