

# Synthesis and Characterization of Novel Polyurethanes Based on $N^1, N^4$ -Bis[(4-hydroxyphenyl)methylene]succinohydrazide Hard Segment

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**ABSTRACT:** This article deals with the synthesis and characterization of novel polyurethanes (PUs) by the reaction between two aromatic diisocyanates (4,4'-diphenylmethane diisocyanate and tolylene 2,4-diisocyanate) and two aliphatic diisocyanates (isophorone diisocyanate and hexamethylene diisocyanate) with  $N^1, N^4$ -bis[(4-hydroxyphenyl)methylene]succinohydrazide, which acted as hard segment. UV-vis, FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and DSC/TGA analytical technique has been used to determine the structural characterization and thermal proper-

ties of the hard segmented PUs. X-ray diffraction revealed that PUs contained semicrystalline and amorphous regions that varied depending upon the nature of the backbone structures. PUs were soluble in polar aprotic solvents. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2315–2320, 2008

**Key words:** polyurethanes; hydrazide; hard segments; phase separation; spectroscopy; morphology; thermal properties

## INTRODUCTION

Polyhydrazides have many special properties like high thermal stability, flame resistant and good mechanical<sup>1,2</sup> thermally stable films<sup>3</sup> and in the fields of polymer electronics and polymer light emitting device.<sup>4–8</sup> Hydrogen bonding is usually considered the strongest secondary force in the hard segmented polyurethanes (PUs) and polyureas. Many PUs and polyureas were found to be insoluble in common organic solvents due to their rigid backbones,<sup>9,10</sup> thereby inhibiting their applications due to difficulty in their processing. To overcome such difficulties, polymer structure modification is necessary, wherein one can introduce asymmetric or bulky groups on the pendant polymer backbone or incorporate noncoplanar structural units on the main polymer chain.<sup>11–14</sup> In our previous papers,<sup>15–17</sup> Schiff-based PUs, chalcone-based PUs and azo-based diol containing PUs have been prepared using 2,2'-(ethane-1,2-diylbis(nitri-

lomethylylidene))diphenol, 2,2'-(hexane-1,6-diylbis(nitri-lomethylylidene)) diphenol, 2,2'-(1,4-phenylenebis[nitri-lomethylylidene])diphenol, 2,2'-(4,4'-methylene di-2-methylphenylene-1,1'-bis[nitri-lomethylylidene])diphenol, 2,6-bis(4-hydroxy-benzylidene)cyclohexanone, 4,4'-[1,4-phenylenedi-diazene-2,1-diyl]bis(2-carboxyphenol), and 4,4'-[1,4-phenylenedi-diazene-2,1-diyl]-bis(2-chlorophenol) with different diisocyanates.

In continuation of our studies, we now propose the synthesis of other PUs based on dihydrazide groups containing a diol like  $N^1, N^4$ -bis[(4-hydroxyphenyl)methylene]succinohydrazide as hard segment with 4,4'-diphenylmethane diisocyanate (MDI), tolylene 2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI), and hexamethylene diisocyanate (HDI). The structure of  $N^1, N^4$ -bis[(4-hydroxyphenyl)methylene]succinohydrazide was established by UV-vis, Fourier transform infrared (FTIR) spectroscopy, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectral data. The synthesized PUs were further characterized by UV-vis, FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, DSC, and X-ray diffraction techniques. Results of this study are discussed in terms of their structure-morphology based considerations.

## EXPERIMENTAL

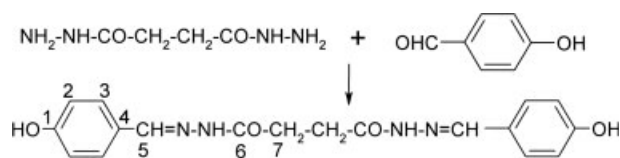
### Materials

MDI, TDI, IPDI, 1,6-hexamethylene diisocyanate (HDI) and dibutyltin dilaurate (DBT) were purchased from

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**Scheme 1** Preparation of BHPMSD.

Aldrich (Milwaukee, WI) and were used without further purification. Diethyl succinate, *p*-hydroxybenzaldehyde, hydrazine hydrate, xylene, ethyl methyl ketone, toluene, *n*-hexane, chloroform, tetrahydrofuran, dimethyl formamide (DMF), dimethylsulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), and dimethyl acetamide (DMAc) were all of analytical reagent (AR) grade samples purchased from s.d. fine chemicals (Mumbai, India). All the solvents were purified before following the standard procedures.

### Preparation of succinohydrazide

In a 500 mL round bottom flask containing ethanol (100 mL), diethyl succinate (0.05 mol), and hydrazine hydrate (0.1 mol) were added and fitted with a condenser. The reaction mixture was refluxed for 5 h, allowed to cool, solid was washed with a small amount of ethanol, and dried. Recrystallisation of the product was done in ethanol. MP = 180–182°C. FTIR assignments of these compounds are given below.

FTIR (KBr): 3350, 3054, 2907, 1671, 1612, 1543, 1520, 1461, 1381, 1249, 1199, 968, 837, and 720  $\text{cm}^{-1}$ .

### Preparation of $N^1,N^4$ -bis[(4-hydroxyphenyl)methylene]succinohydrazide

In a 500 mL round bottom flask fitted with a condenser and a mechanical stirrer containing ethanol (160 mL), *p*-hydroxybenzaldehyde (0.2 mol), and succinohydrazide (0.1 mol) were added. The reaction mixture was refluxed for 5 h, allowed to cool, the solid was washed with a small amount of ethanol, and dried. Recrystallization of the product was done in ethanol. MP = 296–298°C.

UV-vis, FTIR, and NMR assignments of this compound are given below.

UV-vis ( $\lambda_{\text{max}}$ ): 265 and 308 nm.

FTIR (KBr): 3363, 3222, 3037, 2897, 1658, 1606, 1533, 1506, 1447, 1360, 1243, 1198, 966, 831, and 725  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (DMSO- $d_6$ , TMS):  $\delta$ , 2.33 (s, 4H,  $-\text{CH}_2-\text{CO}-$ ), 6.81 (d, 4H,  $\text{C}_2-\text{H}$ , Ar-H), 7.49 (d, 4H,  $\text{C}_3$  and  $\text{C}_4-\text{H}$ , ArH), 7.88 (s, 2H, imine H), 9.01 and 9.91 (br, 2H, amide NH) and 11.05 and 11.24 (br, 2H, phenolic OH).

$^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$ , 29.78 ( $\text{C}_7$ ), 116.53 ( $\text{C}_2$ ), 129.18 ( $\text{C}_3$ ), 143.7 ( $\text{C}_4$ ), 159.83 ( $\text{C}_1$ ), 160.06 ( $\text{C}_5$ ), and 171.68 ( $\text{C}_6$ ).

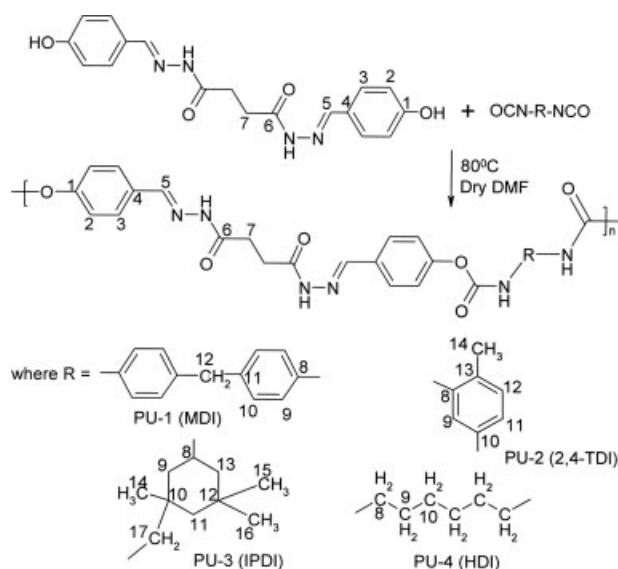
The reaction Scheme 1. displays the formation of  $N^1,N^4$ -bis[(4-hydroxyphenyl)methylene]succinohydrazide (BHPMSD) based on the above cited spectral assignments.

### Polymer synthesis

Typical general procedure used to synthesize PUs was carried out in a three-necked 100 mL round bottom flask equipped with magnetic stirrer, condenser and dropping funnel under an inert nitrogen atmosphere. BHPMSD was dissolved in dry DMF under dry nitrogen atmosphere with a constant stirring. One drop of DBT catalyst was added. Then, equimolar quantity of diisocyanates (MDI, TDI, IPDI, or HDI) with respect to above diol taken in dry DMF was added to this solution over a period of 1 h. The reaction mixture was stirred continuously for 8 h at 80°C, cooled, poured into distilled water, and then filtered. The solid powder polymer obtained was washed with double distilled water, and dried under reduced pressure at 30°C. Chemical structures of PUs are shown in Scheme 2.

### Preparation of poly[ $N^1,N^4$ -bis(4-phenyl)methylenenitriloimino]succinyl methylene-di-1,4-phenyl di(oxyiminocarbonyl)]

Poly[ $N^1,N^4$ -bis(4-phenyl)methylenenitriloimino]succinyl methylene-di-1,4-phenyl di(oxyiminocarbonyl)] (PU-1) was prepared by taking MDI (1.76 g, 0.007 mol) and BHPMSD (2.478 g, 0.007 mol) to yield 3.0 g



**Scheme 2** Reaction schemes for the formation of PUs (i.e., PU-1 to PU-4).

(92.6%). UV-vis, FTIR, and NMR assignments are given below.

UV-vis ( $\lambda_{\max}$ ): 268 and 315 nm.

FTIR (KBr): 3350, 3294, 3134, 3032, 2923, 1657, 1601, 1543, 1511, 1412, 1312, 1234, 1124, 1040, 915, 816, and 779  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (DMSO- $d_6$ , TMS):  $\delta$ , 2.34 (s,  $\text{C}_7\text{—CH}_2$ ), 3.78 (s,  $\text{C}_{13}\text{—CH}_2$ ), 6.70–7.60 (m, ArH), 8.01 (s,  $\text{C}_5\text{—CH}[\text{dbond}]\text{N}$ ) and 8.52 and 9.80 (s, amide and urethane  $\text{—NH—}$ ).

$^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$ , 28.52 ( $\text{C}_7$ ), 35.82 ( $\text{C}_{13}$ ), 114.08 ( $\text{C}_{10}$ ), 118.39 ( $\text{C}_2$ ), 118.72 ( $\text{C}_{11}$ ), 128.72 ( $\text{C}_{12}$ ), 128.90 ( $\text{C}_3$ ), 134.99 ( $\text{C}_4$ ), 137.61 ( $\text{C}_9$ ), 152.62 ( $\text{C}_1$ ), 155.52 ( $\text{C}_5$ ), and 171.93 ( $\text{C}_6$  and  $\text{C}_8$ ).

#### Preparation of poly[ $N^1, N^4$ -bis{(4-phenyl)methylenenitriloimino}succinyl tolylene 2,4-di(oxy carbonylimino)] (PU-2)

Poly[oxy $N^1, N^4$ -bis{(4-phenyl)methylenenitriloimino}succinyl tolylene 2,4-di(oxy carbonylimino)] (PU-2) was prepared by taking TDI (1.56 g, 0.007 mol) and BHPMSD (2.478 g, 0.007 mol) with a yield of 3.75 g (92.86%). UV-vis, FTIR, and NMR assignments are given below.

UV-vis ( $\lambda_{\max}$ ): 262 and 312 nm.

FTIR (KBr): 3325, 3246, 3085, 2967, 1661, 1606, 1545, 1447, 1329, 1237, 1197, 1001, 963, 831, and 749  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (DMSO- $d_6$ , TMS):  $\delta$ , 2.11 (s,  $\text{C}_{15}\text{—CH}_3$ ), 2.14 (s,  $\text{C}_7\text{—CH}_2$ ), 6.70–7.90 (m, ArH), 8.02 (s, imine H), 9.83 and 11.07 (s, amide and urethane  $\text{—NH—}$ ).

$^{13}\text{C}$  NMR (DMSO- $d_6$ , TMS):  $\delta$ , 17.09 ( $\text{C}_{15}$ ), 28.49 ( $\text{C}_7$ ), 115.70 ( $\text{C}_2$ ,  $\text{C}_{10}$  and  $\text{C}_{12}$ ), 125.44 ( $\text{C}_{14}$ ), 128.34 ( $\text{C}_{13}$ ), 128.68 ( $\text{C}_3$ ), 130.20 ( $\text{C}_4$ ), 137.73 ( $\text{C}_9$ ), 142.83 ( $\text{C}_{11}$ ), 159.05 ( $\text{C}_1$  and  $\text{C}_5$ ), 173.32 ( $\text{C}_6$ ), and 174.98 ( $\text{C}_8$ ).

#### Preparation of poly[ $N^1, N^4$ -bis{(4-phenyl)methylenenitriloimino}succinyl 3-(oxycarbonyliminomethyl)-3,5,5-trimethylcyclohexyl iminocarbonyloxy] (PU-3)

PU-3 was prepared by taking IPDI (1.18 g, 0.007 mol) and BHPMSD (2.478 g, 0.007 mol) to yield 3.46 g (94.58%). UV-vis, FTIR, and NMR assignments are given below.

UV-vis ( $\lambda_{\max}$ ): 275 and 319 nm.

FTIR (KBr): 3381, 3059, 2959, 2924, 1719, 1664, 1609, 1502, 1385, 1205, 1165, 1100, 1049, 961, 840, and 753  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (DMSO- $d_6$ , TMS):  $\delta$ , 1.26 (s,  $\text{C}_{15}\text{—CH}_3$ ), 1.31 (s,  $\text{C}_{16}\text{—CH}_3$ ), 1.46 (s,  $\text{C}_{17}\text{—CH}_3$ ), 2.07 (s,  $\text{C}_7\text{—CH}_2$ ), 2.8–3.10 (m,  $\text{C}_9$ ,  $\text{C}_{10}$ ,  $\text{C}_{12}$ , and  $\text{C}_{14}$  isophorone  $\text{—CH}_2$ ), 6.70–8.05 (m, ArH), 8.15 (s, imine H) 9.51 and 11.27 (Ar, amide and urethane  $\text{—NH—}$ ),

$^{13}\text{C}$  NMR (DMSO- $d_6$ , TMS):  $\delta$ , 26.01, 26.07, 27.40 ( $\text{C}_{15}$ ,  $\text{C}_{16}$  and  $\text{C}_{17}$ ), 28.55 ( $\text{C}_7$ ), 29.18, 29.76, 30.04, 38.92, 40.48 (isophorone  $\text{CH}_2$ ), 115.70 ( $\text{C}_2$ ), 128.68

( $\text{C}_3$ ), 131.08 ( $\text{C}_4$ ), 152.20 and 154.03 ( $\text{C}_1$ ), 158.22 ( $\text{C}_5$ ), 171.57 ( $\text{C}_6$ ) and 173.61 ( $\text{C}_8$ ).

#### Preparation of poly[ $N^1, N^4$ -bis{(4-phenyl)methylenenitriloimino}succinyl hexa methylene 1,6-di(oxy carbonylimino)] (PU-4)

PU-4 was prepared by taking HDI (1.29 g, 0.007 mol) and BHPMSD (2.478 g, 0.007 mol) with a yield 3.53 g (93.68%). UV-vis, FTIR, and NMR assignments are given below.

UV-vis ( $\lambda_{\max}$ ): 272 and 306 nm.

FTIR (KBr): 3310, 3234, 3062, 2932, 2856, 1715, 1662, 1548, 1501, 1444, 1376, 1206, 1167, 1097, 945, 841, and 727  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (DMSO- $d_6$ , TMS):  $\delta$ , 1.13 (m,  $\text{C}_{10}\text{—CH}_2\text{—}$ ), 1.49 (m,  $\text{C}_{11}\text{—CH}_2\text{—}$ ), 2.88 (m,  $\text{C}_9\text{—CH}_2\text{—}$ ), 6.7–8.00 (m, ArH), 8.14 (s, imine H), 4.84 (br, amide NH) and 11.27 (br, urethane NH).

$^{13}\text{C}$  NMR (DMSO- $d_6$ , TMS):  $\delta$ , 28.54 ( $\text{C}_7$ ), 29.96 ( $\text{C}_{10}$ ), 31.49 ( $\text{C}_{11}$ ), 35.81 ( $\text{C}_9$ ), 115.68 ( $\text{C}_2$ ), 128.32 ( $\text{C}_3$ ), 131.05 ( $\text{C}_4$ ), 152.17 ( $\text{C}_1$ ), 162.15 ( $\text{C}_5$ ), 171.12 ( $\text{C}_6$ ), and 172.60 ( $\text{C}_8$ ).

Scheme 2 displays the chemical reactions during the formation of different PUs mentioned above.

### Characterization

Melting points of the monomers were determined in open capillary tubes. UV-vis (Secomam, France) were recorded for the monomer and PUs in DMF. FTIR spectra were recorded on a Perkin-Elmer 881 spectrophotometer (Madison, WI).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra in DMSO- $d_6$  were recorded on Bruker's 300 MHz NMR spectrophotometer (Silberstreifen, Rheinstetten, Germany). Chemical shifts,  $\delta$ , were taken with tetramethyl silane (TMS) as a reference liquid. Thermogravimetry (TGA) and differential thermal analysis (DTA) were recorded on a Perkin, Elmer Diamond analyzer (Shelton, CT) from ambient temperature to 800°C under nitrogen gas flow rate of 100 mL/min. The sample weighing about 10 mg was placed in a platinum crucible and DTA/TGA runs were recorded using  $\alpha$ -alumina at the heating rate of 10°C/min. X-ray diffractograms of the PUs were recorded using Rigaku Geigerflex diffractometer (Tokyo, Japan) equipped with Ni-filtered CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Dried PUs were spread on a sample holder and diffractograms were recorded in the 2 $\theta$  angle range of 5–50° at the speed of 5°/min.

### RESULTS AND DISCUSSION

PUs of this study are novel and all were obtained in quantitative yields. Since BHPMSD is incorporated, physical, chemical, and thermal properties of PUs

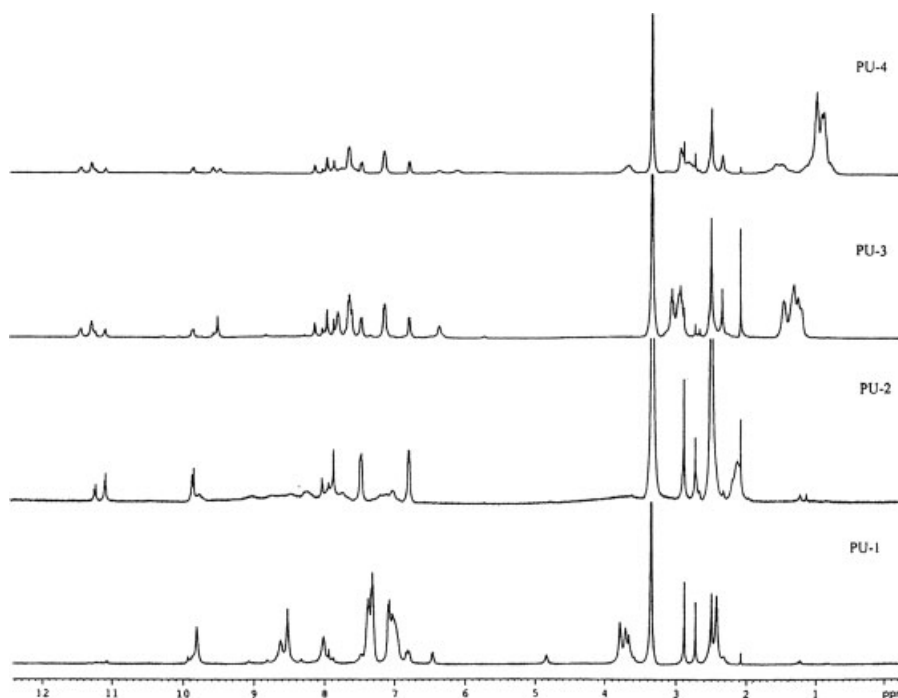


Figure 1  $^1\text{H}$  NMR spectra of PU-1 to PU-4.

were substantially different than those containing aliphatic chains.

### Solubility

All the PUs were soluble in polar aprotic solvents such as *N*'-methyl-2-pyrrolidone (NMP), DMAc, DMF, and DMSO as well as acidic solvents like *m*-cresol, con.  $\text{H}_2\text{SO}_4$ , but were insoluble in water, acetone, methanol, tetrahydrofuran, carbon tetrachloride, ethyl acetate, dioxane, xylene, ethyl methyl ketone, toluene, *n*-hexane, chloroform, and carbon disulfide.

### Spectral data

UV-vis spectra of the diol and PUs were recorded by taking a small amount of the sample in DMF at ambient temperature. In the spectra of Schiff base PUs, absorption bands observed around 262–275 nm are attributed to benzene  $\pi$ - $\pi^*$  transitions.<sup>18</sup> The bands at 306–319 nm are assigned to imine  $n$ - $\pi^*$  transitions.<sup>19</sup> From the absorption spectra, it is concluded that there is no significant difference in the diol and PUs of this study.

Structures of both the monomer and PUs were characterized by NMR and FTIR. FTIR spectra showed a disappearance of both phenolic hydroxyl group and isocyanate group as well as the formation of several characteristic stretching vibrations due to N—H, and C=O bonds. In all the PUs, sharp bands appearing between 3234 and 3381  $\text{cm}^{-1}$  are due to

the presence of hydrogen-bonded N—H group. However, the hydrogen-bonded broad carbonyl groups of amide and urethane are shown in the region 1657–1719  $\text{cm}^{-1}$ .

NMR analysis revealed the disappearance of -OH and -NCO groups as well as the formation of urethane polymer chain.  $^1\text{H}$  NMR spectra of PUs have shown characteristic signals as displayed in Figure 1. Resonance peaks observed in the region 1.13–3.78 ppm correspond to methyl/methylene/isophorone protons of the diol as well as PUs. Aromatic protons showed signals between 6.70 and 8.05 ppm. The resonance peaks of CH=N protons appear in the region of  $\delta$  8.01–8.15 ppm. The resonance peaks of amide and urethane protons occur at  $\delta$  8.14–11.27 ppm.

$^{13}\text{C}$  NMR spectra of all the PUs have shown characteristic signals as displayed in Figure 2. Chemical shifts ranging between 17.09 and 40.48 are due to aliphatic and isophorone carbons. Resonance signals observed in the region between 115.56 and 158.75 ppm are due to aromatic carbons. Peaks observed in the region from 171 to 173 ppm are ascribed to urethane and amide carbonyl.

### Thermal properties

Thermal behavior of all the PUs was studied in a nitrogen atmosphere using DSC/TGA. DSC data are presented in Table I, while the curves are displayed in Figure 3. The existence of multiple endotherms has been documented on thermal characteristics of

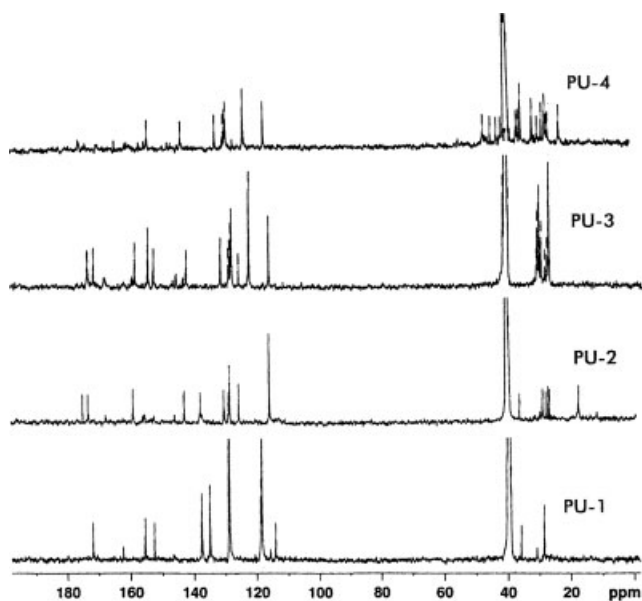


Figure 2  $^{13}\text{C}$  NMR spectra of PU-1 to PU-4.

the segmented PU block copolymers.<sup>20–22</sup> Koberstein and Galambos<sup>23</sup> suggested that the origin of multiple endotherms in PUs is dependent upon the specimen preparation procedure. Martin et al.<sup>24</sup> suggested that five endotherms observed were possibly due to the melting of various hard segment length populations. On the other hand, van Bogart et al.<sup>25</sup> identified three endothermic transitions associated with the ordering of MDI/1,4-butanediol hard segments in materials subjected to third thermal cycle. Blackwell and Lee<sup>26</sup> studied the multiple melting in MDI-based PUs that have been oriented and thermally annealed. Recently, Raghu et al.<sup>9,10,15–17</sup> observed 2–5 endothermic transitions associated with the hard segmented PUs and polyureas. In the light of these reports, it is obvious that the melting behavior of PUs is highly dependent upon the procedure adopted for sample preparation. Indeed, the origin of multiple melting peaks is inherently different for materials prepared under varying conditions.

In the present article, we observe multiple melting phenomena in identical PUs prepared from only hard segments in the main chain. The DSC of PU-1 shows three endotherm peaks, while PU-2, PU-3,

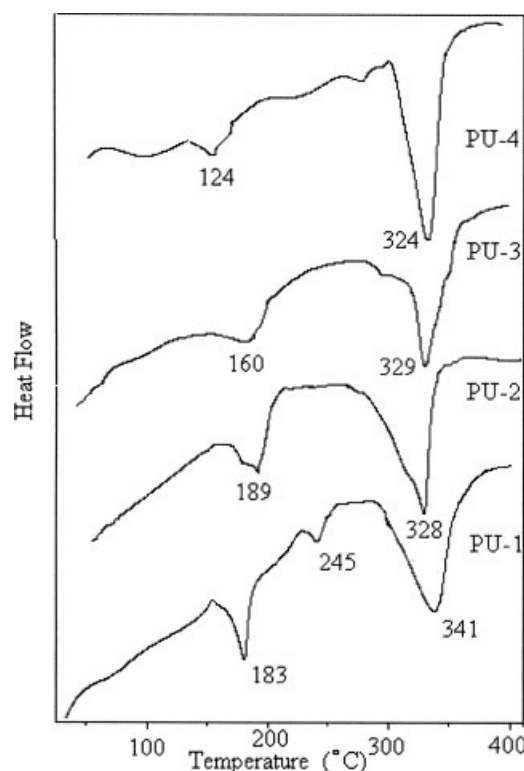


Figure 3 DSC thermograms of PU-1 to PU-4.

and PU-4 show two endotherm peaks, respectively. In case of DSC of PU-1, the lowest endotherm ( $T_1$ ) observed at 183°C is due to the restructuring of the hard-segment units within the hard microdomains. An intermediate temperature endotherm ( $T_2$ ) was observed at 245°C, which is associated with the destruction of long-range order of an unspecified nature. Higher temperature endotherm ( $T_3$ ) observed at 341°C is ascribed to the melting of microcrystalline regions within the hard microdomains. In PU-2, the lowest endotherm ( $T_1$ ) observed at 189°C is due to local restructuring of hard-segment units within hard microdomains. Higher melting temperature ( $T_3$ ) was observed at 328°C. In PU-3, the lowest endotherms ( $T_1$ ) observed at 160°C due to local restructuring of hard-segment units within the hard microdomains. The melting of microcrystalline regions within hard microdomain ( $T_3$ ) is also observed at 329°C. In PU-4, the lowest endotherm ( $T_1$ ) observed at 124°C is due to the restructuring of hard-segment units within hard microdomains. Higher temperature endotherm ( $T_3$ ) observed at 324°C can be ascribed to the melting of microcrystalline regions within hard microdomains. It is thus concluded that  $T_g$  of the hard segmented PUs is found in the range of 124–189°C, while  $T_m$  of the hard segmented PUs observed at higher range of 324–341°C. The MDI-based PUs display the high melting temperature compared to other PUs.

TABLE I  
Different Melting Endotherms from DSC for PUs

Code	$T_1$ (°C)	$T_2$ (°C)	$T_3$ (°C)
PU-1	183	245	341
PU-2	189		328
PU-3	160		329
PU-4	124		324

$T_1$  is the lowest temperature endotherm,  $T_2$  is the intermediate temperature endotherm, and  $T_3$  is the melting temperature endotherm.

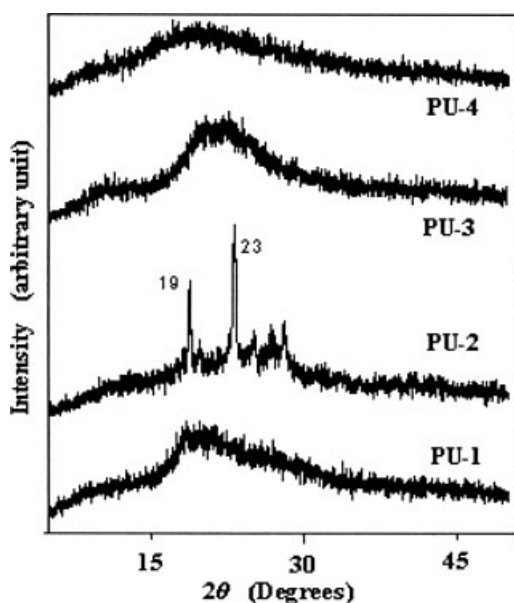


Figure 4 X-ray diffractograms of PU-1 to PU-4

Unfortunately, above 500°C, the degradation of PUs occurs during the TGA study because of the high content of dihydrazide unit in the main chain, which prevented the further study.<sup>27</sup>

### X-ray diffraction

X-ray diffraction curves of the PUs are shown in Figure 4. The semicrystalline form of hard segments seems to depend upon their structures as well as on the crystallization conditions. PU-2 displays semicrystalline nature. PU-1, PU-3, and PU-4 show the amorphous nature. All the PUs display the amorphous nature, while PU-2 exhibits semicrystallinity. These results are in good agreement with our previous reports.<sup>9,10,15–17</sup> This could be due to variations in the unsaturated nature of the diol.

### CONCLUSIONS

Novel PUs based on BHPMSD with MDI, 2,4-TDI, IPDI, and HDI were synthesized. The structures of the diol and PUs were confirmed by UV-vis, FTIR, and NMR studies. All the PUs were soluble in polar aprotic solvents like DMF, DMSO, DMAc, and NMP. DSC displayed multiple endotherms that are in good agreement with the reported data. Above 500°C, degradation of PUs was observed by the TGA, which could be ascribed to the presence of dihydra-

zide unit in the main chain. Semicrystalline and amorphous nature of the PUs was also studied by X-ray diffraction.

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