Synthesis, Characterization of Novel Dihydrazide Containing Polyurethanes Based on N^1,N^2-Bis[(4-hydroxyphenyl)methylene]ethanedihydrazide and Various Diisocyanates

A. V. Raghu, Han Mo Jeong

Department of Chemistry, University of Ulsan, Ulsan 680-749, Republic of Korea

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ABSTRACT: Four novel types of polyurethanes (PUs) were prepared from N^1,N^2-bis[(4-hydroxyphenyl)methylene]ethanedihydrazide with two aromatic diisocyanates (4,4′-diphenylmethane diisocyanate and tolylene 2,4-diisocyanate) and two aliphatic diisocyanates (isophorone diisocyanate and hexamethylene diisocyanate). The chemical structure of both diol and PUs was confirmed by UV–vis, fluoroscence, FTIR, ^{1}H NMR, and ^{13}C NMR spectral data. DSC data show that PUs have multiple endotherm peak. X-ray diffraction revealed that the PUs contained semicrystalline and amorphous regions that varied with the nature of the backbone structures. PUs were soluble in polar aprotic solvents. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3401–3407, 2008

Key words: hydrazide containing PUs; hard segment; spectroscopy; DSC; XRD

INTRODUTION

In our earlier publications,[1–5] we have reported the synthesis and characterization of novel linear segmented polyurethanes (PUs) containing Schiff base, chalcone, and azo-based diols like 4,4′-(ethane-1,2-diylidenedinitrilo)diphenol, 4,4′-(pentane-1,5-diylidenedinitrilo)diphenol, 2,2′-{1,4-phenylenebis[nitrilomethylylidene]}diphenol, 2.2′-{4,4′-methylenedi-2-methylphenylene-1,1′-bis[nitrilomethylylidene]}diphenol, 4-{(4-hydroxy-phenyl)imino]methyl}phenol, 2,6-bis(4-hydroxybenzylidene)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 various diisocyanates. We observed all the PUs display the multiple endotherms peaks via differential scanning calorimetry (DSC). In this study, we have extended our previous work to include a dihydrazide diol moiety in the main chain like N^1,N^2-bis[(4-hydroxyphenyl)methylene]ethanedihydrazide (BHPMED) with 4,4′-diphenylmethane diisocyanate (MDI), tolylene 2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI), and hexamethylene diisocyanate (HDI).

Polyhydrazides have been extensively utilized in a dyeability of synthetic fibers and improve elasticity over other types of polymers.[6,7] They possess good absorption characteristics when the hydrazide link in the main chain of polymer backbone.[8] Azo group is of special interest because of the existence of cis-trans isomerism and its effect on the photochromic properties of the polymers.[9,10] Therefore, polymers that contain the azo group have potential use in a various applications.[11–15] Many PUs and polyureas were found to be insoluble in acidic as well as organic solvents due to their rigid backbones,[16,17] thereby inhibiting their applications due to difficulty in processing. To overcome such difficulties, the polymer structure modification is necessary, wherein one can introduce bulky or asymmetric groups on the pendant polymer backbone or incorporate noncoplanar structural units on the main polymer backbone.

In continuation of our above-mentioned studies, we now propose the synthesis of four novel type of PUs based on dihydrazide groups containing diol like BHPMED as hard segments with MDI, TDI, IPDI, and HDI. The structure of BHPMED and PUs were established by Fourier transform infrared (FTIR) spectroscopy, UV–vis, fluorescence, ^{1}H NMR, and ^{13}C NMR spectral data. The synthesized PUs were further characterized by DSC and X-ray diffraction techniques. Results of this study are discussed in terms of their structure-morphology-based considerations. Theoretical data were also important in the polymer processing. Solubility parameter of the PUs

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Correspondence to: A. V. Raghu (gsraghu2003@yahoo.co.in) or H. M. Jeong (hmjeong@mail.ulsan.ac.kr).

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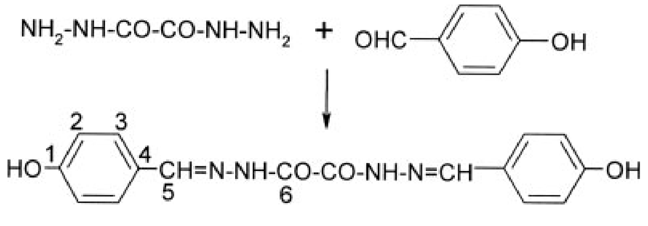


Scheme 1 Preparation of BHPMED.

has also been calculated from the group contribution method suggested by van Krevelen.[18]

EXPERIMENTAL

Materials

p-Hydroxybenzaldehyde, MDI, TDI, IPDI, HDI, and dibutyltin dilaurate (DBT) were purchased from Aldrich (Milwaukee, WI) and used without further purification. Diethyl oxalate, hydrazine hydrate, xylene, toluene, *n*-hexane, tetrahydrofuran (THF), dimethyl formamide (DMF), dimethylsulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMAc), ethanol, methanol, acetone, chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), and hexane were all are of analytical reagent (A.R.) grade samples purchased from S.D. fine chemicals, Mumbai, India. All the solvents were purified before use by following the standard procedures.

Preparation of ethanedihydrazide

In a 500-mL round-bottomed flask containing ethanol (100 mL), diethyl oxalate (10.96 mL, 0.075 mol), and hydrazine hydrate (7.51 mL, 0.150 mol) were added and fitted with condenser. The reaction mixture was refluxed for 5 h and allowed to cool. The obtained solid is washed with small amount of ethanol and dried. Recrystallization of the product was done in ethanol. Product yield was 13.5 g (76%); m.p. 240°C–44°C. FTIR and NMR assignments of these compounds are given below.

FTIR (KBr): 3284, 3181, 3150, 3010, 2805, 1780, 1687, 1613, 1536, 1362, 1278, 1105, 986, 871, and 790 cm^{-1}. ^{1}H NMR (DMSO-d_6, TMS): δ, 2.10 (4H, —NH$_2$) and 8.00 (2H, —NH). ^{13}C NMR (DMSO-d_6): δ, 160.15 (carbonyl carbon).

Preparation of N^1,N^2-bis[(4-hydroxyphenyl)methylene]ethanedihydrazide

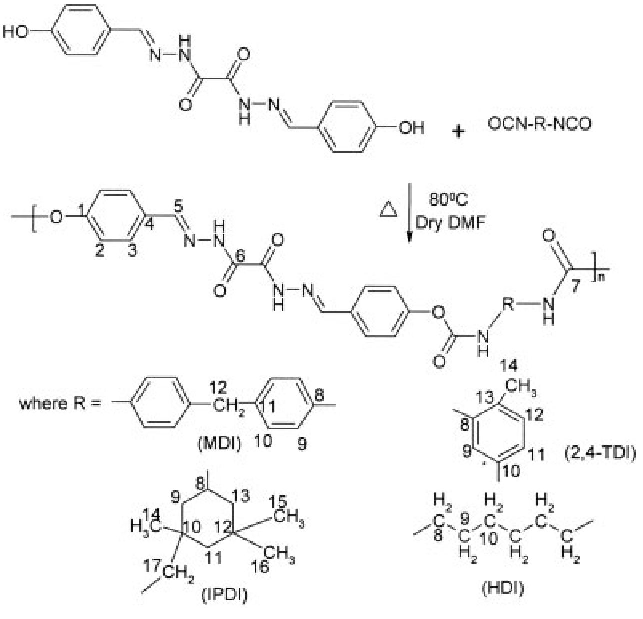
In a 500-mL round-bottomed flask containing ethanol (80 mL), *p*-hydroxybenzaldehyde (12.2 g, 0.1 mol) and ethanedihydrazide (5.9 mL, 0.05 mol) were added and fitted with a condenser. The reaction mixture was refluxed for 7 h and allowed to cool. The solid is washed with small amount of ethanol and recrystallization of the product was done in ethanol. Product yield was 10.3 g (54%); m.p. 296°C–98°C. FTIR and NMR assignments of these compounds are given below.

FTIR (KBr): 3352, 3237, 3037, 1628, 1604, 1505, 1447, 1367, 1229, 1168, 969, 831, and 723 cm^{-1}. ^{1}H NMR (DMSO-d_6, TMS): δ, 6.83 (d, *J* = 8.5 Hz, C$_2$—H, Ar—H), 7.55 (d, *J* = 8.5 Hz, C$_3$—H, ArH), 8.48 (s, —CH=N—), 10.05 (Br, amide NH) and 12.07 (Br, phenolic OH). ^{13}C NMR (DMSO-d_6): δ, 116.65: C$_2$; 125.69: C$_4$; 130.17: C$_3$; 152.20: C$_1$; 156.88: C$_5$; 160.73: C$_6$.

The reaction Scheme 1 displays the formation of BHPMED based on the above-cited spectral assignments.

Synthesis of polyurethanes

Typical general procedure used to synthesize linear segmented PUs was carried out in a three-necked 100-mL round-bottomed flask equipped with a magnetic stirrer, condenser, and dropping funnel under dry nitrogen atmosphere. The BHPMED (0.005 mol) was dissolved in 10-mL dry DMF under dry nitrogen atmosphere with constant stirring and single drop of DBT was added. Then, equimolar quantity of diisocyanates (MDI, TDI, IPDI, or HDI) with respect to the above diol taken in 10-mL dry DMF was added to this solution over a period of 1 h. The reaction mixture was stirred continuously for 6 h at 80°C, cooled, poured into double distilled water, and then filtered. The solid powder polymer obtained was recrystallized from DMF and dried under reduced pressure at 30°C. Chemical structures of PUs are shown in Scheme 2.



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

Preparation of poly[N^1,N^2-bis[(4-phenyl)methylene]ethanedihydrazide 4,4′-methylene diphenylene diurethane] (PU-1)

PU-1 was prepared by taking MDI (1.26 g, 0.005 mol) and BHPMED (1.63 g, 0.005 mol) to yield 2.75 g (95.15 %). FTIR and NMR assignments are given below.

FTIR (KBr): 3315, 3230, 3034, 2922, 1659, 1608, 1510, 1358, 1236, 1166, 1054, 964, 830, and 724 cm^{-1}. ^{1}H NMR (DMSO-*d*$_6$, TMS): δ, 3.78 (s, C_{12}—CH_2), 6.70–7.60 (m, ArH), 8.48 (s, C_5—CH=N), 10.01 (Br, amide —NH) and 12.09 (Br, urethane —NH). ^{13}C NMR (DMSO-*d*$_6$): δ, 38.88: C_{12} merged in DMSO-*d*$_6$ carbon peaks; 115.76: C_9; 118.32: C_2 and C_{10}; 128.86: C_{11}; 129.26: C_3; 134.92: C_4; 137.62: C_8; 151.29: C_1; 155.99: C_5; 159.87: C_6 and C_7.

Preparation of poly[N^1,N^2-bis[(4-phenyl)methylene]ethanedihydrazide tolylene 2,4-diurethane] (PU-2)

PU-2 was prepared by taking TDI (0.88 g, 0.005 mol) and BHPMED (1.63 g, 0.005 mol) with a yield of 2.44 g (97.21%).

FTIR (KBr): 3343, 3231, 3034, 2921, 2859, 1659, 1609, 1538, 1503, 1244, 1159, 1055, 962, 839, and 724 cm^{-1}. ^{1}H NMR (DMSO-*d*$_6$, TMS): δ, 2.15 (s, C_{14}—CH_3), 6.70–8.00 (m, ArH), 8.48 (s, —CH=N—), 10.03 (Br, amide NH) and 12.09 (Br, urethane —NH—). ^{13}C NMR (DMSO-*d*$_6$, TMS): δ, 17.47: C_{14}; 115.84: C_2, C_{11} and C_{13}; 124.90: C_9; 129.33: C_3 and C_{10}; 130.23: C_4; 138.01: C_8 and C_{12}; 151.40: C_1; 156.08: C_5; 159.98: C_6 and C_7.

Preparation of poly[N^1,N^2-bis[(4-phenyl)methylene]ethanedihydrazide isophorone diurethane])] (PU-3)

PU-3 was prepared by taking IPDI (1.13 g, 0.005 mol) and BHPMED (1.63 g, 0.005 mol) to yield 2.57 g (93.11%).

FTIR (KBr): 3365, 3252, 2957, 1658, 1601, 1510, 1440, 1384, 1244, 1236, 1046, and 833 cm^{-1}. ^{1}H NMR (DMSO-*d*$_6$, TMS): δ, 0.86 (s, C_{14}—CH_3), 0.90 (s, C_{15}—CH_3), 0.98 (s, C_{16}—CH_3), 1.12–2.88 (m, C_8, C_9, C_{11}, and C_{13} isophorone—CH_2), 6.70–8.00 (m, ArH), 8.48 (s, —CH=N—), 10.02 (Br, amide NH) and 12.09 (Br, urethane —NH—), ^{13}C NMR (DMSO-*d*$_6$, TMS): δ, 23.26: C_{15}; 27.63: C_{16}; 31.57: C_{14}; 35.06: C_{10}; 35.81: C_{11}; 36.14: C_{12}; 40.17: C_{13}; 42.35: C_{14}; 46.65: C_{14}; 53.03: C_{17}; 115.83: C_2; 124.89: C_3; 129.32: C_4; 151.37: C_1; 156.07: C_5; 159.50: C_6; 162.36: C_7.

Preparation of poly[N^1,N^2-bis[(4-phenyl)methylene]ethanedihydrazide hexamethylene 1,6-diurethane] (PU-4)

PU-4 was prepared by taking HDI (0.845 g, 0.005 mol) and BHPMED (1.63 g, 0.005 mol) with a yield 2.35 g (94.95%).

FTIR (KBr): 3358, 3252, 2957, 2915, 1665, 1601, 1503, 1361, 1237, 1159, 1054, and 836 cm^{-1}. ^{1}H NMR (DMSO-*d*$_6$, TMS): δ, 1.22 (m, C_9—CH_2—), 1.32 (m, C_{10}—CH_2—), 2.94 (m, C_8—CH_2), 6.83 (d, *J* = 8.50 Hz, C_2—H), 7.53 (d, *J* = 8.50 Hz, C_3—H), 8.48 (s, C_5—H, —CH=N—), 10.04 (Br, amide NH) and 12.08 (Br, urethane NH). ^{13}C NMR (DMSO-*d*$_6$, TMS): δ, 26.11: C_{14}; 29.04: C_{15}; 30.06: C_{16}; C_{10}; 34.15: C_9; 35.09: C_{13}; 39.15: C_{11}; 41.25: C_{12}; 41.41: C_{10}; 46.50: C_8; 115.84: C_2; 124.85: C_3; 129.32: C_4; 151.37: C_1; 156.06: C_5; 160.00: C_6 and C_7.

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

Characterization

Melting points (m.p.) of the monomers were determined in open capillary tubes. UV–vis spectra (Secomam, Anthelie, France) were recorded in the wavelength range of 200–600 nm for dilute diol and PUs solution of $5 \times 10^{-4}M$ prepared in a spectroscopic grade DMF. Fluorescence spectra (Varian, USA) were also recorded in the wavelength range of 200–800 nm by using the above-mentioned solution. FTIR spectra were recorded on a PerkinElmer 881 spectrophotometer (Madison, WI). Solution ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker's 300 MHz NMR spectrophotometer (Silberstreifen, Rheinstetten, Germany) in DMSO-*d*$_6$, and chemical shifts are reported in parts per minute downfield of tetramethyl silane (TMS). DSC characterization was conducted under nitrogen on a PerkinElmer Diamond analyzer (Shelton, CT) from ambient temperature to 400°C under nitrogen gas flow rate of 50 mL/min. The sample weighing about 10 mg was placed in a platinum crucible at the heating rate of 10°C/min. All samples were heated at 10°C/min heating rate from 30 to 100°C for the first scan and then cooled at room temperature. X-ray diffractograms of the PUs were recorded using Rigaku Geigerflex diffractometer (Tokyo, Japan) equipped with Ni-filtered Cu Kα radiation (λ = 1.5418 Å). Dried PUs were spread on a sample holder, and diffractograms were recorded in the 2θ angle range of 5°–50° at the speed of 5°/min.

RESULTS AND DISCUSSION

Polyurethanes of this study are novel and are obtained in quantitative yields (93–97%). Becasue Schiff base and dihydrazide contain BHPMED is incorporated, their chemical, physical, and thermal properties PUs are substantially different from those containing aliphatic soft segment chains.

Solubility properties

The solubility of the resulting PUs was investigated in different organic solvent by dissolving 25 mg of

TABLE I
Absorption and Emission Peaks for Diol and Different Pus

Code	Absorption λ_{max} (nm)	Emission λ_{max} (nm)
BHPMED[a]	325	455
PU-1	319	460
PU-2	327	458
PU-3	320	459
PU-4	318	465

[a] BHPMED, *N′*^{1},*N′*^{2}-bis[(4-hydroxyphenyl)methylene] ethanedihydrazide.

PUs in 2.5 mL of solvent at room temperature. It can be seen that all the PUs exhibited good solubility in polar organic solvents such as NMP, DMAc, DMF, DMSO, and *m*-cresol. The solubility should be the result of the introduction of the CH=N group in PU backbone chain. It can also be seen that all the PUs are insoluble in low boiling point solvents such as methanol, acetone, $CHCl_3$, ethanol, hexane, CCl_4, and THF at room temperature and upon heating.

Spectral data

The absorption and emission spectra of the Schiff-based diol and PUs were determined using DMF as a solvent at the ambient temperature. The data are presented in Table I. Both diol and PUs show absorption bands around 318–327 nm, which are attributed to π–π^* transitions of imine transitations.[19] The emission from these diol and PUs appeared around 455–465 nm. From the absorption and emission spectra, it can be concluded that there is no significant difference in the diol and PUs. It may be noted that the observed absorption and emission spectral data are in close agreement with our earlier report.

FTIR spectra showed a disappearance of both the phenolic hydroxyl group (3352) and the isocyanate group (2270) as well as the formation characteristic stretching vibrations due to N—H and C=O bonds as shown in Figure 1. Hydrogen bonding in PUs is of great interest, becasue it plays an important role in determining the phase segregation.[20,21] In all PUs, sharp bands appearing between 3230 and 3365 cm^{-1} are due to the presence of hydrogen-bonded N—H group.[22] However, the hydrogen-bonded broad carbonyl groups of both urethane and amide are merged with Schiff base have appeared in 1657–1665 cm^{-1}.

NMR analysis revealed the disappearance of —OH and —NCO groups as well as the formation of urethane polymer chain. ^{1}H NMR spectra of PUs have shown characteristic signals as displayed in Figure 2. Resonance peaks observed in the region 0.86–3.78 ppm correspond to methyl/methylene/isophorone protons of the diol as well as the PUs. The resonance peaks of —NH—COO— and —NH—CO— protons of all the PUs appeared around 12.01–12.09 ppm, but in the monomer, —OH protons were found to be around 12.07 ppm. Aromatic protons showed signals between 6.70 and 8.00 ppm. The —CH=N— protons displayed signals in the region 8.48 ppm.

^{13}C NMR spectra of all the diol and PUs have shown characteristic signals. The chemical shifts ranging between 17.47 and 53.03 ppm are due to aliphatic and isophorone carbons. Resonance signals observed in the region between 115.76 and 151.40 ppm are due to the aromatic carbons. Peaks observed in the region from 155.99 and 156.08 ppm were ascribed to —CH=N— carbons. Peaks observed in the region from 159.50 to 162.36 ppm are ascribed to —NH—COO— carbons and —NH—CO— carbonyl carbons.

DSC

DSC of all the PUs was studied under nitrogen atmosphere. These data are presented in Table II, while the curves are displayed in Figure 3. The existence of multiple endotherms has been documented

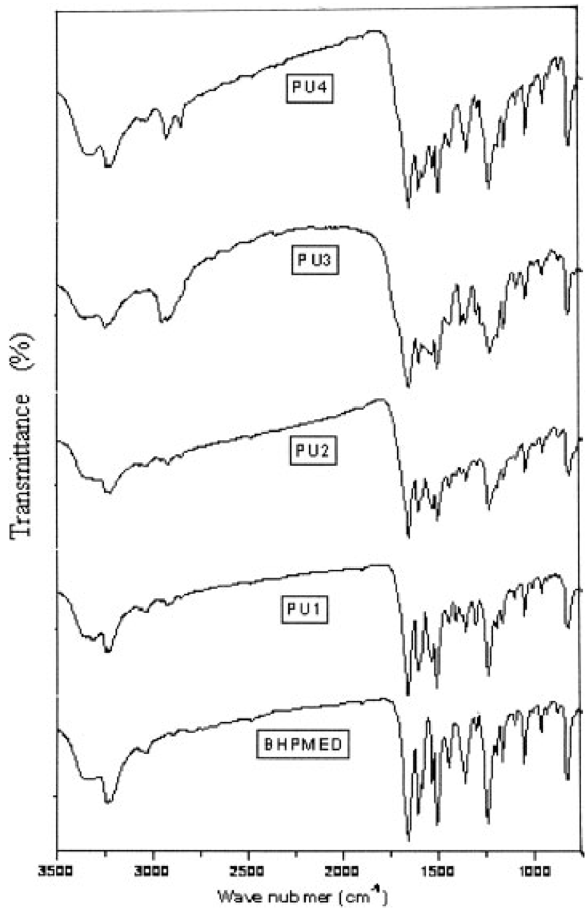


Figure 1 FTIR spectra of BHPMED and PU-1 to PU-4.

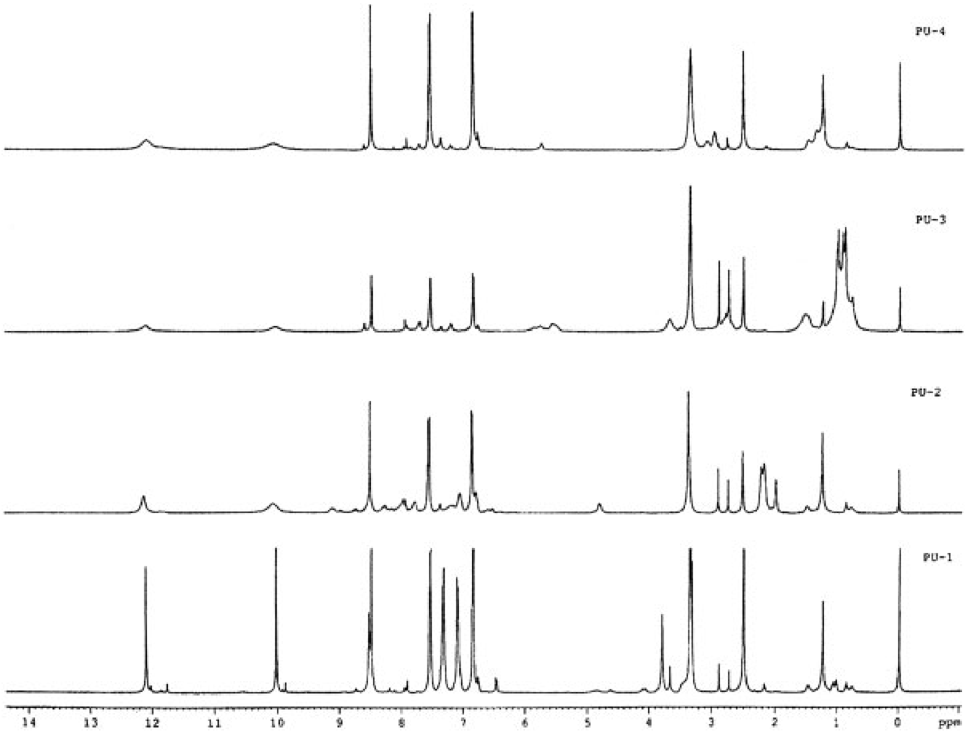


Figure 2 ^{1}H NMR spectra of PU-1 to PU-4.

on thermal characteristics of the segmented PU block copolymers. Koberstein and Galambos[23] suggested that the origin of multiple endotherms in PUs is dependent upon the specimen preparation procedure. Martin et al.[24] 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.[25] identified three endothermic transitions associated with the ordering of MDI/1,4-butanediol hard segments in materials subjected to the third thermal cycle. Blackwell and Lee[26] studied the multiple melting in MDI-based PUs that have been oriented and thermally annealed. 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 origins of multiple melting peaks are inherently different for materials prepared under varying conditions.

TABLE II
Different Melting Endotherms from DSC

Code	T_1 (°C)	T_2 (°C)	T_3 (°C)
PU-1	148	335	362
PU-2	111		355
PU-3	140	305	320
PU-4	190	260	330

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

In this work, we observe two to three melting endothermic peaks phenomena in identical PUs prepared from only hard segments in the main chain. In all PUs, T_g is not clearly shown due to the presence of alternative hard segment. The DSC of PU-2

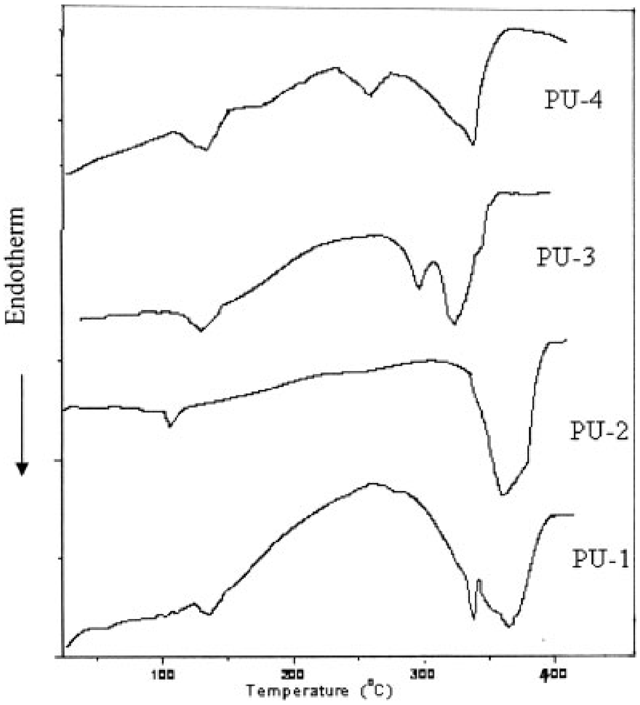


Figure 3 DSC thermograms of PU-1 to PU-4.

shows two endotherm peaks, while PU-1, PU-3, and PU-4 show three endotherm peaks. In case of DSC of PU-1, the lowest endotherm (T_1) observed at 148°C is due to a local restructuring of the hard-segment units within the hard microdomains. An intermediate temperature endotherm (T_2) was observed at 335°C, which is associated with the destruction of long-range order of an unspecified nature. Higher temperature endotherm (T_3) observed at 362°C is ascribed to the melting of microcrystalline regions within hard microdomains. In PU-2, the lowest endotherms (T_1) has shown small peaks at 140°C due to the local restructuring of hard-segment units within the hard microdomains, while an intermediate temperature endotherm (T_2) has displayed at 305°C. The melting of microcrystalline regions within hard microdomain (T_3) is also observed at 320°C. In PU-3, the lowest endotherm (T_1) observed at 111°C is due to a local restructuring of the hard-segment units within the hard microdomains. Higher melting temperature (T_3) was observed at 355°C. In PU-4, the lowest endotherm (T_1) observed at 190°C is due to a local destructing of the hard microdomains. An intermediate temperature endotherm (T_2) was observed at 260°C, which has been associated with the destruction of long-range order of an unspecified nature. Higher temperature endotherm (T_3) observed at 330°C can be ascribed to the melting of microcrystalline regions within the hard microdomains.

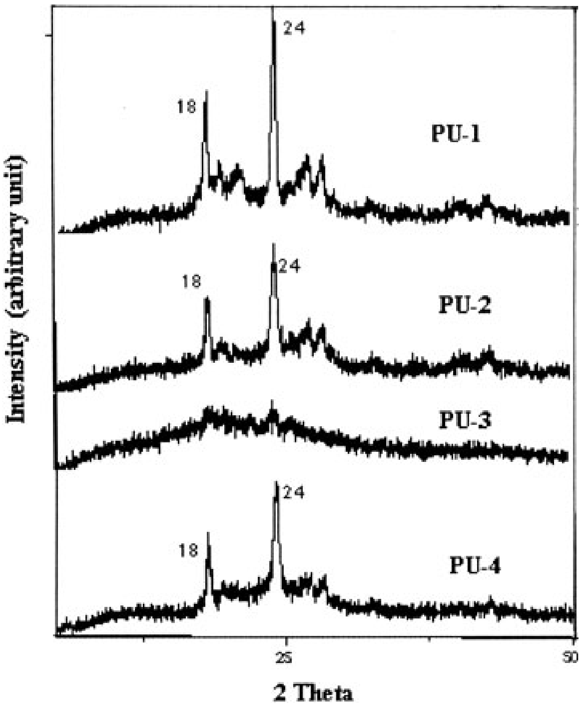


Figure 4 X-ray diffractograms of PU-1 to PU-4.

TABLE III
Solubility Parameter Values from van Krevelen

Code	Molecular weight of PU repeating unit (g/mol)	Volume (cm^3/mol)	Density (g/cc^3)	δ [(J/cm^3)$^{0.5}$]
PU-1	576	509.28	1.1310	16.89
PU-2	500	446.42	1.1120	16.20
PU-3	548	475.28	1.1530	18.59
PU-4	494	434.85	1.1360	16.88

X-ray diffraction

X-ray diffraction curves of the PUs are shown in Figure 4. The semicrystalline and amorphous form of hard segments seem to depend upon their structures as well as on the crystallization conditions.[27] Except PU-3, other PUs display the semicrystalline nature. Semicrystallinity followed in the order: PU-1 > PU-2 > PU-4. PU-3 display the amorphous nature. These results are in good agreement with our previous reports. This could be due to variations in the unsaturated cis-trans nature of the diol.

Solubility parameter

The calculated values from group contribution method (wherein constants were taken from van Krevelen[18]) for solubility parameter are displayed in Table III. Solubility parameters calculated for all PUs ranged between 16.20 and 18.59 (J/cm^3)$^{0.5}$. These values are comparable with our previous report.

CONCLUSIONS

Linear novel segmented PUs based on BHPMED with MDI, 2,4-TDI, IPDI, and HDI were synthesized. The structures of diol and PUs were confirmed by UV–vis spectrophotometer, fluorescence spectroscopy, and FTIR spectra in addition to ^{1}H NMR and ^{13}C NMR studies. All PUs were soluble in polar aprotic solvents and exhibited the fluorescent properties. The solubility parameter values of all the PUs calculated from the group contribution method. DSC displayed the two to three endotherms peaks are close agreement with our previous data. Semicrystalline and amorphous nature of the PUs have been confirmed by X-ray diffraction.

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