

Synthesis and Characterization of Novel Schiff Base Polyurethanes

A. V. Raghu,^{1,2} G. S. Gadaginamath,¹ Han Mo Jeong,² N. T. Mathew,³ S. B. Halligudi,³ T. M. Aminabhavi¹

¹Center of Excellence in Polymer Science, Karnatak University, Dharwad, India 580 003

²Department of Chemistry, University of Ulsan, Ulsan, Republic of Korea 680-749

³Catalysis Division, National Chemical Laboratory, Pune, India 411 008

Received 25 January 2007; accepted 20 February 2008

DOI 10.1002/app.28257

Published online 29 April 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Eight different types of novel polyurethanes (PUs) were synthesized through the polyaddition reaction of 4,4'-(ethane-1,2-diylidenedinitrilo)diphenol and 4,4'-(pentane-1,5-diylidenedinitrilo)diphenol with four different diisocyanates: 4,4'-diphenylmethane diisocyanate, toluene 2,4-diisocyanate, isophorone diisocyanate, and hexamethylene diisocyanate. The resulting PUs were soluble in polar, aprotic solvents. Structures of the diols and PUs were established with ultraviolet-visible, fluorescence, Fourier transform infrared (FTIR), ¹H-NMR, and ¹³C-NMR spectroscopy data. FTIR and NMR spectral data indicated the

disappearance of both hydroxyl and isocyanate groups in the PUs. The thermal properties were investigated with thermogravimetry and differential scanning calorimetry. The weight losses, glass transitions, onset temperatures, and crystalline melting temperatures were measured. All the PUs exhibited semicrystalline and amorphous morphologies, as indicated by X-ray diffraction. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2747–2754, 2009

Key words: amorphous; polyurethanes; morphology; synthesis; thermal properties

INTRODUCTION

Previous articles from our laboratories^{1–5} have dealt with investigations of segmented polyurethanes (PUs) prepared from 2,2'-[ethane-1,2-diylbis(nitrilomethylidene)]diphenol, 2,2'-[hexane-1,6-diylbis(nitrilomethylidene)]diphenol, 2,2'-[1,4-phenylene bis(nitrilomethylidene)]diphenol, 2,2'-[4,4'-methylene-2-methylphenylene-1,1'-bis(nitrilomethylidene)]diphenol, 2,6-bis(4-hydroxybenzylidene)cyclohexanone, 4,4'-(1,4-phenylenediazene-2,1-diyl)bis(2-carboxyphenol), 4,4'-[1,4-phenylenediazene-2,1-diyl]bis(2-chlorophenol), and *N*¹,*N*⁴-bis[(4-hydroxyphenyl)methylene]succinohydrazide as hard segments. As a continuation of those studies, we present here the preparation schemes and characterization of eight novel types of PUs, based on similar, previously developed diols,^{1,2} that were produced through changes in the position of the hydroxyl groups and the use of different aliphatic

dialdehydes instead of diamine units as hard segments of the PUs. Usually, Schiff base polymers exhibit interesting base properties because of the presence of CH=N linkages. Polyazomethine-based conjugated polymers⁶ have the potential to be used in electronic applications because of their environmental stability and good electrical, optoelectronic, electrochemical, nonlinear optical, and mechanical properties.^{7–12} Generally, aromatic polyazomethines are insoluble in common organic solvents but precipitate from the reaction medium before high molecular weights are obtained.^{13,14}

Earlier, we developed PUs and polyureas that were insoluble in common organic solvents because of their rigid backbones^{15,16} which posed difficulties in processing. For the preparation of soluble PUs, we present here novel methods used to prepare eight different types of PUs through the reaction of 4,4'-diphenylmethane diisocyanate (MDI), tolylene 2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI), and 1,6-hexamethylene diisocyanate (HDI) with 4,4'-(ethane-1,2-diylidenedinitrilo)diphenol (EDP) and 4,4'-(pentane-1,5-diylidenedinitrilo)diphenol (PDP). Structures of the diols were established with ultraviolet-visible, fluorescence, Fourier transform infrared (FTIR), ¹H-NMR, and ¹³C-NMR spectral methods, and the PUs were characterized with differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and X-ray diffraction (XRD) techniques to determine their thermal and morphological properties. The results of this

This article is CEPS Communication 133.

Correspondence to: A. V. Raghu (raghu.anjanapura@ril.com) or T. M. Aminabhavi (aminabhavi@yahoo.com).

Contract grant sponsor: University Grants Commission (New Delhi, India); contract grant number: F1-41/2001/CPP-II (to support the Center of Excellence in Polymer Science from 2002 to 2007).

Journal of Applied Polymer Science, Vol. 113, 2747–2754 (2009)
© 2009 Wiley Periodicals, Inc.

study are discussed in terms of their backbone structures and morphologies.

EXPERIMENTAL

Materials

p-Aminophenol, MDI, TDI, IPDI, HDI, and dibutyltin dilaurate (DBT) were purchased from Aldrich (Milwaukee, WI); all were used without further purification. Glyoxal, glutaraldehyde, methanol, and dimethylformamide (DMF) were all purchased from S.D. Fine Chemicals (Mumbai, India). All the solvents were purified before use according to the standard procedures.

Monomer synthesis

Preparation of EDP

To a stirred solution of glyoxal (6.612 g, 0.1 mol) in hot (70°C) methanol (150 mL) was added dropwise a methanolic solution (150 mL) of *p*-aminophenol (23.80 g, 0.2 mol). The reaction mixture was refluxed for 4 h at 70°C. Half of the solvent was removed, and the mixture was cooled to the ambient temperature (30°C) and poured into distilled water (500 mL). The precipitated EDP was filtered, washed with distilled water and then with petroleum ether (40–60°C), and recrystallized from ethanol and dried. The yield was 19.0 g (69%); the melting point was 309–310°C. FTIR and NMR assignments of these compounds are given next.

FTIR (KBr): 3402, 3025, 2823, 1620, 1506, 1459, 1383, 1272, 1162, 1106, 1013, 928, 826, 639 cm^{-1} . $^1\text{H-NMR}$ [deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$), tetramethylsilane (TMS), δ]: 6.83 (d, $J = 8.5$ Hz, 4H, ortho H to $-\text{OH}$), 7.32 (d, $J = 8.5$ Hz, ortho H to $-\text{N}=\text{CH}-$), 8.42 (s, 2H, $-\text{N}=\text{CH}-$), 9.78 (br, 2H, phenolic $-\text{OH}$). $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$, TMS, δ): 115.95 (Ar carbons ortho to $-\text{OH}$), 123.28 (Ar carbons ortho to $-\text{N}=\text{CH}-$), 141.31 (Ar carbons linked to $-\text{N}=\text{CH}-$), 156.43 (Ar carbon linked to $-\text{OH}$), 157.82 ($-\text{N}=\text{CH}-$ carbons).

Preparation of PDP

PDP was synthesized in the usual manner as described previously with glutaraldehyde (10 mL, 0.01 mol) instead of glyoxal. The yield was 17.0 g (62%); the melting point was 309–310°C. FTIR and NMR assignments are given next.

FTIR (KBr): 3390, 3048, 2923, 1632, 1510, 1462, 1380, 1268, 1159, 1112, 936, 835, 645 cm^{-1} . $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, TMS, δ): 1.15 (m, $-\text{N}=\text{CH}-\text{CH}_2-\text{CH}_2-$), 2.79 (m, $-\text{N}=\text{CH}-\text{CH}_2-$), 6.15–7.90 (m, ArH and $-\text{N}=\text{CH}-$ protons), 9.10 (br, 2H, phenolic $-\text{OH}$). $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$, TMS, δ): 28.51

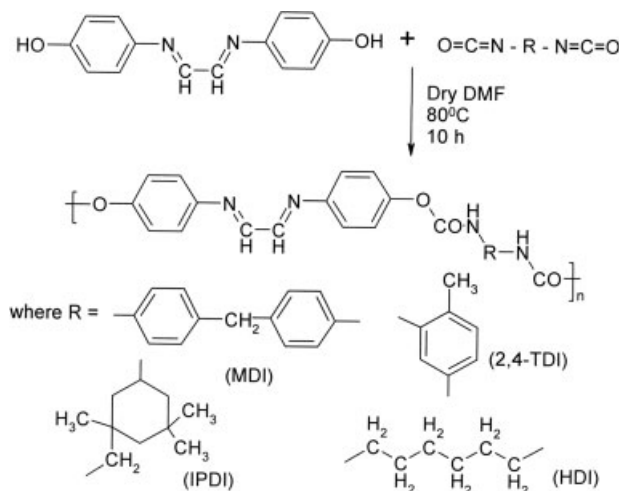
($-\text{N}=\text{CH}-\text{CH}_2-$ carbons), 34.92 ($-\text{N}=\text{CH}-\text{CH}_2-\text{CH}_2-$ carbons), 114.91 (Ar carbons ortho to $-\text{OH}$), 125.30 (Ar carbons ortho to $-\text{N}=\text{CH}-$), 143.69 (Ar carbons linked to $-\text{N}=\text{CH}-$), 155.39 (Ar carbon linked to $-\text{OH}$), 159.73 ($-\text{N}=\text{CH}-$ carbons).

Polymer synthesis

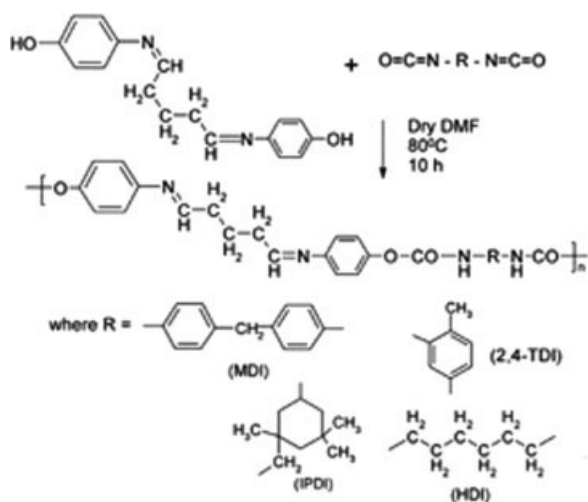
The PUs prepared in this work were novel and were obtained in quantitative yields. After the incorporation of Schiff base diols into the polymer backbone, their physical, chemical, and thermal properties were substantially improved in comparison with those containing aliphatic chains. Typical general procedures used in the synthesis of PUs involved carrying out the reaction in a three-necked, 100-mL, round-bottom flask equipped with a magnetic stirrer, condenser, and dropping funnel under a dry nitrogen atmosphere. The respective diols, EDP and PDF, were dissolved in 10 mL of dry DMF with one drop of the DBT catalyst added to it. Then, an equimolar quantity of a diisocyanate (MDI, TDI, IPDI, or HDI) with respect to each Schiff base diol in 10 mL of dry DMF was added to this solution over a period of 1 h. The reaction mixture was stirred continuously for 10 h at 80°C, cooled, poured into distilled water, and filtered. The solid PUs in powder form were washed with distilled water, recrystallized from DMF, and dried under reduced pressure at 30°C. Chemical structures of the PUs are shown in Schemes 1 and 2.

Preparation of poly[4,4'-(ethane-1,2-diyliidenedinitrilo)diphenyl, methylene bis(4-phenyl carbamate)] (PU-1)

PU-1 was prepared with MDI (2.502 g, 0.01 mol) and EDP (2.4 g, 0.01 mol) to produce a yield of 4.45 g (90.8%). FTIR and NMR assignments are given next.



Scheme 1 Reaction scheme for the formation of PU-1 to PU-4.



Scheme 2 Reaction scheme for the formation of PU-5 to PU-8.

FTIR (KBr): 3308, 3039, 2916, 1664, 1553, 1608, 1553, 1451, 1310, 1094, 1048, 1013, 843, 641 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6 , TMS, δ): 3.79 (s, Ar-CH₂-Ar), 6.60-8.70 (m, ArH), 8.54 (s, -N=CH-), 9.76 (s, -NH-COO-). $^{13}\text{C-NMR}$ (DMSO- d_6 , TMS, δ): 40.35 (Ar-CH₂-Ar carbons merged with DMSO- d_6 methyl carbon peaks), 115.26 (Ar carbons ortho to -O-), 115.96 (Ar carbons ortho to -NH-), 119.13 (Ar carbons ortho to -N=CH-), 128.88 (Ar carbons ortho to -CH₂-), 134.97 (Ar carbons linked to -CH₂-), 137.70 (Ar carbons linked to -NH-), 141.40 (Ar carbons linked to -N=CH- group), 152.92 (Ar carbon linked to -O-), 156.49, 157.79 (-NH-COO- carbons).

Preparation of poly[4,4'-(ethane-1,2-diylidenedinitrilo)diphenyl, tolylene 2,4-(biscarbamate)] (PU-2)

PU-2 was prepared with TDI (1.742 g, 0.01 mol) and EDP (2.4 g, 0.01 mol) to produce a yield of 3.8 g (92%). FTIR and NMR assignments are given next.

FTIR (KBr): 3319, 3050, 2925, 1675, 1608, 1553, 1459, 1375, 1272, 1094, 861, 750 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6 , TMS, δ): 2.16 (s, -CH₃), 6.60-8.20 (m, ArH), 8.39 (s, -N=CH-), 9.74 (s, -NH-COO-). $^{13}\text{C-NMR}$ (DMSO- d_6 , TMS, δ): 17.14 (-CH₃ carbons), 104.35, 106.69 (Ar carbons ortho to -O-), 115.93 (Ar carbons ortho to -NH-), 120.41 (Ar carbons ortho to -N=CH-), 123.23 (Ar carbons linked to -CH₃), 137.91 (Ar carbons linked to -NH-), 141.36 (Ar carbons linked to -N=CH-), 152.84 (Ar carbons linked to -O-), 156.48 (-N=CH- carbons), 157.78 (-NH-COO- carbons).

Preparation of poly[4,4'-(ethane-1,2-diylidenedinitrilo)diphenyl, isophorone(biscarbamate)] (PU-3)

PU-3 was prepared with IPDI (2.22 g, 0.01 mol) and EDP (2.4 g, 0.01 mol) to produce a yield of

4.1 g (89%). FTIR and NMR assignments are given next.

FTIR (KBr): 3345, 3040, 2934, 1728, 1672, 1570, 1524, 1459, 1383, 1001, 843, 748 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6 , TMS, δ): 0.88 (s, -CH₃), 0.90 (s, -CH₃), 0.99 (s, -CH₃), 1.00-2.90 (m, isophorone ring and -CH₂-NH-), 5.75 (br, -NH-COO-), 6.60-7.50 (m, ArH), 8.40 (s, -N=CH- protons), 9.76 (br, -NH-COO-). $^{13}\text{C-NMR}$ (DMSO- d_6 , TMS, δ): 27.57 (-CH₃ carbons), 29.87 (-CH₃ carbons), 30.79 (-CH₃ carbons), 31.44, 34.99, 35.74, 36.07, 44.45, 45.52 (isophorone carbons), 46.67 (-CH₂-NH- carbons), 115.13 (Ar carbons ortho to -O-), 118.20 (Ar carbons ortho to =N-), 137.41, 141.34 (Ar carbons linked to -N=CH- group), 151.91 (Ar carbons linked to -O-), 157.78 (-CH=N- carbons), 159.99, 162.26 (-NH-COO- carbons).

Preparation of poly[4,4'-(ethane-1,2-diylidenedinitrilo)diphenyl, hexamethylene(biscarbamate)] (PU-4)

PU-4 was prepared with HDI (1.682 g, 0.01 mol) and EDP (2.4 g, 0.01 mol) to produce a yield of 3.8 g (93%). FTIR and NMR assignments are given next.

FTIR (KBr): 3381, 3045, 2945, 1664, 1661, 1518, 1456, 1386, 1334, 1284, 1167, 835, 736 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6 , TMS, δ): 1.32 (m, -NH-CH₂-CH₂-), 1.46 (m, -NH-CH₂-CH₂-CH₂-), 3.06 (m, -NH-CH₂-), 6.60-8.00 (m, ArH), 8.45 (s, -N=CH-), 9.80 (br, -NH-COO-). $^{13}\text{C-NMR}$ (DMSO- d_6 , TMS, δ): 25.93 (-NH-CH₂-CH₂- carbons), 29.12 (-NH-CH₂-CH₂-CH₂- carbons), 39.10 (-NH-CH₂- carbons, merged with solvent peaks), 115.97 (Ar carbons ortho to -O-), 122.37 (Ar carbons ortho to -N=CH-), 146.37 (Ar carbons linked to =N-CH-), 150.88 (Ar carbons linked to -O-), 158.13, 159.56 (-NH-COO- carbons).

Scheme 1 displays the chemical reactions involved in the formation of PU-1 to PU-4.

Preparation of poly[4,4'-(pentane-1,5-diylidenedinitrilo)diphenyl, methylene bis(4-phenylcarbamate)] (PU-5)

PU-5 was prepared with MDI (2.502 g, 0.01 mol) and PDP (2.76 g, 0.01 mol) to produce a yield of 4.9 g (85.5%). FTIR and NMR assignments are given next.

FTIR (KBr): 3308, 3039, 2925, 1675, 1608, 1515, 1404, 1310, 1094, 1013, 832, 745 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6 , TMS, δ): 1.25 (m, -N=CH-CH-CH₂-), 2.87 (m, -N=CH-CH₂-), 3.66, 3.78 (s, Ar-CH₂-Ar), 6.30-7.90 (m, ArH and -N=CH- protons), 8.50 (br, -NH-COO-). $^{13}\text{C-NMR}$ (DMSO- d_6 , TMS, δ): 29.21 (-N=CH-CH₂- carbons), 35.74 (-N=CH-CH₂-CH₂- carbons), 40.34 (Ar-CH₂-Ar carbon merged with DMSO- d_6 ,

CH₃ carbons), 114.12 (ortho Ar carbons to —O—), 118.45 (ortho Ar carbons to —NH—), 128.72, 128.86 (Ar carbons ortho to —N=CH—), 129.01 (Ar carbons ortho to —CH₂—), 134.95, 135.76 (Ar carbons linked to —CH₂—), 137.47 (Ar carbons linked to —NH—), 137.69 (Ar carbons linked to —N=CH—), 152.62 (Ar carbons linked to —O—, —NH—COO— carbons and —N=CH— carbons).

Preparation of poly[4,4'-(pentane-1,5-diylidenedinitrilo)diphenyl, tolylene 2,4-(biscarbamate)] (PU-6)

PU-6 was prepared with TDI (1.742 g, 0.01 mol) and PDP (2.76 g, 0.01 mol) to produce a yield of 4.1 g (91%). FTIR and NMR assignments are given next.

FTIR (KBr): 3318, 3042, 2922, 1670, 1605, 1518, 1462, 1310, 1094, 998, 840, 753 cm⁻¹. ¹H-NMR (DMSO-*d*₆, TMS, δ): 1.17 (m, —N=CH—CH₂—CH₂—), 2.16 (s, —CH₃), 2.87 (m, —N=CH—CH₂—), 6.30–8.70 (m, ArH), 9.07 (br, —NH—COO—). ¹³C-NMR (DMSO-*d*₆, TMS, δ): 17.15 (—CH₃ carbons), 30.77 (—N=CH—CH₂— carbons), 35.75 (—N=CH—CH₂—CH₂— carbons), 104.08 (Ar ortho carbons to —O—), 106.45 (Ar ortho carbons to —N—), 129.88 (Ar carbons linked to —N— and —CH₃), 152.46 (Ar carbons linked to —O—), 162.31 (—NH—COO— carbons and —N=CH— carbons).

Preparation of poly[4,4'-(pentane-1,5-diylidenedinitrilo)diphenyl, isophorone(biscarbamate)] (PU-7)

PU-7 was prepared with IPDI (2.22 g, 0.01 mol) and PDP (2.76 g, 0.01 mol) to produce a yield of 4.6 g (92%). FTIR and NMR assignments are given next.

FTIR (KBr): 3345, 3047, 2945, 1664, 1553, 1375, 1305, 1059, 835, 756 cm⁻¹. ¹H-NMR (DMSO-*d*₆, TMS, δ): 0.86 (s, —CH₃), 0.90 (s, —CH₃), 0.98 (s, —CH₃), 1.00–3.00 (m, isophorone protons and —N=CH—CH₂—CH₂—), 5.54 (br, —NH—COO—), 6.30–8.00 (m, ArH).

Preparation of poly[4,4'-(pentane-1,5-diylidenedinitrilo)diphenyl, hexamethylene(biscarbamate)] (PU-8)

PU-8 was prepared with HDI (1.682 g, 0.01 mol) and PDP (2.76 g, 0.01 mol) to produce a yield of 4.35 g (92%). FTIR and NMR assignments are given next.

FTIR (KBr): 3315, 3039, 2937, 1710, 1637, 1506, 1357, 1272, 1039, 836, 760 cm⁻¹. ¹H-NMR (DMSO-*d*₆, TMS, δ): 1.22 (m, —N=CH—CH₂—CH₂—), 1.32 (m, —NH—CH—CH₂—), 2.87 (m, —N=CH—CH₂—CH₂—), 2.94 (—NH—CH₂—), 2.07 (—NH—CH₂—CH₂—CH₂—) 5.75–7.80 (m, ArH), 7.90 (m, —N=CH— and —NH—COO—).

Scheme 2 displays the formation of PU-5 to PU-8.

Characterization

Melting points of the diols were determined in open capillary tubes. Ultraviolet–visible (Secomam, Anthelie, France) and fluorescence spectra (F-2000, Hitachi, Tokyo, Japan) were recorded for diols and PUs in DMF. FTIR spectra were recorded on a PerkinElmer (Madison, WI) 881 spectrophotometer. ¹H-NMR and ¹³C-NMR spectra in DMSO-*d*₆ were recorded on a Bruker 300-MHz NMR spectrophotometer (Silberstreifen, Rheinstetten, Germany). Chemical shifts were measured with TMS as the reference. TGA and differential thermal analysis (DTA) were recorded on a PerkinElmer (Shelton, CT) diamond analyzer from the ambient temperature to 1000°C under an inert nitrogen atmosphere with a flow rate of 100 mL/min. A sample weight of about 5–10 mg was placed in a platinum crucible, and DTA/TGA runs were recorded with α-alumina at the heating rate of 10°C/min. X-ray diffractograms of the PUs were recorded with a Rigaku (Tokyo, Japan) Geigerflex diffractometer 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 angle range of 5–50° at the speed of 5°/min.

RESULTS AND DISCUSSION

Solubility

All PUs were insoluble in common organic solvents such as methanol, chloroform, xylene, toluene, carbon disulfide, tetrahydrofuran, carbon tetrachloride, ethyl acetate, ethyl methyl ketone, acetone, benzene, ether, and hexane because of hydrogen bonding. However, they were soluble in polar aprotic solvents such as DMF, *N*-methylpyrrolidone, and DMSO.

Spectral data

Table I shows absorption and emission spectral values for the PUs and diols for comparison. Both PUs

TABLE I
Absorption and Emission Peaks of Different Monomers and PUs

Code	Maximum absorption (emission) wavelength (nm)
EDP	278 (350), 380 (455)
PU-1	284 (338), 381 (454)
PU-2	275 (334), 379 (453)
PU-3	275 (335), 382 (427)
PU-4	268 (347), 381 (428)
PDP	270 (335), 378 (457)
PU-5	271 (345), 382 (430)
PU-6	273 (338), 381 (450)
PU-7	272 (342), 384 (452)
PU-8	278 (341), 380 (451)

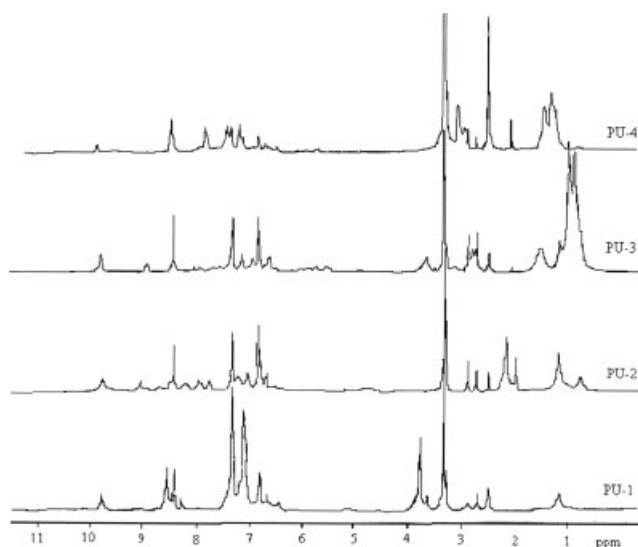


Figure 1 ^1H -NMR spectra of PU-1 to PU-4.

and diols show absorption peaks around 268–284 nm, which are attributed to benzene π - π^* transitions, whereas peaks around 378–384 nm have been assigned to imine n - π^* transitions.¹⁷ Emissions from these diols and PUs appear around 334–350 and 430–455 nm, respectively. From the absorption and emission spectra, it can be concluded that there is no significant difference in the diols and PUs prepared. However, the observed absorption and emission spectral data are in good agreement with our earlier report.¹

Structures of both the diols and PUs were characterized with FTIR and NMR. FTIR spectra indicate the disappearance of bands due to both hydroxyl (at 3390 and 3402 cm^{-1}) and isocyanate (at 2268 cm^{-1}) groups, but they exhibit several characteristic stretching vibrations due to N–H, C=O, CH=N, and C–H moieties. Hydrogen bonding in PUs is of great interest because it is important¹⁸ in determining the phase segregation. In all the PUs, sharp bands appearing between 3308 and 3363 cm^{-1} are due to the presence of hydrogen-bonded N–H groups.¹⁹ However, the hydrogen-bonded carbonyl bands²⁰ of the urethane merge with the imine bands appearing between 1664 and 1728 cm^{-1} .

NMR analysis also confirms the disappearance of –OH and –NCO groups and the formation of the urethane polymer chain. ^1H -NMR spectra of PUs show characteristic signals (Fig. 1). Resonance peaks in the region of 0.88–3.79 ppm correspond to methyl, isophorone, and methylene protons of diol as well as PUs. Resonance peaks of –NH–COO– protons of all the PUs occur around 9.07–9.80 ppm, except that of PU-7 (IPDI-based polymer). In PU-7, the –NH–COO– protons appear at 5.75 ppm, which is in agreement with our earlier reports.^{1,21} The

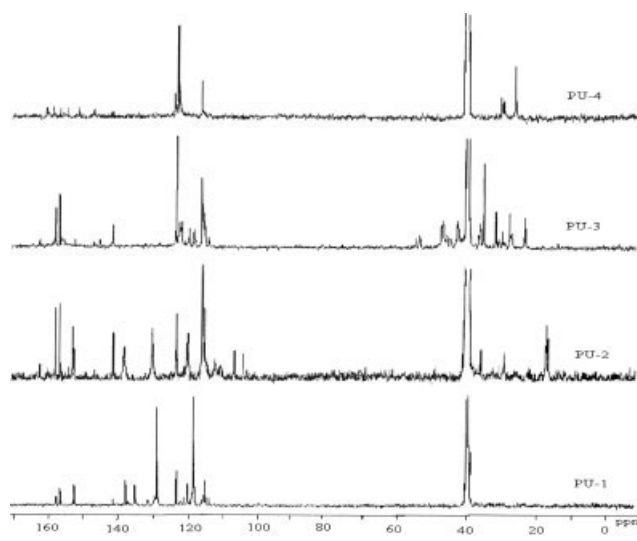


Figure 2 ^{13}C -NMR spectra of PU-1 to PU-4.

–OH proton signals of the diols are observed at δ values of 9.50 and 9.78 ppm; these peaks have disappeared in PUs. Resonance peaks of CH=N protons appear in the region of 8.39–8.54 ppm, but the multiplet due to aromatic protons occurs from 6.30 to 8.70 ppm.

The ^{13}C -NMR spectra of all the PUs show characteristic signals, as displayed in Figure 2. The δ values ranging from 17.14 to 45.52 ppm are due to methyl, methylene, and isophorone carbons. Resonance signals observed in the region between $\delta = 104.55$ ppm and $\delta = 152.92$ ppm are due to aromatic carbons. Peaks observed in the region from 156.48 to 162.26 ppm are ascribed to CH=N and urethane carbonyl carbons.

Thermal properties

The thermal properties of all the PUs were investigated with DTA/TGA, and these data are presented in Table II and Figure 3. The existence of multiple endotherms has been documented in several studies

TABLE II
Different Melting Endotherms of PUs from DTA/TGA

Code	T_1 ($^{\circ}\text{C}$)	T_2 ($^{\circ}\text{C}$)	T_3 ($^{\circ}\text{C}$)
PU-1	133	245	335
PU-2	76	297	327
PU-3	62	335, 349	359, 384
PU-4	80	187, 231	347, 368
PU-5	76		339
PU-6	69		229
PU-7	66		351
PU-8	72		317, 366

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

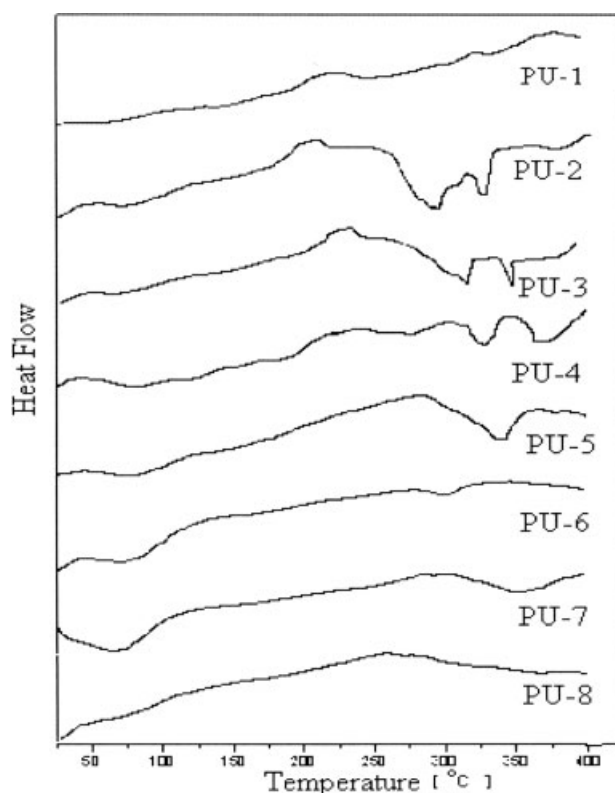


Figure 3 DTA thermograms of PU-1 to PU-8.

of the thermal behavior of segmented PU block copolymers.^{22–24} Koberstein and Galambos²⁵ indicated that the origin of multiple endotherms in PUs is dependent on their preparation procedure. Martin et al.²⁶ suggested that the five endotherms are possibly due to the melting of various hard-segment length populations. Van Bogart et al.²⁷ identified three endothermic transitions associated with the ordering of MDI/1,4-butane diol hard segments in PUs subjected to a third thermal cycle. Blackwell and Lee²⁸ studied multiple melting in MDI-based PUs that were oriented and thermally annealed. In the light of these reports, one can conclude that the

melting behavior of PUs is highly dependent on the procedure adopted for sample preparation. Indeed, the origins of multiple melting may be inherently different for polymers prepared under various conditions.

In this study, multiple melting has been observed, which is similar to that of PUs prepared from only hard segments of the main chain. DSC data for PU-5, PU-6, and PU-7 show two endothermic peaks, whereas those of PU-1 and PU-8 display three endotherms, but PU-3 and PU-4 exhibit five endotherms. The lowest endotherms in the region of 60–80 °C are due to the local restructuring of hard-segment units within the hard microdomains, which may be considered to be the glass-transition temperature of the polymer. The intermediate temperature endotherms are also observed around 187–297 °C and are associated with the destruction of long-range order of an unspecified nature. Higher temperature endotherms observed around 317–384 °C are ascribed to the melting of microcrystalline regions within the hard microdomains.

Weight-loss (TGA) data of all the PUs, presented in Table III and graphically displayed in Figure 4, suggest that 10 and 50% weight losses have occurred in the temperature ranges of 199–253 and 337–499 °C, respectively. PUs exhibit an onset temperature range of 219–304 °C. These curves show a major weight loss between 230 and 490 °C, but the residual weight remaining at 600 °C is about 13–41%. This variation in weight loss is due to the differences in the structures of the hard segments of the PUs. TGA data indicate that the MDI-based PUs exhibited better thermal stability than the diisocyanate-based PUs, and this is attributed to the presence of biphenyl groups on the main chains.

XRD

XRD tracings of the PUs are presented in Figures 5 and 6, respectively. EDP-based PUs show semicrys-

TABLE III
Thermal Properties of PUs

Code	Decomposition temperature (°C)		Major weight-loss transition (°C)	Residual weight loss at 600 °C by TGA in N ₂ (%)	Onset temperature
	T ₁₀	T ₅₀			
PU-1	251	499	230–361	41	219
PU-2	248	394	216–490	33	260
PU-3	244	368	272–448	20	276
PU-4	235	337	210–484	13	277
PU-5	253	421	247–478	36	273
PU-6	199	409	223–490	32	255
PU-7	147	354	275–472	26	304
PU-8	245	392	242–477	31	235

T₁₀ is the temperature at which 10% weight loss was observed by TGA, and T₅₀ is the temperature at which 50% weight loss was observed by TGA.

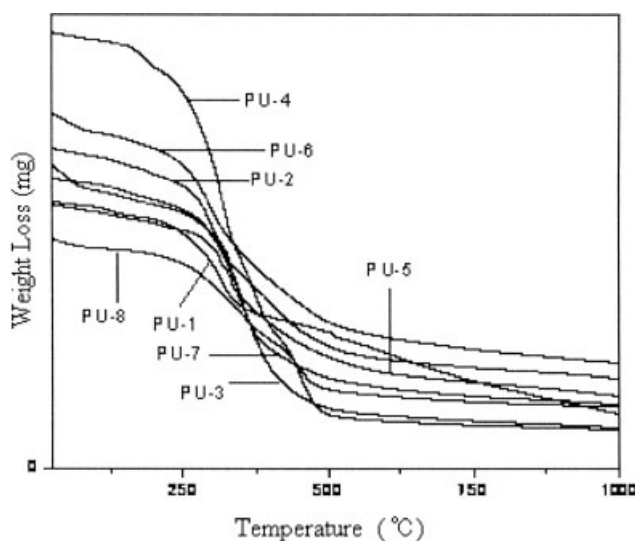


Figure 4 TGA tracings of PU-1 to PU-8.

talline domains, whereas PDP-based ones show amorphous domains. The semicrystalline nature of the PUs is in agreement with the DSC data. In the case of EDP-based PUs, three to four endotherms are observed.

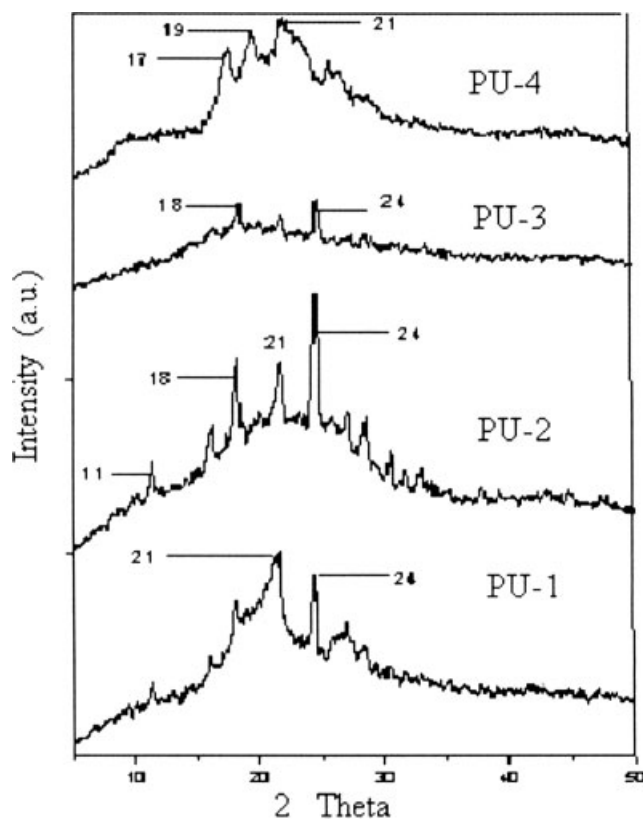


Figure 5 X-ray diffractograms of PU-1 to PU-4.

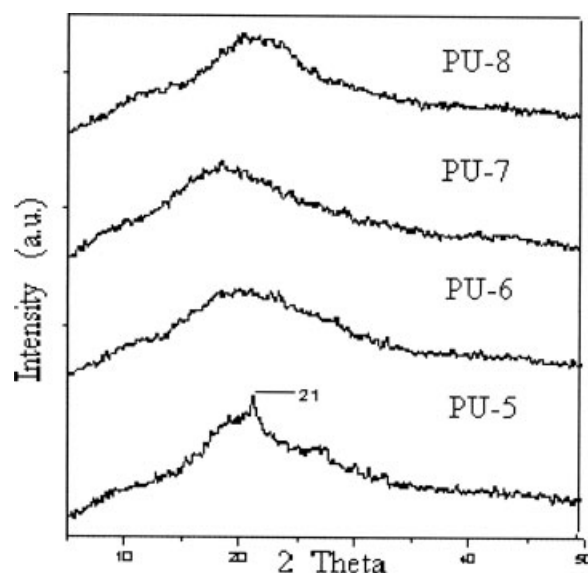


Figure 6 X-ray diffractograms of PU-5 to PU-8.

CONCLUSIONS

This article reports on the synthesis and characterization of eight novel types of PUs based on EDP and PDP with MDI, TDI, IPDI, and HDI. These PUs are soluble in polar organic solvents. Structures of the PUs were confirmed with ultraviolet, fluorescence, FTIR, and NMR methods. FTIR and NMR data showed the disappearance of both hydroxyl and isocyanate groups in the resulting PUs. TGA data indicated an onset temperature beyond 219°C, but the curves exhibited a major weight loss between 230 and 490°C. The MDI-based PUs exhibited better thermal stability than the other diisocyanate-based PUs. DSC displayed multiple endotherms that were in good agreement with the reported data. Semicrystalline and amorphous morphologies of the PUs were confirmed by XRD data.

References

- Raghu, A. V.; Jawalkar, S. S.; Gadaginamath, G. S.; Halligudi, S. B.; Aminabhavi, T. M. *J Polym Sci Part A: Polym Chem* 2006, 44, 6032.
- Raghu, A. V.; Gadaginamath, G. S.; Mathew, N. T.; Halligudi, S. B.; Aminabhavi, T. M. *J Appl Polym Sci* 2007, 106, 299.
- Raghu, A. V.; Anita, G.; Barigaddi, Y.; Gadaginamath, G. S.; Aminabhavi, T. M. *J Appl Polym Sci* 2007, 104, 81.
- Raghu, A. V.; Gadaginamath, G. S.; Mathew, N. T.; Halligudi, S. B.; Aminabhavi, T. M. *React Funct Polym* 2007, 67, 503.
- Raghu, A. V.; Gadaginamath, G. S.; Priya, M.; Seema, P.; Jeong, H. M.; Aminabhavi, T. M. *J Appl Polym Sci* 2008, 110, 2315.
- Hall, H. K., Jr. *J Macromol Sci Chem* 1988, 25, 729.
- Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem Rev* 1988, 88, 192.
- Li, X.; Jiao, Y.; Li, S. *Eur Polym J* 1991, 27, 1345.
- El-Shekeil, A. G.; Hamid, S.-A. M. K.; Ali, D. A. *Angew Makromol Chem* 1994, 195, 1877.
- Ng, S. C.; Chan, H. S. O.; Wong, K. L.; Tan, K. L.; Tan, B. T. G. *Polymer* 1988, 39, 4963.

11. El-Shekeil, A. G.; Al-Saady, H. A.; Al-Yusufy, F. A. *New Polym Mater* 1988, 5, 131.
12. Saegusa, Y.; Kuriki, M.; Nakamura, S. *Macromol Chem Phys* 1994, 195, 1877.
13. Kimura, K.; Zhuang, J. H.; Shirabe, K.; Yamashita, Y. *Polym Commun* 2003, 44, 476.
14. Adams, R.; Nulloc, J. E.; Wilson, W. C. *J Am Chem Soc* 1923, 45, 521.
15. Raghu, A. V.; Gadaginamath, G. S.; Aminabhavi, T. M. *J Appl Polym Sci* 2005, 96, 2236.
16. Raghu, A. V.; Gadaginamath, G. S.; Mallikarjuna, N. N.; Aminabhavi, T. M. *J Appl Polym Sci* 2006, 100, 576.
17. Kim, D. H.; Cho, H. I.; Zyung, T.; Do, L. M.; Ki, Bark, K. M.; Shin, G. C.; Shin, S. C. *Eur Polym J* 2002, 38, 133.
18. Evans, D.; Hicks, T. A.; Williamson, W. R. N.; Dawson, W.; Meacock, S. C. R.; Kitchen, E. A. *Eur J Med Chem* 1996, 31, 635.
19. Christenson, C. P.; Harthcock, M. A.; Meadows, M. D.; Spell, H. L.; Howard, W. L.; Creswick, M. W.; Guerra, R. E.; Turner, R. B. *J Polym Sci Part B: Polym Phys* 1986, 24, 1401.
20. Buruiana, E. C.; Olaru, M.; Simionescu, B. C. *Eur Polym J* 2002, 38, 1079.
21. Prabhakar, A.; Chattopadhyay, D. K.; Jagadeesh, B.; Raju, K. V. S. N. *J Polym Sci Part A: Polym Chem* 2005, 43, 1196.
22. Seymour, R. W.; Cooper, S. L. *Macromolecules* 1973, 6, 48.
23. Hesketh, T. R.; van Bogart, J. W. C.; Copper, S. L. *Polym Eng Sci* 1980, 20, 190.
24. Jacques, C. H. M. In *Polymer Alloys*; Klemperer, D. K.; Frisch, K. C., Eds.; Plenum: New York, 1977; p 287.
25. Koberstein, J. T.; Galambos, A. F. *Macromolecules* 1992, 25, 5618.
26. Martin, D. J.; Meijs, G.; Fgunatillake, P. A.; McCarthy, S. J.; Renvvick, G. M. *J Appl Polym Sci* 1997, 64, 803.
27. van Bogart, J. W. C.; Bluemke, D. A.; Cooper, S. L. *Polymer* 1981, 22, 1428.
28. Blackwell, J.; Lee, C. D. *J Polym Sci Polym Phys Ed* 1984, 22, 769.