

Synthesis, Characterization, and Acoustic Properties of New Soluble Polyurethanes Based on 2,2'-[1,4-Phenylenebis(nitrilomethylidene)diphenol and 2,2'-[4,4'-Methylene-di-2-methylphenylene-1,1'-bis(nitrilomethylidene)]diphenol

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ABSTRACT: Eight novel polyurethanes based on 2,2'-[1,4-phenylenebis(nitrilomethylidene)]diphenol and 2,2'-[4,4'-methylene-di-2-methylphenylene-1,1'-bis(nitrilomethylidene)]diphenol acting as hard segments with two aromatic and two aliphatic diisocyanates (4,4'-diphenylmethane diisocyanate, toluene 2,4-diisocyanate, isophorone diisocyanate, and hexamethylene diisocyanate) were prepared and characterized with Fourier transform infrared, UV spectrophotometry, fluorescence spectroscopy, ¹H-NMR and ¹³C-NMR spectroscopy,

thermogravimetric analysis, and differential thermal analysis. All the polyurethanes contained domains of semi-crystalline and amorphous structures, as indicated by X-ray diffraction. The acoustic properties and solubility parameters were calculated with the group contribution method. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 299–308, 2007

Key words: infrared spectroscopy; NMR; phase behavior; polyurethanes; thermal properties

INTRODUCTION

In our previous article,¹ we reported segmented polyurethanes (PUs) based on 2,2'-[ethane-1,2-diylbis(nitrilomethylidene)]diphenol and 2,2'-[hexane-1,6-diylbis(nitrilomethylidene)]diphenol acting as hard segments. In a continuation of that research, we present here the preparation and characterization of novel PUs based on similar diols described previously¹ through the incorporation of aromatic units instead of aliphatic units. These moieties can act as hard segments of the PU chains. Schiff base polymers continue to be interesting materials because of their outstanding film- and fiber-forming properties,² semiconductor applications,^{3,4} nonlinear optics,^{5–7} and liquid-crystalline properties,^{8–12} in addition to their thermal stability.^{13,14} A variety of different types of Schiff base polymers have been synthesized and characterized with spectroscopic techniques.^{15,16}

Generally, the polymers derived from substituted aromatic bisazomethine diols exhibit a high degree of crystallinity, which induces very low solubility. However, the utility of substituted aromatic monomers prevents the close packing of macromolecular chains, so improved solubility of the polymers is exhibited.¹⁷

As part of our continuing research into the synthesis of PUs^{1,18} and polyureas,¹⁹ we have prepared eight novel PUs by reacting 4,4'-diphenylmethane diisocyanate (MDI), toluene 2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI), and hexamethylene diisocyanate (HDI) with 2,2'-[1,4-phenylenebis(nitrilomethylidene)]diphenol (PbNMD) and 2,2'-[4,4'-methylene-di-2-methylphenylene-1,1'-bis(nitrilomethylidene)]diphenol (MdMPbNMD). The structures of PbNMD and MdMPbNMD have been confirmed with Fourier transform infrared (FTIR) spectroscopy, ¹H-NMR, and ¹³C-NMR spectral data. The synthesized PUs have been further characterized with ultraviolet-visible (UV-vis), fluorescence, FTIR, ¹H-NMR, ¹³C-NMR, differential thermal analysis (DTA)/thermogravimetric analysis (TGA), and X-ray diffraction (XRD) techniques. The results are discussed in terms of structure-morphology considerations. In addition, we have calculated the solubility parameter and acoustic properties with the group contribution method.

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EXPERIMENTAL

Materials

MDI, TDI, IPDI, dibutyltin dilaurate (DBTDL), HDI, and hexamethylenediamine were purchased from Aldrich (Milwaukee, WI) and used without further purification. Salicylaldehyde, *p*-phenylenediamine, *o*-toluidine, formalin, chloroform, benzene, diethyl ether, tetrahydrofuran, hexane, ethanol, methanol, dimethylformamide (DMF), acetic acid and hydrochloric acid were all analytical-reagent-grade samples purchased from S.D. Fine Chemicals (Mumbai, India). All the solvents were purified before use with the following standard procedures.

Characterization

The melting points 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 PU solutions of 5×10^{-4} M prepared in a spectroscopic-grade DMF solvent. Fluorescence spectra (F-2000, Hitachi, Tokyo, Japan) were also recorded in the wavelength range of 200–800 nm. FTIR spectral measurements were scanned between 400 and 4000 cm^{-1} with a Nicolet (Madison, WI) Impact 410 spectrophotometer to confirm the structures of the monomers and PU polymers in KBr pellets prepared under a hydraulic pressure of 400–600 kg/cm^2 . $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra in CDCl_3 or dimethyl sulfoxide- d_6 ($\text{DMSO-}d_6$) were recorded on a Bruker 300-MHz NMR spectrophotometer (Silberstreifen, Rheinstetten, Germany). The chemical shifts (δ) were measured with tetramethylsilane (TMS) as a reference liquid. TGA and DTA were recorded on a PerkinElmer (Shelton, CT) Diamond analyzer in the temperature interval from the ambient temperature to 1000°C under a nitrogen flow rate of 100 mL/min. A sample of about 5–10 mg was placed in a platinum crucible to record TGA and differential scanning calorimetry (DSC) spectra against 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 $K\alpha$ radiation (wavelength = 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.

Preparation of the monomers

Preparation of 4,4'-methylene bis(2-methylaniline) [MB(MA)]

To *o*-toluidine (21.4 g, 0.2 mol) in distilled water (200 mL) was slowly added hydrochloric acid (36.5%, 50 mL) under constant stirring with cooling

to 10°C. The reaction mixture was charged with a formalin (50 mL, 0.1 mol) solution with an increase in the temperature to 60°C and stirring up to 5 h. The resulting solution was neutralized with 10% sodium hydroxide, and the precipitated solid was filtered, washed with water, dried, and recrystallized from aqueous alcohol. The product yield was 26 g (57%). FTIR and NMR assignments of these compounds are given next.

FTIR (KBr): 3431, 3353, 3028, 2981, 2914, 2852, 1636, 1512, 1279, 1166, 907, 762, 633, and 560 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3 , TMS, δ): 2.20 (s, 6H, CH_3), 3.50 (br, 4H, $-\text{NH}_2$), 3.75 (s, 2H, $-\text{CH}_2-$), 6.60–6.89 (m, 6H, ArH). $^{13}\text{C-NMR}$ (CDCl_3 , TMS, δ): 17.78 (C_8), 40.68 (C_7), 115.00 (C_5), 122.87 (C_3), 127.60 (C_1), 131.27 (C_2), 132.65 (C_6), and 142.82 (C_4).

Scheme 1 displays the formation of MB(MA) based on the aforementioned spectral assignments.

Preparation of PbNMD

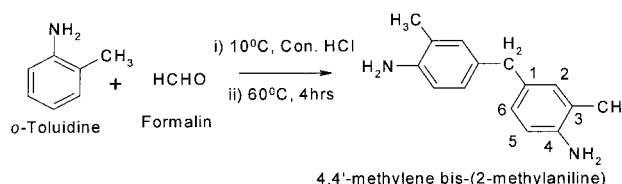
To a stirred solution of *p*-phenylenediamine (5.4 g, 0.05 mol) in hot (70°C) ethanol (50 mL) was added dropwise a solution of salicylaldehyde (12.21 g, 0.1 mol) in ethanol (75 mL). The mixture was stirred for 4 h at 70°C. After cooling, the resultant solid precipitate was filtered, washed with ethanol, and dried in air to give a yield of 12.1 g (76%) and a melting point of 164–165°C. FTIR and NMR assignments of these compounds are given next.

FTIR (KBr): 3254, 3055, 2935, 2847, 1635, 1567, 1450, 1280, 1202, 1046, 899, 779, 649, and 563 cm^{-1} . $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, TMS, δ): 6.80–7.80 (m, 12H, ArH), 9.04 (s, 2H, $-\text{CH}=\text{N}-$), and 13.07 (br, 2H, phenolic $-\text{OH}$). $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$, TMS, δ): 117.05 (C_9), 119.61 (C_2), 119.85 (C_6), 122.95 (C_4), 132.96 (C_3), 133.74 (C_5), 147.18 (C_8), 160.75 (C_1), and 163.52 (C_7).

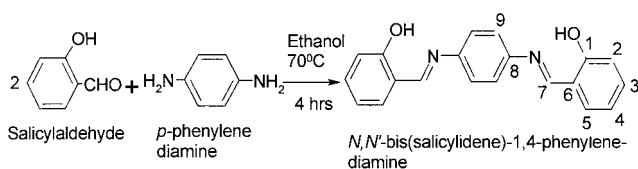
Scheme 2 displays the formation of PbNMD based on the aforementioned spectral assignments.

Preparation of MdMPbNMD

MdMPbNMD was synthesized in the usual manner, as described in Scheme 2, by the reaction of salicylaldehyde (8.68 g, 0.02 mol) with MB(MA) (5.81 g, 0.05 mol) in ethanol. Purification was accomplished by recrystallization from ethanol, giving a yield of 13.1 g



Scheme 1 Preparation of MB(MA).



Scheme 2 Preparation of PbNMD.

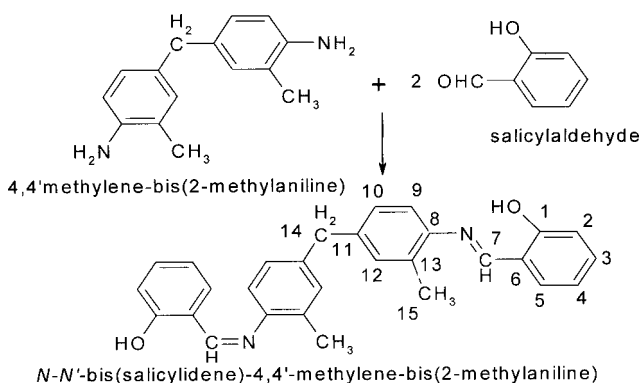
(68%) and a melting point of 75–78°C. FTIR and NMR assignments of these compounds are given next.

FTIR (KBr): 3384, 3055, 3013, 2916, 2838, 1619, 1564, 1479, 1280, 1195, 890, 762, and 639 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6 , TMS, δ): 2.32 (s, 6H, $-\text{CH}_3$), 3.94 (s, 2H, $-\text{CH}_2-$), 6.80–7.80 (m, 14H, ArH), 8.89 (s, 2H, $-\text{CH}=\text{N}-$), and 13.42 (br, 2H, phenolic $-\text{OH}$). $^{13}\text{C-NMR}$ (DMSO- d_6 , TMS, δ): 18.19 (C_{15}), 39.85 (C_{14} merged with DMSO $-\text{CH}_3$ peaks), 116.98 (C_9), 118.45 (C_2), 119.46 (C_{13}), 119.87 (C_6), 127.82 (C_{12}), 131.30 (C_4), 132.24 (C_5), 132.91 (C_{10}), 133.51 (C_3), 140.43 (C_{11}), 145.36 (C_8), 160.87 (C_1), and 162.89 (C_7).

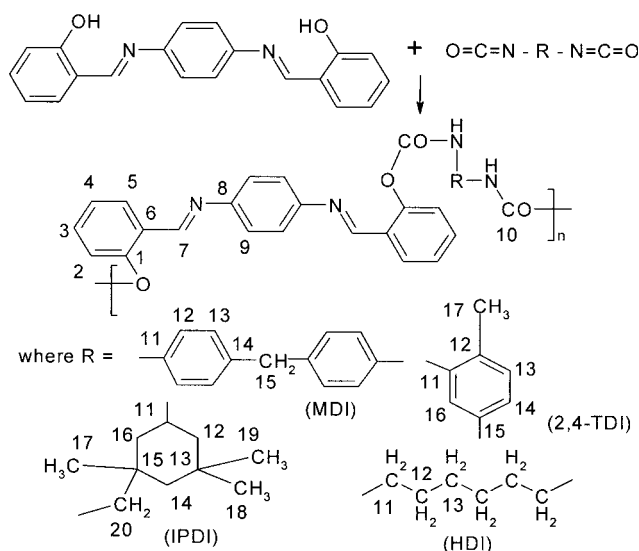
Scheme 3 displays the formation of MdMPbNMD based on the aforementioned spectral assignments.

Polymer synthesis

In a 100-mL, three-necked, round-bottom flask equipped with a magnetic stirrer, a condenser, and a dropping funnel under a dry nitrogen atmosphere, 0.005 mol of Schiff's base diol (PbNMD/MdMPbNMD) was dissolved in dry DMF (25 mL). About two drops of the DBTDL catalyst were added under a dry nitrogen atmosphere with constant stirring, and then 0.005 mol of diisocyanate (MDI/TDI/IPDI/HDI) in dry DMF (25 mL) was added for about 1 h. The reaction mixture was then stirred continuously for 10 h at 80°C and was cooled, poured into water, and filtered. The obtained yellowish polymer powder was washed with double-distilled water and dried under reduced pressure at 30°C. Chemical structures of the PUs formed are shown in Schemes 4 and 5.



Scheme 3 Preparation of MdMPbNMD.

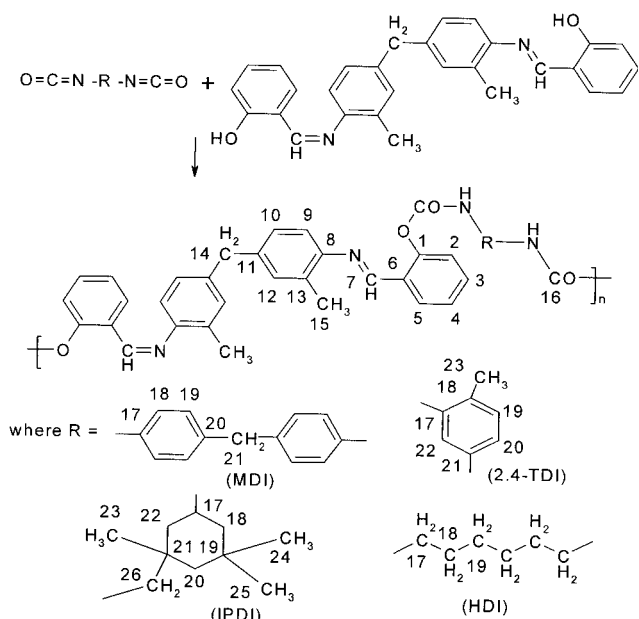


Scheme 4 Reaction scheme for the formation of PU-1 to PU-4.

Poly{2,2'-[1,4-phenylenebis(nitrilomethylidene)]diphenyl-4,4'-methylene diphenyl diurethane} (PU-1)

PU-1 was prepared with 1.26 g of MDI (0.005 mol) and 1.58 g of PbNMD (0.005 mol), which gave a yield of 2.5 g (88%). FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and TGA data are given next.

FTIR (KBr): 3353, 3043, 2927, 2849, 1710, 1638, 1600, 1453, 1235, 1051, 963, 857, 758, and 507 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6 , TMS, δ): 3.78 (s, $-\text{CH}_2-$), 6.70–8.60 (m, ArH), 9.02 (s, $-\text{CH}=\text{N}-$), and 13.06 (br, $-\text{NH}-\text{CO}-$). $^{13}\text{C-NMR}$ (DMSO- d_6 , TMS, δ): 40.24 (C_{15} , merged with DMSO $-\text{CH}_3$ carbons),



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

114.19 (C₁₂), 116.55 (C₉), 118.81 (C₂), 119.41 (C₆), 121.93 (C₄), 129.63 (C₁₃), 130.89 (C₃), 132.77 (C₁₄), 133.31 (C₅), 137.82 (C₁₁), 146.72 (C₈), 152.58 (C₁), 160.33 (C₇), and 162.80 (C₁₀).

TGA. A 10% weight loss was observed at 264°C, and a 50% weight loss was observed at 340°C. A major weight-loss transition was observed at 242–394°C with a residual weight of 16% at 800°C and an onset temperature at 237°C.

Poly{2,2'-[1,4-phenylenebis(nitrilomethylidene)]
diphenyl toluene-2,4-diurethane} (PU-2)

PU-2 was prepared with 0.84 g of TDI (0.005 mol) and 1.58 g of PbNMD (0.005 mol), which gave a yield of 2.1 g (85%). FTIR, NMR, and TGA data are given next.

FTIR (KBr): 3332, 3053, 2927, 2896, 1695, 1633, 1579, 1418, 1375, 1283, 1224, 1115, 1041, 978, 859, 760, and 645 cm⁻¹. ¹H-NMR (DMSO-*d*₆, TMS, δ): 2.25 (s, —CH₃), 6.80–7.80 (m, ArH), 9.00 (s, —CH=N—), and 13.06 (br, —NH—COO—). ¹³C-NMR (DMSO-*d*₆, TMS, δ): 17.08 (C₁₇), 114.18 (C₁₆), 116.62 (C₁₄), 118.83 (C₉), 119.18 (C₂), 119.41 (C₄), 122.53 (C₁₂), 130.20 (C₁₃), 130.66 (C₆), 132.55 (C₃), 133.32 (C₅), 146.72 (C₈, C₁₁ and C₁₅), 152.50 (C₁), 160.33 (C₇), 162.69, and 163.09 (C₁₀).

TGA. A 10% weight loss was observed at 268°C, and a 50% weight loss was observed at 328°C. A major weight-loss transition was observed at 251–357°C; the residual weight at 800°C was 5%, and the onset temperature was observed at 285°C.

Poly{2,2'-[1,4-phenylenebis(nitrilomethylidene)]
diphenyl isophorone diurethane} (PU-3)

PU-3 was prepared with 1.2 g of IPDI (0.005 mol) and 1.58 g of PbNMD (0.005 mol) with a yield of 2.5 g (89%). FTIR, NMR, and TGA data are given next.

FTIR (KBr): 3331, 3055, 2961, 2890, 1713, 1652, 1557, 1280, 1143, 1066, 883, 753, and 632 cm⁻¹. ¹H-NMR (DMSO-*d*₆, TMS, δ): 0.86 (s, —CH₃), 0.90 (s, —CH₃), 0.97 (s, —CH₃), 1.00–2.90 (m, isophorone ring and —NH—CH₂— protons), 6.80–7.80 (m, ArH), 5.55 and 5.75 (br, —NH—COO— protons), 9.02 (s, —CH=N— protons), and 13.06 (s, —NH—COO— protons). ¹³C-NMR (DMSO-*d*₆, TMS, δ): 27.61 (C₁₇), 28.98 (C₁₈), 30.78 (C₁₉), 31.55 (C₁₂), 35.04 (C₁₄), 36.12 (C₁₆), 37.92 (C₁₅), 43.18 (C₁₃), 46.65 (C₂₀), 47.08 (C₁₁), 116.62 (C₂), 118.98 (C₉), 119.17 (C₄), 121.86 (C₆), 132.55 (C₃), 133.31 (C₅), 140.81 (C₈), 157.73 (C₁), 160.69 (C₇), 162.28, and 163.08 (C₁₀).

TGA. A 10% weight loss at 280°C and a 50% weight loss at 340°C were observed. A major weight-loss transition was observed at 267–407°C, but the residual weight at 800°C was 9%, and the onset temperature was observed at 280°C.

Poly{2,2'-[1,4-phenylenebis(nitrilomethylidene)]
diphenyl hexamethylene 1,6-diurethane} (PU-4)

PU-4 was prepared with 0.82 g of HDI (0.005 mol) and 1.58 g of PbNMD (0.005 mol) with a yield of 2.2 g (91%). FTIR, NMR, and TGA data are given next.

FTIR (KBr): 3323, 3058, 2935, 2864, 1704, 1635, 1541, 1290, 1030, 840, 762, 658, and 570 cm⁻¹. ¹H-NMR (DMSO-*d*₆, TMS, δ): 1.22 (m, —NH—CH₂—CH₂—), 1.97 (m, —NH—CH₂—CH₂—CH₂—), 2.88 (m, —NH—CH₂—), 6.40–8.20 (m, ArH), 9.02 (s, —CH=N—), and 13.06 and 13.25 (br, —NH—COO—). ¹³C-NMR (DMSO-*d*₆, TMS, δ): 26.50 (C₁₂), 29.34 (C₁₃), 39.50 (C₁₁), 118.89 (C₉), 119.39 (C₂), 119.58 (C₄), 130.67 (C₆), 132.57 (C₃), 133.26 (C₅), 146.69 (C₈), 152.67 (C₁), 160.36 (C₇), and 162.68 (C₁₀). TGA. A 10% weight loss was observed at 268°C, whereas a 50% weight loss occurred at 364°C. A major weight-loss transition was seen at 235–376°C; the residual weight at 800°C was 27%, and the onset temperature was observed at 237°C.

Scheme 4 displays the chemical reactions for the formation of PUs (i.e., PU-1 to PU-4).

Poly{2,2'-[1,4-phenylenebis(nitrilomethylidene)]
diphenyl-4,4'-methylene diphenyl diurethane} (PU-5)

PU-5 was prepared with 1.26 g of MDI (0.005 mol) and 2.17 g of MdMPbNMD (0.005 mol), which gave a yield of 3.1 g (90%). FTIR, NMR, and TGA data are given next.

FTIR (KBr): 3349, 3046, 2935, 2896, 1704, 1645, 1525, 1316, 1221, 1143, 1020, 961, 847, 753, and 632 cm⁻¹. ¹H-NMR (DMSO-*d*₆, TMS, δ): 2.30 (s, —CH₃), 3.79 (s, —CH₂—), 3.92 (s, —CH₂—), 6.30–8.60 (m, ArH), 8.87 (s, —CH=N—), and 13.41 (br, —NH—COO—). ¹³C-NMR (DMSO-*d*₆, TMS, δ): 17.80 (C₁₅), 38.99 (C₁₄ and C₂₁ merged with DMSO —CH₃ peaks), 114.07 (C₁₈), 116.57 (C₉), 118.39 (C₂), 119.35 (C₆), 121.38 (C₄), 126.69 (C₁₃), 127.40 (C₁₂), 129.00 (C₁₀ and C₁₉), 130.88 (C₃), 132.49 (C₅), 134.95 (C₂₀), 137.83 (C₁₁), 140.66 (C₁₇), 144.94 (C₈), 152.59 (C₁), 160.44 (C₇), and 162.81 (C₁₆).

TGA. A 10% weight loss was observed at 308°C, whereas a 50% weight loss was observed at 372°C. A major weight-loss transition was observed at 273–407°C; the residual weight at 800°C was 23% with an onset temperature at 302°C.

Poly{2,2'-[hexane-1,6-diylbis(nitrilomethylidene)]
diphenyl toluene 2,4-diurethane} (PU-6)

PU-6 was prepared with 0.84 g of TDI (0.005 mol) and 2.17 g of MdMPbNMD (0.005 mol), which gave a yield of 2.6 g (86%). FTIR, NMR, and TGA data are given next.

FTIR (KBr): 3380, 3055, 2925, 2847, 1619, 1557, 1280, 1176, 831, 753, and 649 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6 , TMS, δ): 2.30 (s, $-\text{CH}_3$), 3.92 (s, $-\text{CH}_2-$), 6.60–7.80 (m, ArH), 8.86 (s, $-\text{CH}=\text{N}-$), and 13.40 (br, $-\text{NH}-\text{COO}-$). $^{13}\text{C-NMR}$ (DMSO- d_6 , TMS, δ): 17.79 (C_{15} and C_{23}), 39.20 (C_{14} merged with DMSO $-\text{CH}_3$ peaks), 114.22 (C_{22}), 116.57 (C_{20}), 117.75 (C_9), 118.00 (C_2), 119.03 (C_{13} and C_{18}), 119.44 (C_6), 126.70 (C_{12}), 127.40 (C_{10}), 130.28 (C_3), 131.84 (C_5), 133.08 (C_{21}), 137.79 (C_{17}), 140.02 (C_{21}), 144.89 (C_8), 152.67 (C_1), 160.47 (C_7), and 162.43 (C_{16}).

TGA. A 10% weight loss was observed at 285°C, and a 50% weight loss was observed at 370°C. A major weight-loss transition was seen at 248–388°C; the residual weight at 800°C was 24% with an onset temperature at 258°C.

Poly{2,2'-[hexane-1,6-diylbis(nitrilomethylidene)] diphenyl isophorone diurethane} (PU-7)

PU-7 was prepared with 1.2 g of IPDI (0.005 mol) and 2.17 g of MdMPbNMD (0.005 mol) with a yield of 3.15 g (93%). FTIR, NMR, and TGA results are given next.

FTIR (KBr): 3349, 3055, 2942, 1697, 1619, 1563, 1368, 1228, 1065, 961, 831, and 769 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6 , TMS, δ): 0.86 (s, $-\text{CH}_3$), 0.90 (s, $-\text{CH}_3$), 0.98 (s, $-\text{CH}_3$), 1.00–2.90 (m, isophorone ring and $-\text{NH}-\text{CH}_2-$ protons), 2.30 (s, $-\text{CH}_3$), 3.92 (s, $-\text{CH}_2-$), 5.60 (br, $-\text{NH}-\text{COO}-$), 6.80–7.70 (m, Ar-H), 8.87 (s, $-\text{CH}=\text{N}-$), and 13.41 (br, $-\text{NH}-\text{COO}-$). $^{13}\text{C-NMR}$ (DMSO- d_6 , TMS, δ): 17.80 (C_{15}), 23.25 (C_{23}), 27.63 (C_{24}), 29.93 (C_{25}), 31.56 (C_{12}), 35.05 (C_{18}), 36.15 (C_{20}), 39.00 (C_{14} merged with DMSO $-\text{CH}_3$ peaks), 42.40 (C_{21}), 46.67 (C_{22}), 47.13 (C_{17}), 53.23 (C_{26}), 116.56 (C_9), 118.38 (C_2), 119.44 (C_4), 126.69 (C_{12}), 127.40 (C_{10}), 130.87 (C_6), 132.50 (C_3), 133.08 (C_{11}), 144.90 (C_8), 157.72 (C_1), 160.46 (C_7), and 162.46 (C_{16}).

TGA. A 10% weight loss was observed at 291°C, and a 50% weight loss was observed at 335°C. A major weight-loss transition was seen at 273–382°C, and the residual weight at 800°C was 4% with an onset temperature at 303°C.

Poly{2,2'-[hexane-1,6-diylbis(nitrilomethylidene)] diphenyl hexamethylene 1,6-diurethane} (PU-8)

PU-8 was prepared with 0.82 g of HDI (0.005 mol) and 2.17 g of MdMPbNMD (0.005 mol) with a yield of 2.7 g (92%). FTIR, NMR, and TGA results are assigned as follows.

FTIR (KBr): 3332, 3055, 2935, 2847, 1723, 1626, 1567, 1280, 1186, 1020, 831, 762, and 649 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6 , TMS, δ): 1.22 (m, $-\text{NH}-\text{CH}_2-\text{CH}_2-$), 1.33 (m, $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 2.30

(s, $-\text{CH}_3$), 2.94 (m, $-\text{NH}-\text{CH}_2-$), 3.92 (s, Ar- CH_2 -Ar), 6.80–7.50 (m, ArH), 8.87 (s, $-\text{CH}=\text{N}-$), and 13.41 (s, $-\text{NH}-\text{COO}-$). $^{13}\text{C-NMR}$ (DMSO- d_6 , TMS, δ): 17.80 (C_{15}), 26.50 (C_{18}), 29.32 (C_{19}), 39.20 (C_{14} merged with DMSO CH_3 peaks), 40.22 (C_{17} merged with DMSO CH_3 peaks), 116.57 (C_9), 118.03 (C_2), 119.05 (C_{13}), 119.44 (C_6), 127.40 (C_{12}), 130.88 (C_3), 131.83 (C_5), 132.51 (C_{10}), 133.11 (C_{11}), 144.91 (C_8), 160.45 (C_1 and C_7), and 162.48 (C_{16}).

TGA. A 10% weight loss was observed at 299°C, and a 50% weight loss was observed at 344°C. A major weight-loss transition was observed at 267–363°C; the residual weight at 800°C was 13%, and the onset temperature was observed at 283°C.

Scheme 5 displays the chemical reactions for the formation of PUs (i.e., PU-5 to PU-8).

RESULTS AND DISCUSSION

Solubility

Hard-segmented PUs are insoluble in polar organic and acidic solvents.^{18,19} However, because of the presence of Schiff's base moieties in the main chain, these PUs are soluble in polar solvents such as *N'*-methyl-2-pyrrolidone, DMF, and DMSO. All the PUs are insoluble in water, acetone, methanol, chloroform, diethyl ether, tetrahydrofuran, and hexane because of more lyophobic groups on the backbone.

Spectral data

UV and fluorescence spectra of the monomers and PUs were recorded with small samples in DMF at the ambient temperature. Electronic absorption and emission spectral data for both the monomers and the PUs are listed in Table I. In the spectra of the Schiff base PUs, aromatic bands around 266–270 nm are attributed to benzene $\pi-\pi^*$ transitions.²⁰ Bands around 329–379 nm are assigned to azomethine $\pi-\pi^*$ transitions.²¹ The emissions from these monomers

TABLE I
Absorption and Emission Peaks for Different Monomers and PUs

Name	Absorption (emission) wavelength maxima (nm)
PbNMD	267 (336), 378 (423)
PU-1	267 (342), 365 (428)
PU-2	266 (333), 379 (434)
PU-3	267 (339), 375 (433)
PU-4	270 (339), 360 (439)
MdMPbNMD	266 (340), 329 (405)
PU-5	271 (349), 327 (413)
PU-6	270 (337), 332 (405)
PU-7	266 (346), 324 (419)
PU-8	268 (360), 326 (403)

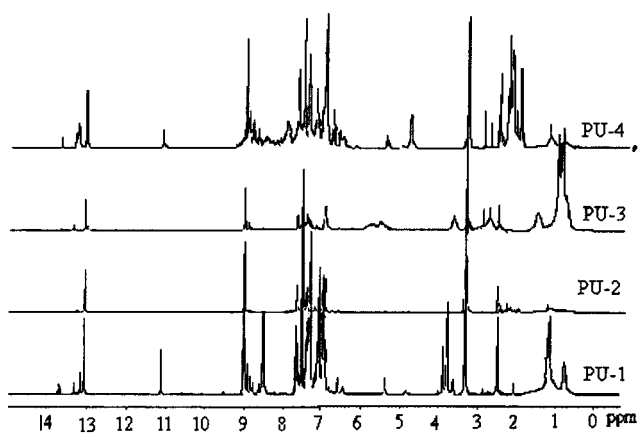


Figure 1 ^1H -NMR spectra of PU-1 to PU-4.

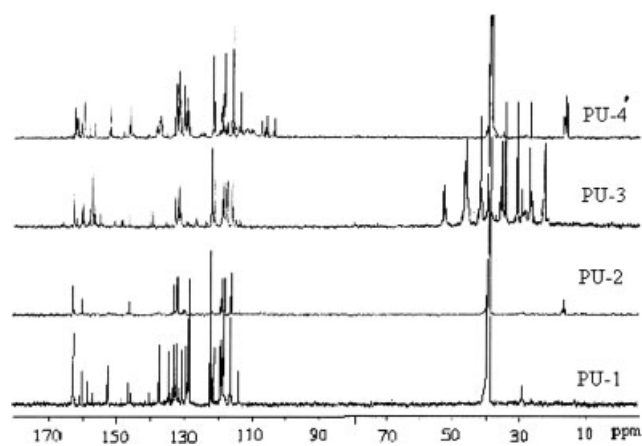


Figure 3 ^{13}C -NMR spectra of PU-1 to PU-4.

and polymers appear around 333–346 and 403–439 nm, respectively. From the absorption and emission spectra, it can be concluded that there is no significant difference in the monomers and PUs prepared.

The structures of both the monomers and the PUs have been characterized with NMR and FTIR. FTIR showed the disappearance of both the hydroxyl group (3254 and 3384 cm^{-1}) and the isocyanate group (2270 cm^{-1}) as well as the formation of several characteristic stretching vibrations due to N-H , C=O , CH=N , and C-H bonds. Hydrogen bonding in PUs is of great interest because it plays an important role²² in determining the phase segregation. In all the PUs, sharp bands appearing between 3280 and 3384 cm^{-1} are due to the presence of hydrogen-bonded N-H groups.²³ However, hydrogen-bonded carbonyl groups of urethane that merged with the Schiff base have appeared in the region of 1645 – 1619 cm^{-1} .

NMR analysis suggests the disappearance of $-\text{OH}$ and $-\text{NCO}$ groups and the formation of urethane polymer chains. ^1H -NMR spectra of PUs show characteristic signals, as displayed in Figures 1 and 2. Resonance peaks in the region of 0.86 – 3.92 ppm

correspond to methyl, methylene, and cyclohexane ring protons of the monomer as well as the PUs. Resonance peaks of $-\text{NH}-\text{COO}-$ protons of all the PUs can be seen around 13.06 – 13.41 ppm , except for the IPDI-based polymers. In IPDI-based PUs, $-\text{NH}-\text{COO}-$ protons appear at $\delta = 5.79$ – 5.95 ppm (less hydrogen-bonded) and $\delta = 13.40$ – 13.60 ppm (more hydrogen-bonded), but the resonance peaks of CH=N protons appear in the region of 8.86 – 9.02 ppm . The multiplet due to aromatic protons occurs in the region from 6.30 to 8.60 ppm .

^{13}C -NMR spectra of all the PUs show characteristic signals, as shown in Figures 3 and 4. For instance, the δ range of 17.08 – 53.23 is due to aliphatic carbons and cyclohexane ring carbons. Resonance in the region between 114.07 and 160.45 ppm is due to aromatic carbons. Peaks observed in the region from 160.33 to 162.81 ppm are due to urethane carbonyl and CH=N carbons.

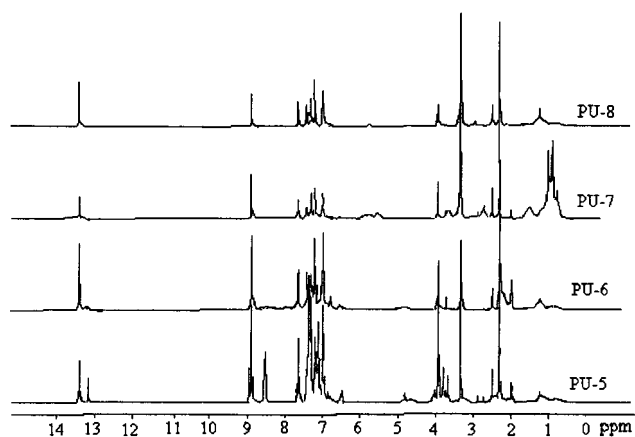


Figure 2 ^1H -NMR spectra of PU-5 to PU-8.

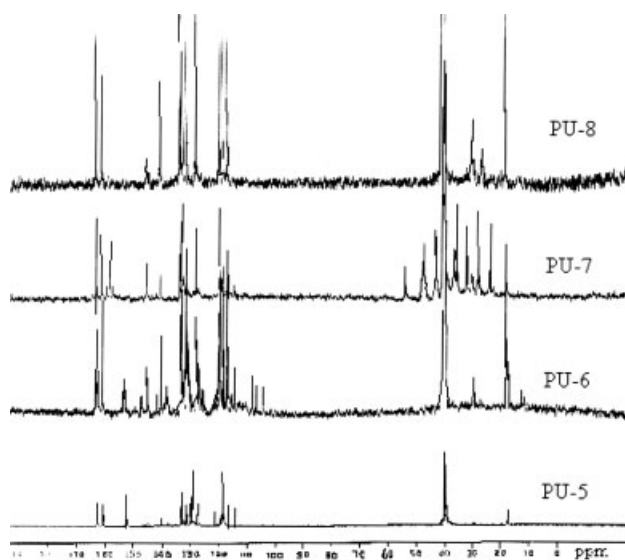


Figure 4 ^{13}C -NMR spectra of PU-5 to PU-8.

Thermal properties

DSC

DSC data are presented in Table II and displayed in Figure 5. The existence of multiple endotherms has been documented for the thermal behavior of segmented PU block copolymers.^{24–26} Koberstein and Galambos²⁷ indicated that the origin of multiple endotherms in PUs is dependent on the specimen preparation method. Martin et al.²⁸ suggested that the five endotherms observed could possibly be due to the melting of various hard-segment-length populations. van Bogart et al.²⁹ identified three endothermic transitions associated with the ordering of MDI/butanediol hard segments when subjected to the third thermal cycle. Blackwell and Lee³⁰ studied multiple melting in the MDI-based PUs that were oriented and thermally annealed. Recently, Raghu and coworkers^{18,19} observed two to five endothermic transitions associated with hard-segmented PUs and polyureas. In light of these reports, it is obvious that the melting behavior of PUs is highly dependent on the procedure adopted for their preparation. Indeed, the origins of multiple melting peaks are inherently different for materials prepared under various conditions.

In this work, we observed multiple melting phenomena in identical PUs prepared from only hard segments of the main chain. DSC data for PU-1, PU-5, PU-6, and PU-7 show three endothermic peaks, whereas those of PU-3, PU-4, and PU-8 display five endotherms. However, PU-2 exhibited four endotherms. The lowest endotherm in the region of 63–189°C is due to local restructuring of hard-segment units within the hard microdomains. However, the intermediate temperature endotherms were also observed around 209–289°C and are associated with the destruction of the long-range order of the hard-segment part of PUs. Higher temperature endotherms observed around 315–380°C could be

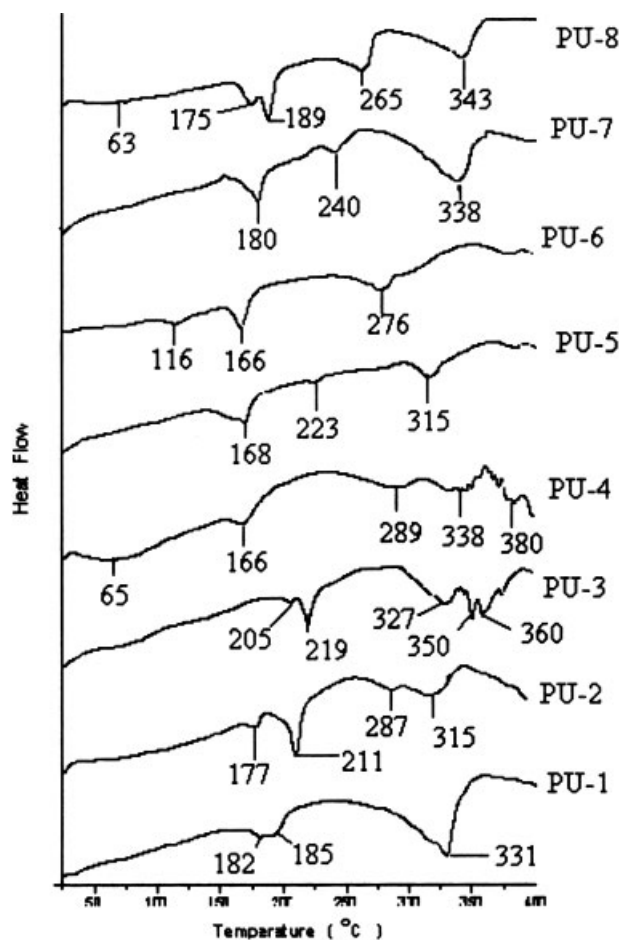


Figure 5 DSC thermograms of polymers PU-1 to PU-8.

ascribed to the melting of microcrystalline regions within the hard microdomains. The PbNMD-based PUs display higher melting temperatures than the MdMPbNMD-based PUs. This is due to the presence of a methyl-substituted benzene ring in the MdMPbNMD-based PUs.

Using the procedures suggested by van Krevelen,³¹ we have calculated the glass-transition and melting temperatures to correlate them with the experimental data, as shown in Table II. The calculated glass-transition and melting temperatures fall in the ranges of 79–138 and 293–344°C, respectively. It is thus concluded that the calculated glass-transition temperature of hard-segmented PUs is higher than 79°C and the calculated melting temperature of hard-segmented PUs is higher than 293°C. Only the calculated melting temperatures are in close agreement with the experimental values.

TGA

Weight-loss data from TGA for all the PUs are presented in the Experimental section, but the TGA curves displayed in Figure 6 suggest that 10 and

TABLE II
Different Melting Endotherms from DSC for PUs

Code	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_g^a	T_m^a
PU-1	182	185	331	138	344
PU-2	177	211, 287	315	123	337
PU-3	205, 219	327	350, 360	102	325
PU-4	65, 166	289	338, 380	91	314
PU-5	168	223	315	119	321
PU-6	116	166	276	121	312
PU-7	180	240	338	94	304
PU-8	63, 175	189, 265	343	79	293

T_1 is the lowest temperature endotherm, T_2 is the intermediate temperature endotherm, T_3 is the melting temperature endotherm, T_g is the glass-transition temperature, and T_m is the melting temperature.

^a From van Krevelen.³¹

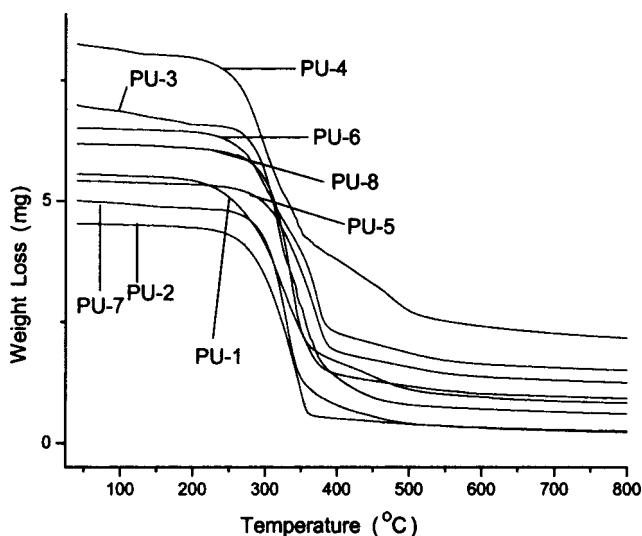


Figure 6 TGA tracings of polymers PU-1 to PU-8.

50% weight losses occurred in the temperature ranges of 264–308 and 328–378°C, respectively. PUs exhibited an onset temperature range of 237–303°C. These curves show a major weight loss between 235 and 407°C, but the residual weight remaining at 800°C varied from 4 to 24%. This variation in weight loss is due to the differences in the structures of the hard segments of the PUs. TGA data indicate that MdMPbNMD-based PUs exhibit good thermal stability in comparison with PbNMD-based PUs; this is attributed to an increase in the phenyl rings of the diols.

XRD

XRD curves of the PUs are shown in Figure 7. The crystalline form of the hard segments depends on their structure and the crystallization conditions.¹ Among the PUs synthesized, PU-3, PU-4, and PU-6 are amorphous, whereas the others are semicrystalline in nature. The semicrystallinity decreases in the order of PU-8 < PU-2 < PU-5 < PU-1 < PU-7. This unusual behavior in the nature of PUs could be due

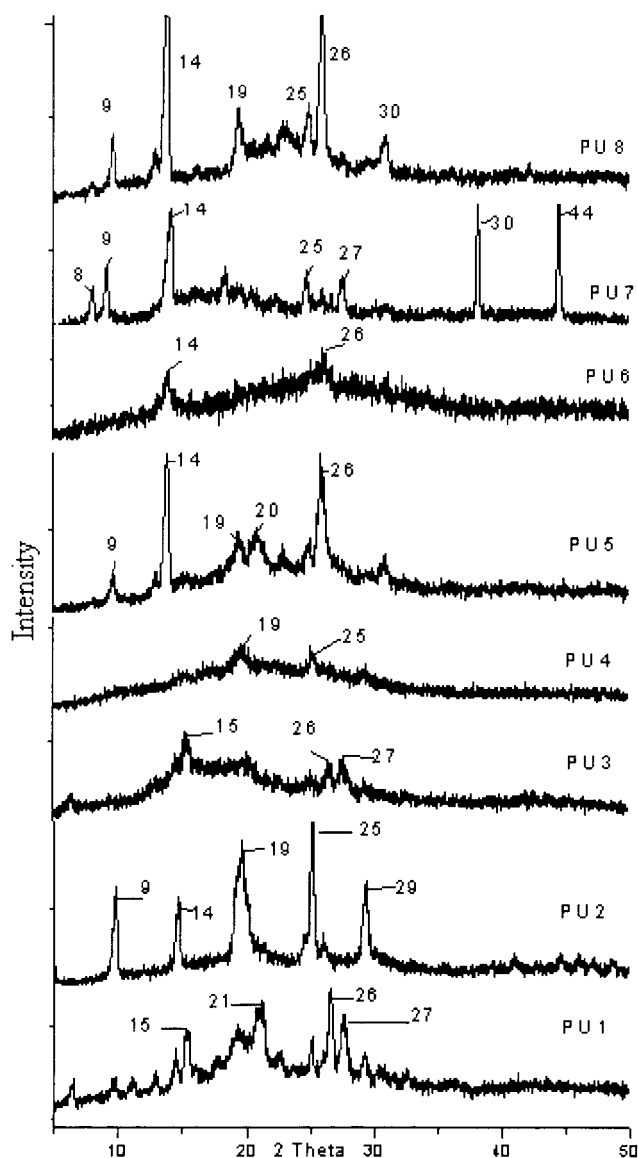


Figure 7 X-ray diffractograms of polymers PU-1 to PU-8.

to the cis and trans structural units of the Schiff base moiety and also due to the conformational variations of the diisocyanates of the PU chain.

TABLE III
Elastic Parameters of PUs Calculated with the Group Contribution Method^a

Code	U_R	U_H	K (10^{10} N/m ²)	G (10^{10} N/m ²)	E (10^{10} N/m ²)	ν
PU-1	28560	22975	3.68	0.99	2.745	0.3757
PU-2	24580	19730	3.41	0.91	2.513	0.3772
PU-3	28760	23165	5.00	1.36	3.754	0.3748
PU-4	24760	19750	3.83	0.988	2.731	0.3814
PU-5	35540	28410	4.21	1.099	3.034	0.3799
PU-6	31560	25165	3.54	0.910	2.517	0.3817
PU-7	35740	28600	5.60	1.471	4.058	0.3792
PU-8	31740	25185	4.599	1.148	3.179	0.3847

^a From van Krevelen.³¹

TABLE IV
Solubility Parameter Values of PUs

Code	Molecular weight of the PU repeat unit (g/mol)	Volume (cm ³ /mol)	Density (g/cm ³) ^a	Solubility parameter [(J/cm ³) ^{0.5}] ^a
PU-1	566	504.72	1.1214	16.88
PU-2	490	439.50	1.1149	16.83
PU-3	538	482.50	1.1150	16.91
PU-4	484	434.11	1.1149	16.88
PU-5	684	613.50	1.1149	17.76
PU-6	608	560.73	1.0843	17.44
PU-7	656	588.34	1.1150	19.10
PU-8	602	539.85	1.1149	17.98

^a From van Krevelen.³¹

Acoustic properties

The acoustic properties of PUs vary, depending on the frequency, temperature, and hydrostatic pressure. Some PUs find applications as underwater acoustic materials in addition to their use as encapsulants, housing, coatings, linings, and so forth. Thus, techniques for accurately predicting acoustic properties are important in designing and selecting polymers to assess their performances.^{32–35} The speeds of longitudinal and transverse (shear) ultrasonic waves can be predicted with two additive molar functions, U_R and U_H , which are the Rao and Hartmann functions, respectively. From these, four important elastic parameters, the bulk modulus (K), shear modulus (G), Young's modulus (E), and Poisson ratio (ν), have been calculated³¹ with eqs. (1)–(4):

$$K = \rho[U_R/V]^6 \quad (1)$$

$$G = \rho[U_H/V]^6 \quad (2)$$

$$E = 3G/[1 + G/3K] \quad (3)$$

$$\nu = (0.5 - G/3K)/(1 + G/3K) \quad (4)$$

where ρ is the density and V is the additive molar volume of the polymer, which was calculated by the group contribution method suggested by van Krevelen.³¹ The calculated results are presented in Table III. Both ρ and V are combined as additive quantities. These values are in close agreement with our previous data.¹

Solubility parameter

The calculated values (the constants were taken from van Krevelen³¹) of the solubility parameter are displayed in Table IV. These data for all the PUs range between 16.83 and 19.10 (J/cm³)^{0.5} and are comparable to the previous data.¹

CONCLUSIONS

Some novel types of PUs based on PbNMD and MdMPbNMD with MDI, 2,4-TDI, IPDI, and HDI have been synthesized. The structures of PUs have been confirmed with UV spectrophotometry, fluorescence, and FTIR spectral data in addition to NMR. All the PUs are moderately soluble in polar organic solvents but exhibit fluorescent properties. TGA data indicate an onset temperature of more than 237°C for all the PUs, but TGA curves show a major weight loss between 235 and 407°C. DSC displays multiple endotherms, which are in good agreement with the reported data. The semicrystalline and amorphous nature of the developed PUs have been confirmed with XRD experiments. MdMPbNMD-based PUs show better thermal properties than PbNMD-based PUs. The acoustic properties and solubility parameters of the PUs are comparable to earlier published results.

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