Synthesis and Characterization of Novel Polyureas Based on Benzimidazoline-2-one and Benzimidazoline-2-thione Hard Segments

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ABSTRACT: Six novel polyureas were prepared from benzimidazolin-2-one and benzimidazolin-2-thione, which acted as hard segments, with two aromatic diisocyanates (4,4′-diphenylmethane diisocyanate and toluene 2,4-diisocyanate) and one aliphatic diisocyanate (hexamethylene diisocyanate). The polymers that formed were fully characterized with Fourier transform infrared spectroscopy, ^{13}C-NMR cross-polarization/magic-angle spinning, differential scanning calorimetry, and thermogravimetry. X-ray diffraction revealed that the polymers contained crystalline and amorphous regions that varied with the nature of the backbone structures. All the polyureas were insoluble in common organic solvents, and this made it difficult to investigate their solution properties. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 576–583, 2006

Key words: heteroatom-containing polymers; morphology; solid-state structure; thermal properties

INTRODUCTION

In another article from this laboratory,[1] we studied segmented polyurethanes (PUs) based on 1,3-bis(hydroxymethyl)benzimidazolin-2-one and 1,3-bis(hydroxymethyl)benzimidazolin-2-thione hard segments. In this article, we focus on the preparation and characterization of novel types of polyureas (PURs) based on the same moieties developed previously.[1] These moieties act as hard segments of PUR chains. The benzimidazole nucleus is a widely studied heterocyclic ring because of its broad range of pharmaceutical applications.[2–14] It is well established that polymers with fully aromatic backbones generally exhibit high thermal stability, mechanical strength, and chemical resistivity to a wide range of aggressive organic solvents.[15] Of these, polybenzimidazoles have outstanding thermal stability coupled with high chemical stability.[16,17] The latter property creates problems associated with processability. Unlike the PUs developed previously,[1] this article reports on the development of novel types of PURs that are prepared with diamines instead of diols as in PUs; this causes phase separation in comparison with PUs extended with diols. Such phase separation improves the mechanical properties, such as the elongation at break, hysteresis, and stress elongation.[18]

Soluble PURs have found various applications as nonlinear optical materials,[19] gas-separation membranes,[20] and ultrafiltration membranes.[21] Aqueous PUR dispersions have been used as coatings for improved hardness and solvent resistance.[22] Therefore, it has been realized that the development of novel types of PURs derived from benzimidazolin-2-one (Bi-2-O) and benzimidazolin-2-thione (Bi-2-S) are polymers of great interest. The high nitrogen, low hydrogen, and heterocyclic contents of such materials are expected to provide thermal stability and high chemical resistivity. In this study, we prepared six different PURs with 4,4′-diphenylmethane diisocyanate (MDI), toluene 2,4-diisocyanate (TDI), and hexamethylene diisocyanate (HDI) with Bi-2-O and Bi-2-S. The prepared PURs were fully characterized with Fourier transform infrared (FTIR) spectroscopy, ^{13}C-NMR cross-polarization/magic-angle spinning (CP–MAS), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and X-ray diffraction. These results are discussed in terms of their structure–morphology correlations.

EXPERIMENTAL

Materials

MDI, TDI, and HDI were purchased from Aldrich (Milwaukee, WI). These were used without purifica-

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tion. *o*-Phenylenediamine, urea, amyl alcohol, 37% formalin, 4-methylpentanone-2, dimethyl formamide, acetic acid, and hydrochloric acid were all purchased from S.D. Fine Chemicals (Mumbai, India). All the solvents and solid *o*-phenylenediamine were purified with the standard procedures.

Preparation of Bi-2-O

A mixture of *o*-phenylenediamine (0.1 mol, 10.8 g) and urea (0.1 mol, 6.0 g) placed in a single-necked, 500-mL, round-bottom flask containing 100 mL of amyl alcohol was refluxed at 130°C for 2 h until the evolution of ammonia ceased. The separated white solid was collected and washed twice with diluted HCl and finally with distilled water. The product was recrystallized from aqueous alcohol (containing 20% water). The yield was 13.0 g (89%), and the melting point was 309–310°C (lit. 310°C). The FTIR and NMR assignments of these compounds are given next.

FTIR (KBr): 3431, 3172, 3123, 3023, 2906, 1745, 1628, 738 cm^{-1}. ^{1}H-NMR [dimethyl sulfoxide-d_6 (DMSO-d_6), tetramethylsilane (TMS), δ]: 6.91 (s, 4H, Ar H), 10.58 (s, 2H, amide NH). ^{13}C-NMR (δ): 108.92 (C_5 and C_6), 120.86 (C_4 and C_7), 130.11 (C_{1a} and C_{3b} ring junctions), 155.71 (C=O).

Preparation of Bi-2-S

A mixture of *o*-phenylenediamine (0.1 mol, 10.8 g), carbon disulfide (6.0 mL), and potassium hydroxide (0.1 mol, 5.6 g) placed in a single-necked, 500-mL, round-bottom flask containing 100 mL of absolute alcohol was refluxed at 50°C for 3 h, charcoal was added for decoloration, and the solution was filtered. To the filtrate, 100 mL of warm water was added and heated to 100°C for 30 min. After the addition of acetic acid (8 mL in 16 mL of distilled water), the colorless crystals were separated and cooled in an ice bath to complete the crystallization. The product was recrystallized from absolute alcohol. The yield was 14 g (93%), and the melting point was 300–301°C (lit. 302°C). The FTIR and NMR assignments of these compounds are given next.

FTIR (KBr): 3442, 3172, 3104, 2968, 2882, 1573, 1017, 739 cm^{-1}. ^{1}H-NMR (DMSO-d_6, TMS, δ): 7.10–7.18 (m, 4H, Ar H), 10.53 (br, 2H, amide NH). ^{13}C-NMR (δ): 109.96 (C_5 and C_6), 122.80 (C_4 and C_7), 132.68 (C_{1a} and C_{3b} ring junctions), 168.51 (C=S).

Synthesis of the polymers

The polyureas (PUR1–PUR6) were synthesized at room temperature under a nitrogen atmosphere by the polyaddition of different diisocyanates with the corresponding diamines Bi-2-O and Bi-2-S, as shown in Schemes 1 and 2. In a typical procedure, the dia-

mine was dissolved in dry dimethylformamide under nitrogen. The solution was stirred until the diamine was completely dissolved. Equal moles of diisocyanate with respect to the diamines were placed in dried 4-methylpentan-2-one. The resulting solution was stirred continuously for 3 h at room temperature. PUR was precipitated by the pouring of the reaction mixture into water, and the solid was collected by filtration. The PURs were obtained in quantitative yields.

Characterization

FTIR spectra were recorded on a PerkinElmer (Madison, WI) FTIR Nicolet instrument with KBr pellets. The ^{13}C-NMR CP–MAS experiments were performed with a Bruker (Germany) DSX-300 NMR spectrometer at the Sophisticated Instrumentation Facilities of the Indian Institute of Science (Bangalore, India; courtesy of Dr. N. Suryaprakash). Chemical shifts were measured with TMS as a reference liquid. Thermal analysis experiments were performed with a Rheometric Scientific (Surrey, UK) DSC SP and a Rheometric Scientific STA 1500. In the DSC analysis, samples of about 10 mg were used, and DSC scans were performed in a nitrogen atmosphere between 20 and 450°C at a heating rate of 10°C/min. The X-ray diffraction measurements of PURs were recorded with a Rigaku Geigerflex diffractometer equipped with Ni-filtered Cu Kα radiation (λ = 1.5418 Å; National Chemical Laboratory, Pune, India; courtesy of Dr. S. B. Halligudi). The dried polymers were spread on a sample holder, and the patterns were recorded in the range of 0–50°C at a speed of 5°C/min.

Preparation of poly[benzimidazolin-2-one,methylene-bis(4-phenylurenyl)] (PUR1)

This compound was prepared with 2.502 g of MDI (0.01 mol) and 1.34 g of Bi-2-O (0.01 mol), with a yield of 3.96 g (97%). FTIR and ^{13}C-NMR CP–MAS assignments are given next.

FTIR (cm^{-1}, KBr): 3389, 3123, 3018, 2909, 1746, 1604, 1536, 857, 746 cm^{-1}. ^{13}C-NMR CP–MAS at 6.0 kHz (ppm, external TMS): 210.0 (urenylene and Bi-2-O carbonyl carbons), 153.3 (2 Ar carbons linked to N), 147.2 (2 Ar carbons linked to N), 135.5 (2 Ar carbons linked to —CH$_2$—), 129.5 (4,5-carbons of Bi-2-O), 119.7 (4 Ar carbons ortho to —CH$_2$—), 115.4 (Ar carbons ortho to —CH$_2$—), 40.0 (Ar CH$_2$—Ar).

Preparation of poly[benzimidazolin-2-one, toluene 2,4-(bisurenyl)] (PUR2)

This compound was prepared with 1.742 g of TDI (0.01 mol) and 1.34 g of Bi-2-O (0.01 mol), with a yield of 3.177 g (97%). FTIR and ^{13}C-NMR CP–MAS assignments are given next.
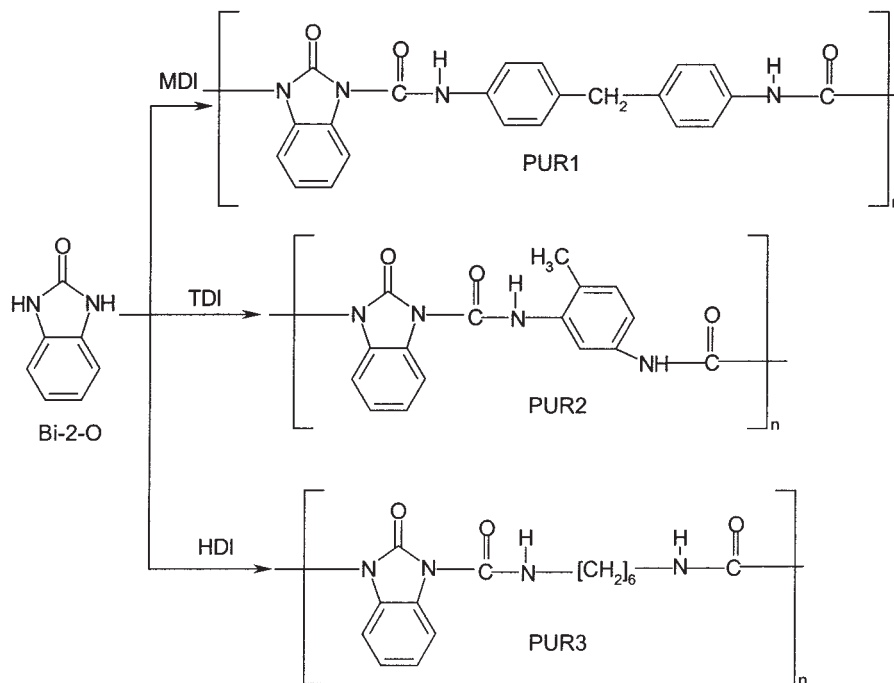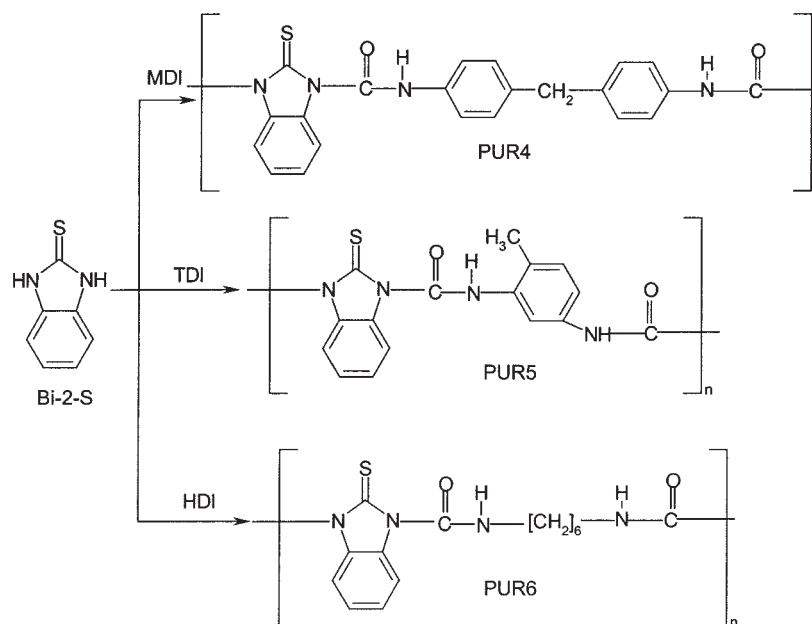
Scheme 1 Reaction pathways for the formation of PUR1 to PUR3.

FTIR (cm^{-1}, KBr): 3302, 3061, 2962, 2912, 1729, 1609, 1414, 812, 763 cm^{-1}. ^{13}C-NMR CP–MAS at 6.0 kHz (ppm, external TMS): 208.0 (urenylene carbonyl carbon) 195.0 (Bi-2-O carbonyl carbon), 153.0 (2 Ar carbons linked to N), 146.6 (2 Ar carbons linked to N), 135.3 (1 Ar carbon linked to —CH$_3$), 125.6 (4,5-Ar carbons of Bi-2-O), 114.6 (1 ortho carbon to —CH$_3$ of tolyl), 110.1 (4 Ar carbons ortho to N), 16.7 (tolyl —CH$_3$ carbon).

Preparation of poly[benzimidazolin-2-one, hexamethylene (bisurenyl)] (PUR3)

This compound was prepared with 1.682 g of HDI (0.01 mol) and 1.34 g of Bi-2-O (0.01 mol), with a yield of 3.14 g (96%). FTIR and ^{13}C-NMR CP–MAS assignments are given next.

FTIR (cm^{-1}, KBr): 3382, 2968, 2925, 1758, 1548, 757 cm^{-1}. ^{13}C-NMR CP–MAS at 8.0 kHz (ppm, external

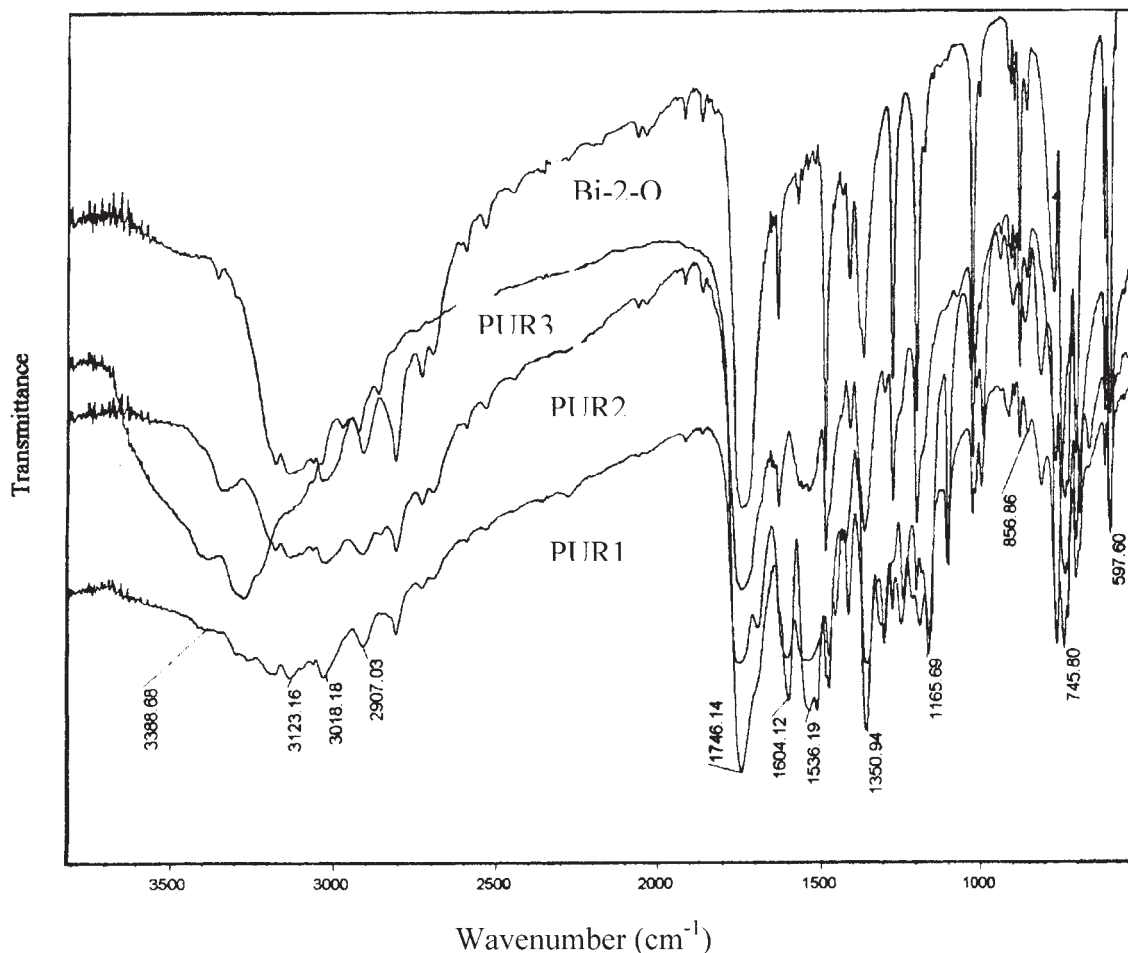**Scheme 2** Reaction pathways for the preparation of PUR4 to PUR6.

Figure 1 Representative FTIR spectra of Bi-2-O-based PURs (PUR1, PUR2, and PUR3).

TMS): 228.0 (urenylene carbonyl carbon), 218.0 (Bi-2-O carbonyl carbon), 160.2 (1 Ar carbon linked to N), 150.1 (1 Ar carbon linked to N), 126.4 (1 Ar carbon meta to N), 123.0 (1 Ar carbon meta to N), 113.6 (1 Ar carbon ortho to N), 110.9 (1 Ar carbon ortho to N), 42.0 (2 methylene carbons linked to N), 30.8 [1 C_3 carbon of —$(CH_2)_6$—], 29.2 [2 C_2 carbons of —$(CH_2)_6$—].

Scheme 1 displays the reaction pathways for the formation of PURs.

Preparation of poly[benzimidazolin-2-thione, methylene-bis (4-phenylurenyl)] (PUR4)

This compound was prepared with 2.502 g of MDI (0.01 mol) and 1.5 g of Bi-2-S (0.01 mol), with a yield of 4.08 g (98%). FTIR and ^{13}C-NMR CP–MAS assignments are given next.

FTIR (cm^{-1}, KBr): 3378, 3135, 2906, 1719, 1657, 1600, 1509, 811, 743 cm^{-1}. ^{13}C-NMR CP–MAS at 6.0 kHz (ppm, external TMS): 210.4 (urenylene carbonyl carbon), 205.6 (Bi-2-S carbonyl carbon), 168.3 (2 Ar carbons linked to N), 155.3 (2 Ar carbons linked to N), 144.8 (2 Ar carbons linked to —CH_2—), 130.4 (4,5-carbons of Bi-2-S), 124.5 (4 Ar carbons ortho to —CH_2—), 118.5 (1 Ar carbon ortho to N), 110.8 (1 Ar carbon ortho to N), 40.7 (Ar—CH_2—Ar).

Preparation of poly[benzimidazolin-2-thione, toluene 2,4-(bisurenyl)] (PUR5)

This compound was prepared with 1.742 g of TDI (0.01 mol) and 1.5 g of Bi-2-S (0.01 mol), with a yield of 3.34 g (97%). FTIR and ^{13}C-NMR CP–MAS assignments are given next.

FTIR (cm^{-1}, KBr): 3376, 3098, 3030, 2919, 1721, 1542, 813, 743 cm^{-1}. ^{13}C-NMR CP–MAS at 7.0 kHz (ppm, external TMS): 230.6 (crystalline urenylene carbonyl carbon), 224.6 (crystalline Bi-2-S carbonyl carbon), 218.0 (amorphous urenylene carbonyl carbon), 210.4 (amorphous Bi-2-S carbonyl carbon), 167.4 (2 Ar carbons linked to N of Bi-2-S), 156.4 (1 Ar carbon linked to N of tolyl), 148.6 (1 Ar carbon linked to N of tolyl), 136.3 (1 Ar carbon linked to CH_3), 123.8 (5,6-Ar carbons of B-2-S), 117 (1 ortho carbon to CH_3 of tolyl), 109.6 (4 Ar carbons ortho to N), 17.5 (tolyl CH_3 carbon).
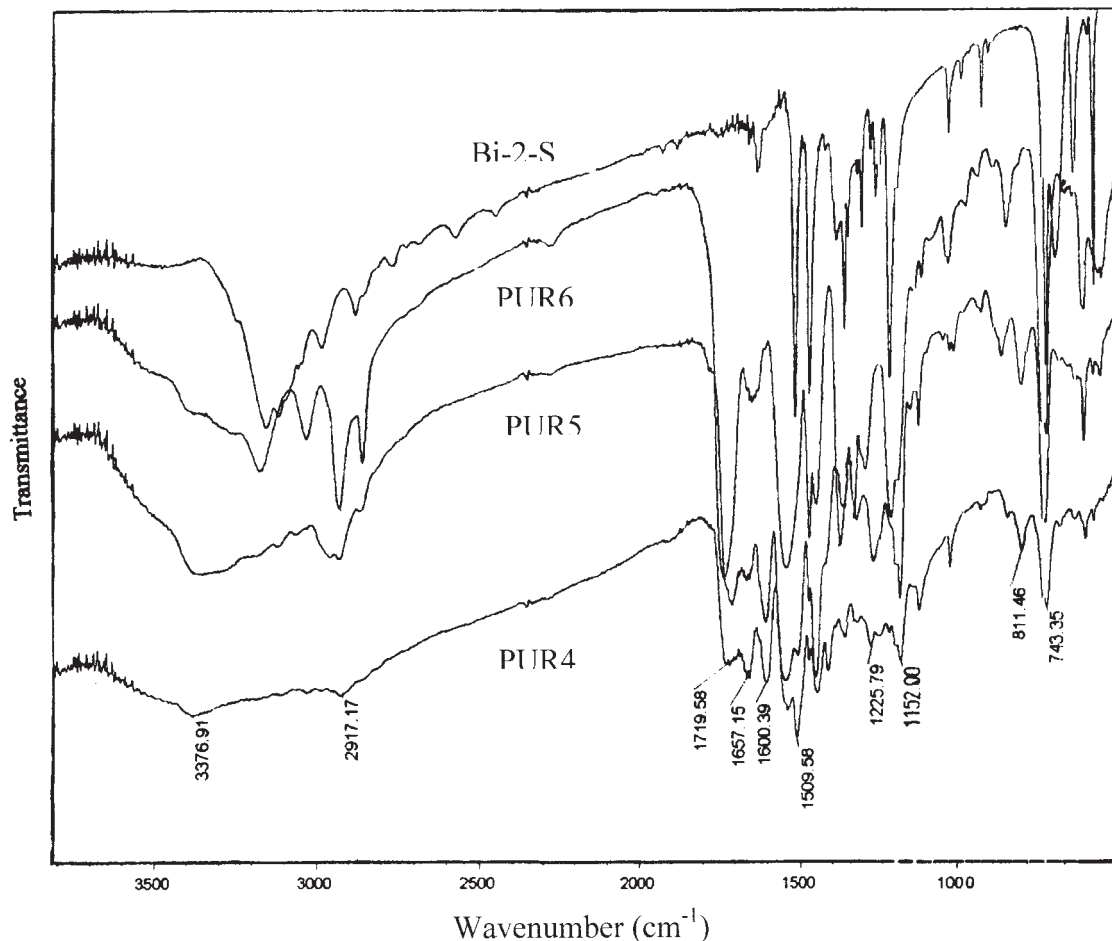
Figure 2   Representative FTIR spectra of Bi-2-S-based PURs (PUR4, PUR5, and PUR6).

Preparation of poly[benzimidazolin-2-thione, hexamethylene (bisurenyl)] (PUR6)

This compound was prepared with 1.682 g of HDI (0.01 mol) and 1.5 g of Bi-2-S (0.01 mol), with a yield of 3.24 g (98%). FTIR and ^{13}C-NMR CP–MAS assignments are given next.

FTIR (cm^{-1}, KBr): 3246, 3172, 3036, 2925, 1726, 1541, 819, 739 cm^{-1}. ^{13}C-NMR CP–MAS at 7.0 kHz (ppm, external TMS): 218.9 (urenylene carbonyl carbon), 209.0 (Bi-2-S carbonyl carbon), 166.4 (1 Ar carbon linked to N), 150.3 (1 Ar carbon linked to N), 129.9 (1 Ar carbon meta to N), 125.2 (1 Ar carbon meta to N), 116.0 (1 Ar carbon ortho to N), 110.4 (1 Ar carbon ortho to N), 42.7 [2 methylene carbons linked to N of —(CH$_2$)$_6$—], 32.3 [1 C$_3$ carbon of —(CH$_2$)$_6$—], 29.7 [2 C$_2$ carbons of —(CH$_2$)$_6$—].

Scheme 2 displays the reaction pathways for the formation of various PURs.

RESULTS AND DISCUSSION

Solubility

All the PURs were almost insoluble in polar aprotic solvents such as N,N'-methyl-2-pyrrolidone, dimeth-ylformamide, and dimethyl sulfoxide as well as acidic solvents such as m-cresol and concentrated H$_2$SO$_4$.

Spectral data

FTIR spectra of each PUR show several characteristic stretching vibrations due to the N—H, C=O and C—H bonds, as shown in Figures 1 and 2. The most significant FTIR feature of the PURs is the disappearance of N=C=O near 2300 cm^{-1}, which indicates its utilization during polymerization. Hydrogen bonding in PURs is also of great interest because it plays an important role[9] in determining the phase segregation. In all the PURs, the broad bands appearing between 3301 and 3400 cm^{-1} are due to the presence of N—H groups. However, the carbonyl groups of urea and Bi-2-O are shown in the region from 1702 to 1758 cm^{-1}.

The ^{13}C-NMR CP–MAS spectra of all the PURs (Figs. 3 and 4) show the characteristic signals. For instance, the NMR range between 16.7 and 42.7 ppm is due to aliphatic carbons, but the resonance in the region of 109.6–168.3 ppm is due to the aromatic carbons. Peaks observed between 195 and 230.6 ppm are due to Bi-2-O and urea carbonyls, respectively.
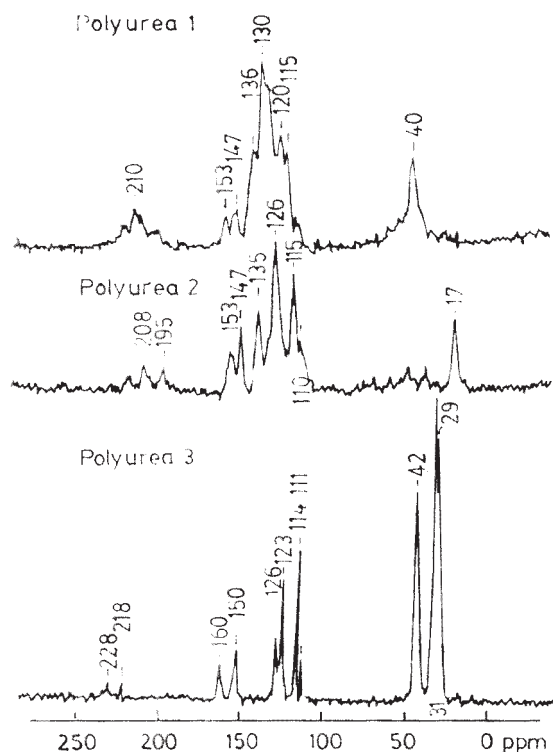
Figure 3 CP–MAS ^{13}C-NMR spectra of PUR1, PUR2, and PUR3.

Thermal properties

The thermal properties of all the PURs were evaluated with DSC and TGA. These data are given in Tables I and II, respectively. The existence of multiple endotherms is in agreement with the results of our other article.[1] In all the PURs, the glass-transition temperature is not clearly shown because of the alternative hard segments.[23] DSC data of PUR1, PUR2, and PUR5 show two endotherm peaks, whereas PUR4 and PUR6 show three endotherm peaks; on the other hand, for PUR3, the DSC curves display five endotherm peaks. The DSC studies of PUR1, PUR2, and PUR5 exhibit the lowest temperature endotherms (T_1's) at 221, 221, and 163°C because of a local restructuring of hard-segment units within the hard microdomains and destruction of the long-range order of an unspecified nature. Higher (or intermediate) temperature endotherms (T_2's) observed at 301, 283, and 296°C, respectively, can be ascribed to the melting of microcrystalline regions within the hard microdomains. In PUR4 and PUR6, T_1's observed at 160 and 130°C are due to local restructuring of the hard-segment units within the hard microdomains. The intermediate temperature endotherm (T_2) observed at 269 and 235°C is related to the melting of microcrystalline regions within the hard microdomains. A higher melting temperature (T_3) has been observed at 319 and 319°C, respectively. In PUR3, T_1 shows two small peaks at 179 and 205°C due
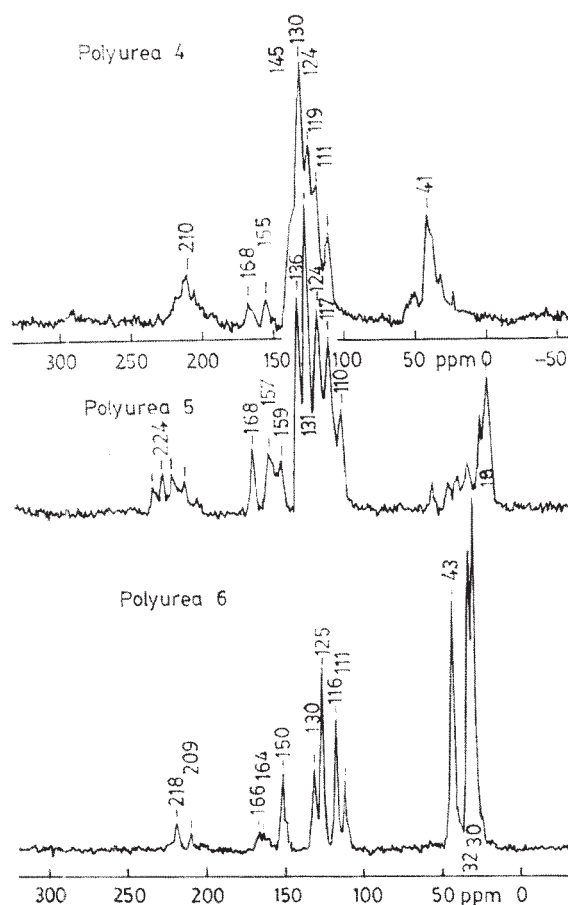

Figure 4 CP–MAS ^{13}C-NMR spectra of PUR4, PUR5, and PUR6.

to local restructuring of the hard-segment units within the hard microdomains, whereas T_2 displays two peaks, one at 261 and another at 300°C. The melting of microcrystalline regions within the hard microdomains (T_3) can be observed at 363°C.
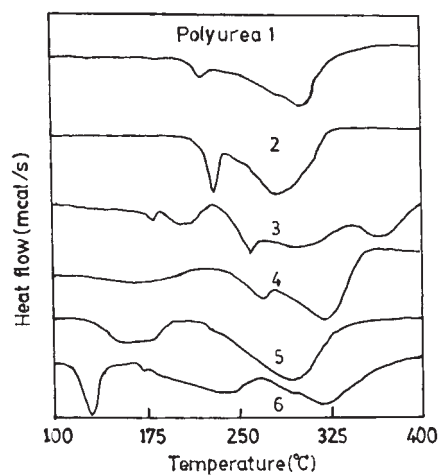

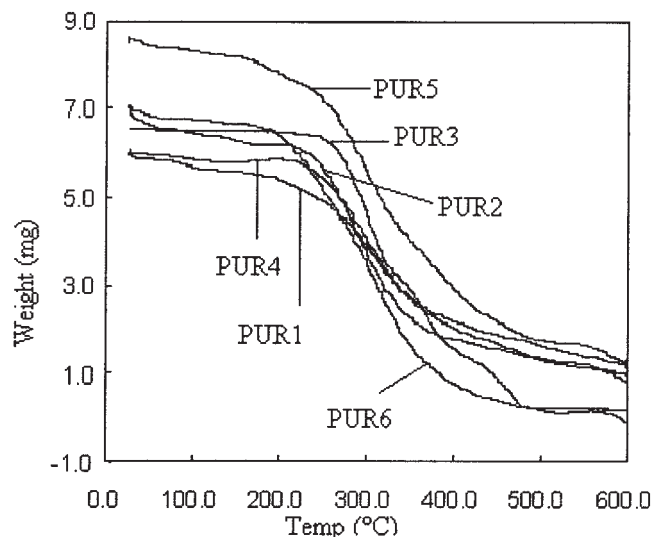**Figure 5** DSC thermograms of PUR1 to PUR6.

Figure 6   TGA tracings of PUR1 to PUR6.

TABLE II
Thermal Properties of PURs Measured by TGA

Polymer	Decomposition temperature (°C) $T_i{}^a$	$T_{50}{}^b$	Major weight-loss transition (°C)	RW at 600°C (%)^c
PUR1	192	331	192–363	15
PUR2	225	302	225–357	14
PUR3	149	334	149–338	04
PUR4	178	332	178–402	12
PUR5	184	336	184–425	15
PUR6	194	301	194–371	01

^{a} Temperature at which 0% weight loss was observed by TGA.
^{b} Temperature at which 50% weight loss occurred in TGA.
^{c} Residual weight observed by TGA at 600°C in N_2.

The weight-loss data from TGA for all the PURs are presented in Table II. These results suggest that zero weight loss occurs at 155°C, whereas the curves show a major weight loss between 155 and 455°C. The residual weight remaining at 600°C is about 1–25%. This variation in the weight loss is due to the differences in the structure of the hard segments in PURs. In PUR1, the weight loss begins at 192°C, but the major weight losses occur around 192 and 363°C. In PUR2, the weight loss begins at 225°C, but the major weight loss occurs around 225–357°C. In PUR3, the weight loss begins at 155°C, whereas the major weight loss occurs around 155–338°C. In PUR4, the weight loss begins at 178°C, and the major weight loss occurs around 178–402°C. In PUR5, the weight loss begins at 184°C, with the major weight loss occurring around 184–425°C. In PUR6, the weight loss begins at 194°C, but the major weight loss occurs in the range of 194–371°C.

X-ray diffraction data

The X-ray diffraction curves of the polymers are shown in Figure 7. All the PURs are amorphous, prob-

ably because of the presence of heterocyclic moieties such as the benzimidazole group and aromatic structures of the main PUR chain, which might limit the molecular mobility of the PURs.

The texture and anisotropic nature of the PURs were studied with a Euromax polarizing microscope equipped with a Linkem HFS91 heating stage and a TP-93 temperature programmer. The anisotropic behavior was observed via heating from the ambient temperature to 250°C and cooling at a rate of 5°C/min. None of the PURs studied exhibited any anisotropic behaviors.

CONCLUSIONS

A novel approach to the preparation of chemically resistant PURs has been presented. The direct polyaddition of different diisocyanates to Bi-2-O and Bi-2-S
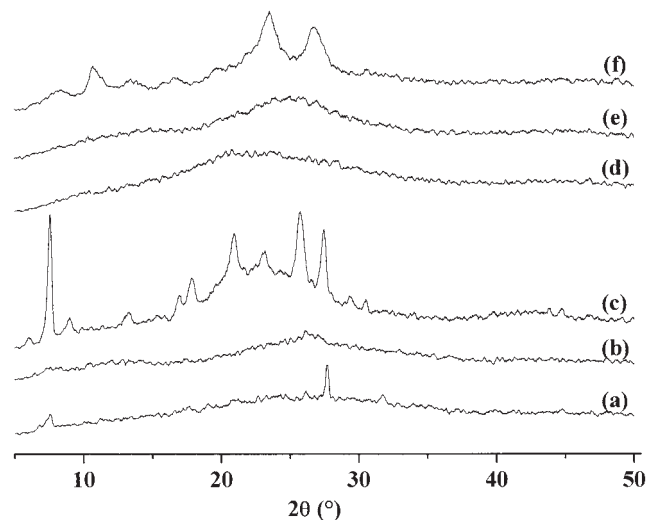
TABLE I
Different Melting Endotherms from DSC

	T_1(°C)	T_2(°C)	T_3(°C)
PUR1	—	221	301
PUR2	—	231	283
PUR3	179	205,261	300,363
PUR4	160	269	319
PUR5	163	296	—
PUR6	130	235	319

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

Figure 7   X-ray diffractograms of (a) PUR1, (b) PUR2, (c) PUR3, (d) PUR4, (e) PUR5, and PUR6 (f).

led to a series of PURs with high yields (up to 97%). The structures of the PURs were confirmed with FTIR and ^{13}C-NMR CP–MAS spectral studies. FTIR showed intermolecular hydrogen bonding between NH and CO, which suggested the insolubility of the PURs. The DSC data showed different endothermic peaks due to the presence of alternative hard segments. These were in good agreement with the reported data. TGA studies indicated that all the PURs were stable up to 149°C, whereas the curves showed major weight loss between 149 and 425°C. The amorphous nature of the PURs was confirmed by X-ray diffraction data.

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