Synthesis and Characterization of Novel Polyurethanes Based on 1,3-Bis(hydroxymethyl) Benzimidazolin-2-one and 1,3-Bis(hydroxymethyl) Benzimidazolin-2-thione Hard Segments*

A. V. Raghu, G. S. Gadaginamath, Tejraj M. Aminabhavi

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

ABSTRACT: Novel polyurethanes (PUs) based on 1,3-bis(hydroxymethyl) benzimidazolin-2-one and 1,3-bis(hydroxymethyl) benzimidazolin-2-thione as hard segments with two aromatic diisocyanates, viz., 4,4'-diphenylmethane diisocyanate and toluene 2,4-diisocyanate, were prepared. Polymer structures were established by Fourier transform infrared and nuclear magnetic resonance spectroscopy. Morphology of the PUs was studied by differential scanning calorimetry and thermogravimetry. All PUs contain domains of crystalline and amorphous structures as indicated by X-ray diffraction experiments. Furthermore, polymers were insoluble in the majority of organic solvents and, hence, their solution characterization was not possible. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2236–2244, 2005

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

INTRODUCTION

Polyurethanes (PUs) are segmented copolymers consisting of soft segment domains derived from a polyol monomer and hard segment domains derived from a diisocyanate and a chain extender.[1] The hard segment domains, dispersing in the soft matrix, act as physical junction points. In conventional PUs, the soft segment is a polyether or polyester polyol, while hard segments contain many aromatic compounds. In the earlier literature, innumerable types of PUs based on number of polyols and diisocyanates were prepared and studied for different applications.[2–6] Several investigations have reported the novel type of PUs based on nonpolar macromolecular polyols such as polyisobutylene, polybutadiene, and *cis*-polyisoprene polyols.[7–9] However, in such nonpolar polyol-based PUs, there is no establishment of hydrogen bonding between soft segments and hard segments, since hydrogen bonding, as well as other interactions, is merely confined to hard segment domains. As a result, segmented PU copolymers exhibit more complete microphase separation than those containing polar polyols. In addition, high tensile strength, superior water-resistant properties, and high modulus are some characteristics[8] of such PUs. Thermodynamic interactions in such systems are considered negligible and, hence, such polymers could serve as model compounds of interest for theoretical understanding of structure–property relationships. Earlier, Higgins and Marvel[10] carried out extensive investigations on the origin of multiple melting endotherms in hard and block segments of PUs using differential scanning calorimetry (DSC). They suggested that phase separation of hard segments could be due to the presence of hard block segments of PU. Several authors[11–13] have suggested that crystalline behavior and morphology of phase segmented PUs is quite complicated due to multiple transitions, as a result of complicated morphology. These systems are sensitive to thermal history.

In this paper, we focus on the development of novel PUs based on 1,3-bis(hydroxymethyl) benzimidazolin-2-one [1,3-B[*HM*]B-2-O], and 1,3-bis(hydroxymethyl) benzimidazolin-2-thione [1,3-B[*HM*]B-2-S] (as hard segments) with 4,4'-diphenylmethane diisocyanate (MDI), toluene 2,4-diisocyanate (TDI), and hexamethylene diisocyanate (HDI). Benzimidazoles are well-known heterocyclic compounds used widely as pharmaceuticals.[14–16] On the other hand, poly(benzimidazoles) have acquired a special place as thermally stable polymers, having very high glass transition temperatures, in addition to exhibiting outstanding chemi-

---

cal stability and mechanical strength properties.[17] Moreover, in the present context, high nitrogen, low hydrogen, and heterocycle contents of such materials are expected to provide good thermal stability and low chemical resistivity. To further contribute in this area, we have prepared six different PUs using MDI, TDI, and HDI with 1,3-bis(hydroxy methyl) benzimidazolin-2-one and 1,3-bis(hydroxy methyl) benzimidazolin-2-thione. The structures of 1,3-bis(hydroxymethyl) benzimidazolin-2-one and 1,3-bis(hydroxymethyl) benzimidazolin-2-thione were confirmed by FTIR, ^{1}H-NMR, and ^{13}C-NMR spectral data. The polyurethanes prepared from the above monomers were characterized by Fourier transform infrared (FTIR) spectroscopy, ^{13}C-NMR, DSC, thermogravimetry (TGA), and X-ray diffraction. The results of this study are discussed in terms of their structure–morphology based considerations.

EXPERIMENTAL

Materials

MDI, TDI, and HDI were purchased from Aldrich (Milwaukee, WI) and were used without further purification. 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 solvents and the solid o-phenylenediamine were purified before use by following the standard procedures.

Preparation of benzimidazolin-2-one

A mixture of o-phenylenediamine (0.1 mol, 10.8 g) and urea (0.1 mol, 6.0 g) taken in a single-neck 500-mL-capacity 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 dil. HCl and finally with distilled water. The product was recrystallized from aqueous alcohol (containing 20% water). Yield: 13.0 g (89%); m.p. 309–310 °C (lit. 310 °C). FTIR and NMR assignments of these compounds are given below.

FTIR (KBr): 3431, 3172, 3123, 3023, 2906, 1745, 1628, and 738 cm^{-1}.

^{1}H-NMR (DMSO-d_6, TMS): δ 6.91(s, 4H, Ar H), and 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) and 155.71 (C = O carbon).

Preparation of 1,3-bis (hydroxymethyl) benzimidazolin-2-one

Benzimidazolin-2-one (0.1 mol, 13.4 g) and 37% formalin (1 mol, 30 mL) taken in a single-neck 500-mL-

capacity round-bottom flask containing 100 mL distilled water were heated to 100 °C under reflux for 1 h. The contents were filtered and diluted with distilled water. The separated solid was recrystallized from distilled water. Yield: 18 g, (92%); m.p. 164–165 °C (lit. 165 °C). FTIR and NMR assignments of these compounds are given below.

FTIR (KBr): 3407, 3357, 3116, 2999, 2956, 2919, 1672, 1622, and 764 cm^{-1}.

^{1}H-NMR (DMSO-d_6, TMS): δ 5.22 (s, 2H, -CH$_2$-O-), 5.24 (s, 2H, -CH$_2$-O-), 6.3–7.26 (m, 4H, Ar H), and 10.54 (s, 2H, -OH).

^{13}C-NMR: δ 63.99 (2C of –CH$_2$OH), 109.12 (C_5 and C_6), 121.77 (C_4 and C_7), 128.87 (C_{1a} and C_{3b} ring junctions), and 153.09 (C = O carbon).

Preparation of benzimidazolin-2-thione

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) taken in a single-neck 500-mL-capacity 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 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 crystallization. The product was recrystallized from absolute alcohol. Yield: 14 g (93%); m.p. 300–301 °C (lit. 302 °C). FTIR and NMR assignments of these compounds are given below.

FTIR (KBr): 3442, 3172, 3104, 2968, 2882, 1573, 1017, and 739 cm^{-1}.

^{1}H-NMR (DMSO-d_6, TMS): δ 7.10–7.18 (m, 4H, Ar H), and 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), and 168.51 (C = S carbon).

Preparation of 1,3-bis(hydroxymethyl) benzimidazolin-2-thione

Benzimidazolin-2-thione (0.1 mol, 15.0 g) and 37% formalin (1 mol, 30 mL) taken in a single-neck 500-mL-capacity round-bottom flask containing 100 mL of distilled water were heated under reflux for 1 h and cooled. The separated colored solid was washed repeatedly with distilled water and filtered and the solid was recrystallized from distilled water. Yield: 19 g (92%); m.p. 158–159 °C. (lit. 160 °C). FTIR and NMR assignments of these compounds are given below.

FTIR (KBr): 3462, 3295, 3165, 2974, 2962, 1609, 1066, and 738 cm^{-1}.

^{1}H-NMR (DMSO-d_6, TMS): δ 5.69 (s, 2H, -CH$_2$-O-), 5.71 (s, 2H, -CH$_2$-O-), 6.61–7.52 (m, 4H, Ar H), and 12.78 (br, 2H, -OH).

^{13}C-NMR: δ 67.53 (2C of –CH$_2$OH), 110.60 (C$_5$ and C$_6$), 123.48 (C$_4$ and C$_7$), 131.57 (C$_{1a}$ and C$_{3b}$ ring junctions), and 169.46 (C = S carbon).

Polymer synthesis

The general synthetic procedure to prepare PUs is well known.[18] However, the PUs prepared in this study are novel and were obtained in quantitative yields. Since highly heterocyclic rings are incorporated, their physical and thermal properties were substantially different than those containing aliphatic chains. The typical general procedure used to synthesize PUs involves reaction in a three-neck 100-mL round-bottom flask equipped with a mechanical stirrer, condenser, and a dropping funnel. The respective diols, viz., 1,3-B[*HM*]B-2-O and 1,3-B[*HM*]B-2-S, were dissolved in dry DMF under nitrogen atmosphere with constant stirring. Then, an equimolar quantity of diisocyanates (MDI, TDI, or HDI) with respect to each diol taken in dry 4-methylpentanone-2 was added to this solution over a period of 1 h. The reaction mixture was heated for 2.5 h at 115 °C to obtain the solid. The mixture was stirred continuously for 3 h, cooled, poured into water, and then filtered. The white solid polymer obtained was chopped in a blender, washed with water, and dried under reduced pressure at 90 °C.

Characterization

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

### Preparation of poly[1,3-bis(methylene)benzimidazolin-2-one, methylene-bis(4-phenylcarbamate)] (PU1)

PU1 was prepared by taking 2.502 g of MDI (0.01 mol) and 1.94 g of 1,3-B[*HM*]B-2-O (0.01 mol), with a yield of 4.3 g (96.8%). The FTIR and NMR assignments are given below.

FTIR (KBr): 3401, 3129, 3061, 2956, 2919, 1709, 1604, 1542, 813, and 764 cm^{-1}.

^{13}C-NMR CPMAS (external TMS): 205.5, 153.6, 136.4, 128.9, 122.5, 109.2, 64.0, and 40.3 ppm.

Preparation of poly[1,3-bis(methylene) benzimidazolin-2-one, toluene 2,4-(biscarbamate)] (PU2)

PU2 was prepared by taking 1.742 g of TDI (0.01 mol) and 1.94 g of 1,3-B[*HM*]B-2-O (0.01 mol), with a yield
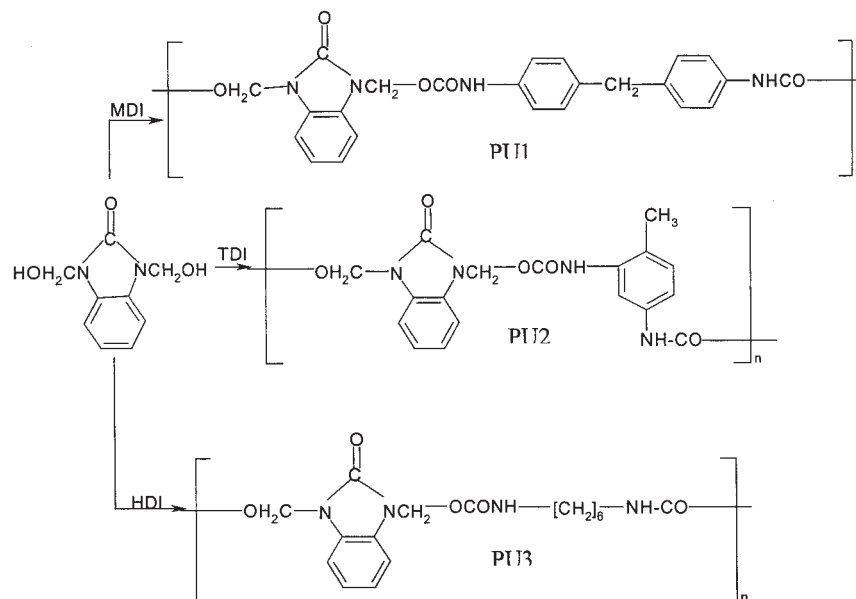
Scheme 1   Reaction pathways for the formation of PUs, i.e., PU1 to PU3.
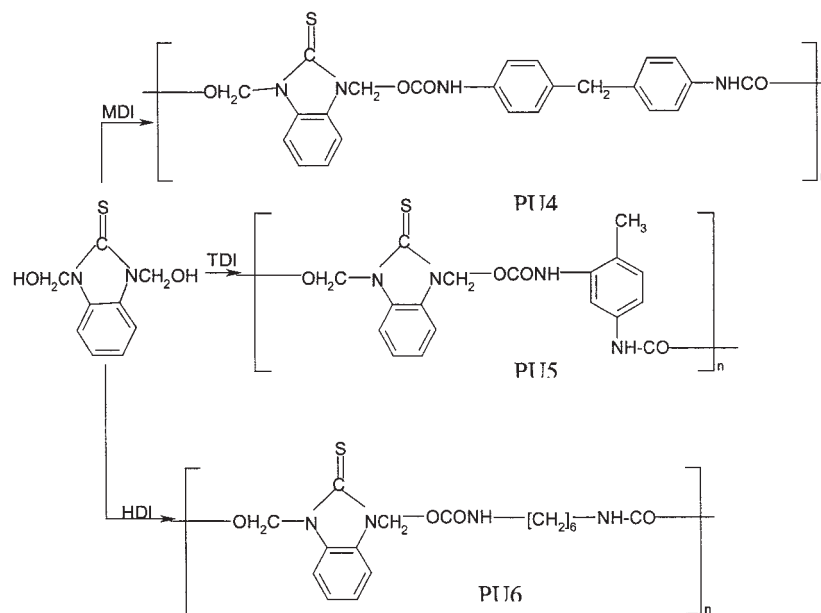
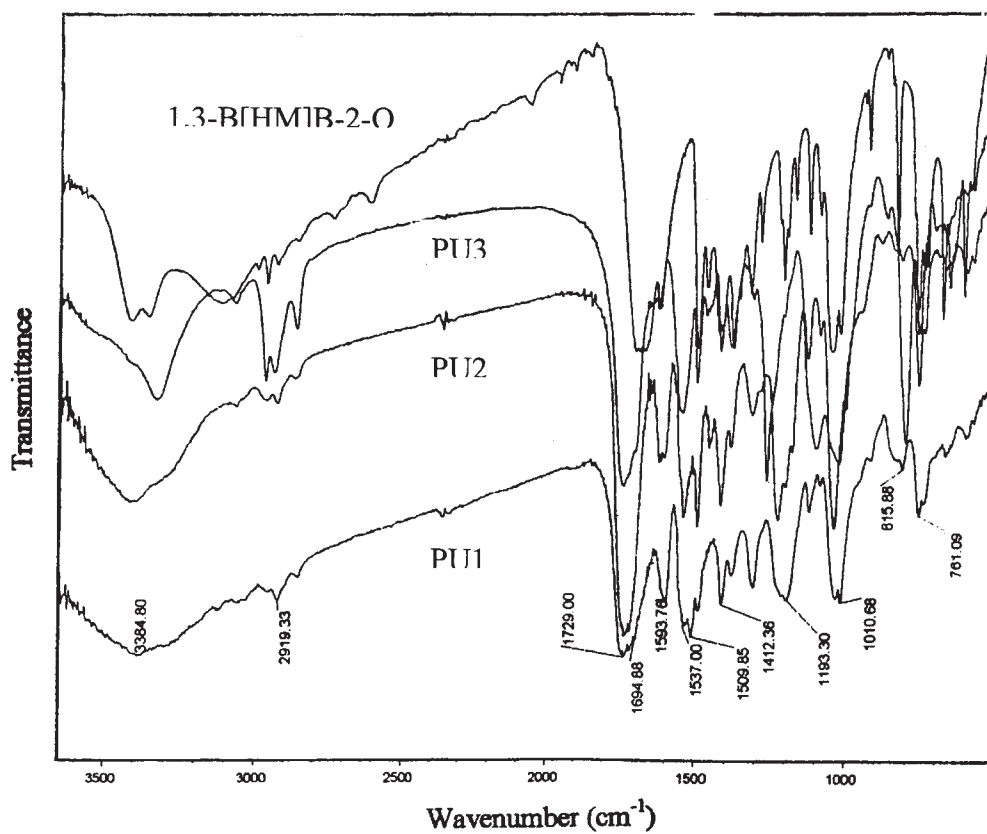Scheme 2 Reaction pathways for the preparation of PUs, i.e., PU4 to PU6.

Figure 1 Representative FTIR spectra of 1,3-bis(hydroxymethyl) benzimidazolin-2-one based PUs (PU1, PU2, and PU3).
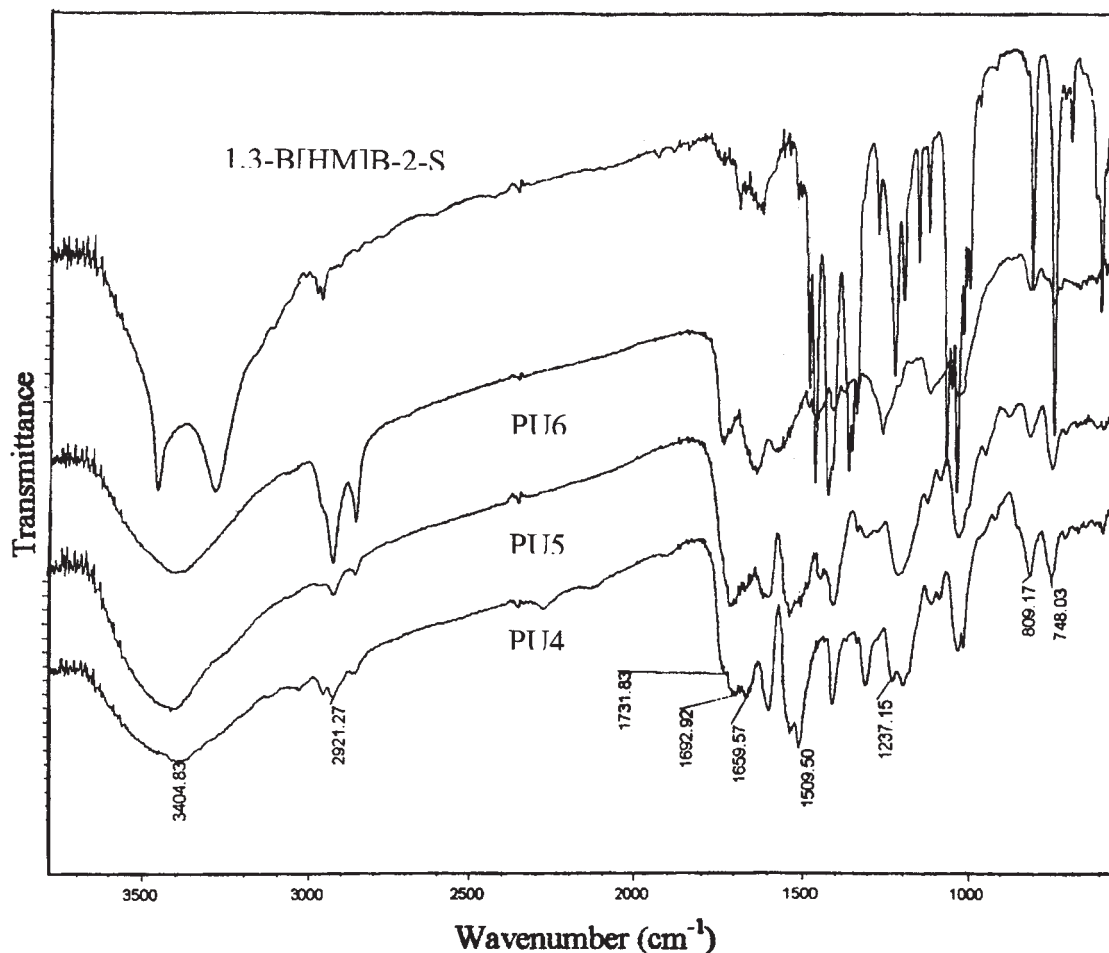
Figure 2 Representative FTIR spectra of 1,3-bis(hydroxymethyl) benzimidazolin-2-thione based PUs (PU4, PU5, and PU6).

of 3.757 g (98%). The FTIR and NMR assignments are given below.

FTIR (KBr): 3302, 3061, 2962, 2912, 1729, 1609, 1414, 812, and 763 cm^{-1}.

^{13}C-NMR CPMAS (external TMS): 202.5, 153.6, 136.6, 128.2, 122.2, 109.4, 64.4, and 16.8 ppm.

Preparation of poly[1,3-bis(methylene) benzimidazolin-2-one, hexamethylene (biscarbamate)] (PU3)

PU3 was prepared by taking 1.682 g of HDI (0.01 mol) and 1.94 g of 1,3-B[*HM*]B-2-O (0.01 mol), with a yield of 3.737 g (97%). The FTIR and NMR assignments are given below.

FTIR (KBr): 3327, 3067, 2956, 2958, 1746, 1542, 1419, and 795 cm^{-1}.

^{13}C-NMR CPMAS (external TMS): 230.0, 217.7, 186.0, 156.2, 153.4, 128.2, 121.5, 114.9, 110.4, 64.7, 48.3, 41.6, and 28.3 ppm.

Scheme 1 displays the chemical reaction pathways for the formation of different PUs mentioned above.

Preparation of poly[1,3-bis(methylene) benzimidazolin-2-thione, methylene-bis (4-phenylcarbamate)] (PU4)

PU4 was prepared by taking 2.502 g MDI (0.01 mol) and 2.10 g of 1,3-B[*HM*]B-2-S (0.01 mol) with a yield of 4.3 g (97%). The FTIR and NMR assignments are given below.

FTIR (KBr): 3395, 3030, 2962, 2926, 1702, 1653, 1597, 814, and 746 cm$-^{-1}$.

^{13}C-NMR CPMAS (external TMS): 266.3, 153.9, 136.2, 129.3, 118.7, 111.7, 118.7, 52.6, and 40.8 ppm.

Preparation of poly[1,3-bis(methylene) benzimidazolin-2-thione, toluene 2,4-(biscarbamate)] (PU5)

PU5 was prepared by taking 1.742 g of TDI (0.01 mol) and 2.10 g of 1,3-B[*HM*]B-2-S (0.01 mol) with a yield of 3.757 g (98%). The FTIR and NMR assignments are given below.

FTIR (KBr): 3401, 2919, 2851, 1704, 1597, 814, and 746 cm^{-1}.

^{13}C-NMR CPMAS (external TMS): 237.4, 153.7, 136.7, 131.2, 124.0, 119.1, 111.7, 68.7, and 17.9 ppm.

Preparation of poly[1,3-bis(methylene) benzimidazolin-2-thione, hexamethylene (biscarbamate)] (PU6)

PU6 was prepared by taking 1.682 g of HDI (0.01 mol) and 2.10 g of 1,3-B[*HM*]B-2-S (0.01 mol) with a yield of 3.737 g (97%). The FTIR and NMR assignments are given below.

FTIR (KBr): 3401, 2919, 2851, 1704, 1597, 814, and 746 cm^{-1}.

^{13}C-NMR CPMAS (external TMS): 237.4, 153.7, 136.7, 131.2, 124.0, 119.1, 111.7, 68.7, and 17.9 ppm.

Scheme 2 displays the chemical reaction pathways for the formation of different PUs.

RESULTS AND DISCUSSION

Solubility properties

All PUs were insoluble in polar aprotic solvents such as *N*-methyl-2-pyrrolidone, dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO) as well as acidic solvents like *m*-cresol and con. H_2SO_4.

Spectral data

FTIR of each PU shows several characteristic stretching vibration modes due to N-H, C = O, and C-H bonds, as shown in Figures 1 and 2. The most significant feature of FTIR of the PUs is the disappearance of N = C = O near 2300 cm^{-1}, which indicates its utilization during polymerization. Hydrogen bonding in PUs is also of great interest since it plays an important role in determining phase segregation.[19] In all PUs, broad bands appearing between 3302 and 3401 cm^{-1} are due to the presence of a N-H group.[18] However, the carbonyl group of urethane and benzimidazolin-2-one is shown in the region 1709 to1758 cm^{-1}.

The ^{13}C-NMR spectra of all PUs (Figs. 3 and 4) have shown characteristic signals. For instance, the ppm range between 16.8 and 68.7 is due to the aliphatic carbons. Resonance in the region between 109.2 and 186.0 ppm is due to aromatic carbons. Peaks observed between 204.7 and 237.4 ppm are due to benzimidazolin-2-one and urethane carbonyls.

Thermal properties

Thermal properties of all PUs were evaluated with DSC (Fig. 5) and TGA (Fig. 6), and the derived data are presented in Tables I and II. The existence of multiple endotherms has been documented in several studies of the thermal behavior of segmented polyurethane block copolymers.[20-22] Koberstein and Galambos[12] indicated that the origin of multiple endotherms in PUs is dependent upon the specimen preparation procedure. Martin et al.[23] suggested that the five endotherms were possibly due to melting of various hard
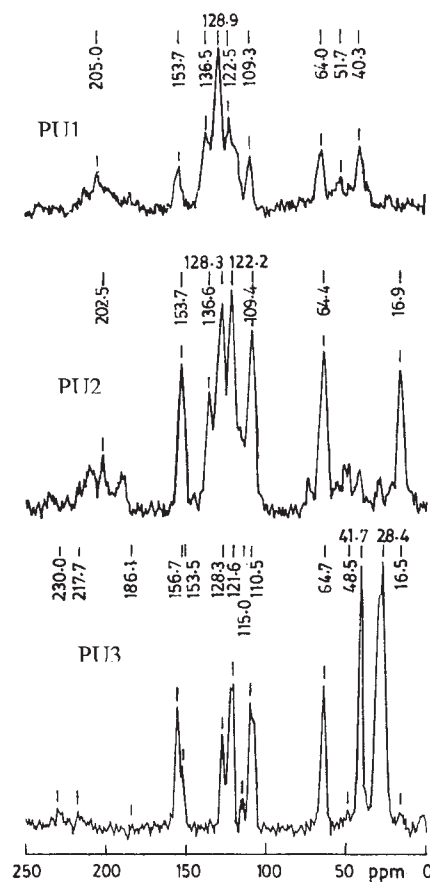

Figure 3 CPMAS ^{13}C-NMR spectra of PU1, PU2, and PU3.

segment length populations. Van Bogart et al.[24] have identified three endothermic transitions associated with the ordering of MDI/BDO hard segments in materials subjected to a third thermal cycle. Blackwell and Lee[25] studied the multiple melting in MDI-based PUs that had been oriented and thermally annealed. In light of the above reports, it is obvious 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 materials prepared under varying conditions.

In the present article, we observe multiple melting phenomena in identical PUs prepared from only hard segments in the main chain. In all PUs, T_g is not clearly shown due to alternative hard segment.[26] DSC data of PU1, PU4, PU5, and PU6 show three endotherm peaks, while in PU2 and PU3, DSC curves display four and five endotherm peaks, respectively. DSC studies of PU1, PU4, PU5, and PU6 exhibited the lowest endotherms (T_1) at 174, 223, 221, and 158 °C due to local restructuring of hard segment units within the hard microdomains. Intermediate temperature endotherms (T_2) were also observed at 236, 252, 300, and 234 °C, which has been associated with the destruction of long-range order of an unspecified nature. Higher temperature endotherms (T_3) observed at 321, 327,
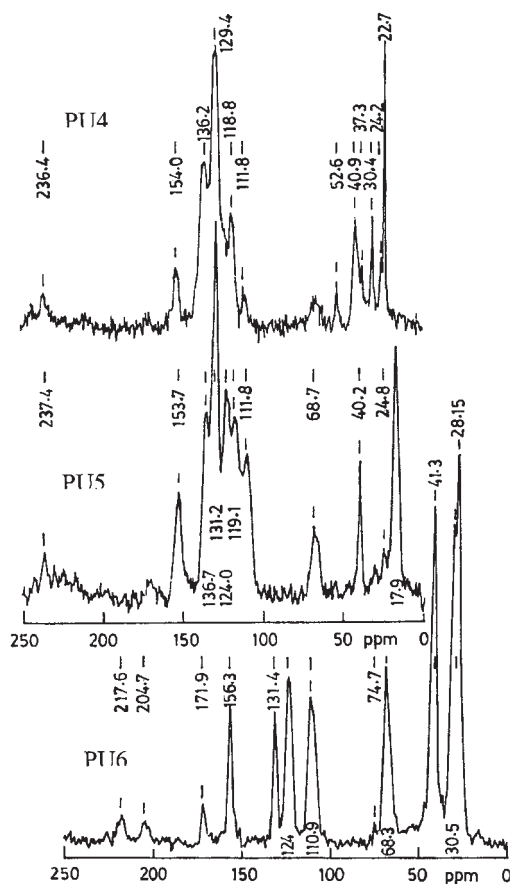
Figure 4 CPMAS ^{13}C-NMR spectra of PU4, PU5, and PU6.

363, and 352 °C, respectively, were generally ascribed to the melting of microcrystalline regions within hard microdomains. In PU2 the lowest endotherms (T_1)
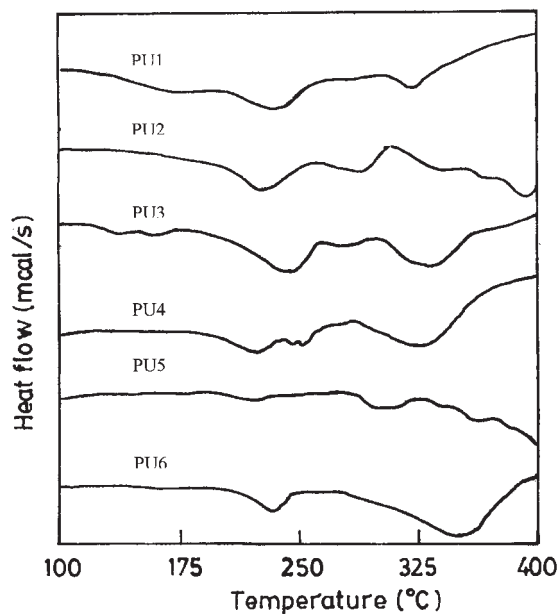

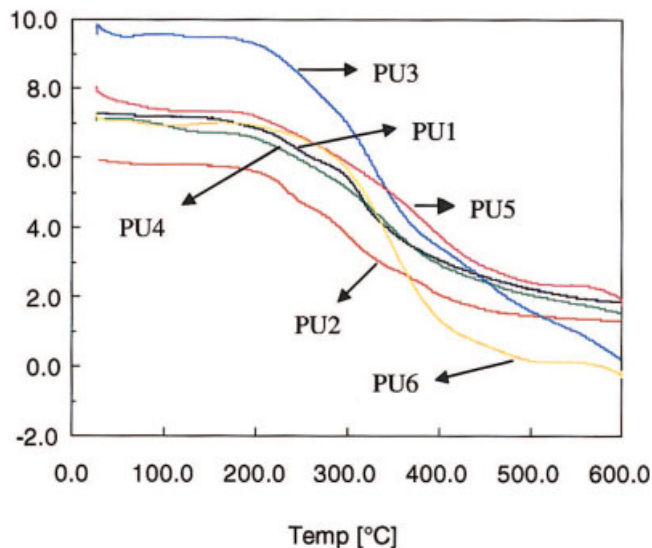**Figure 5** DSC thermograms of PU1 to PU6.

Figure 6 TGA tracings of PU1 to PU6. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

observed at 230 °C are due to a local restructuring of hard segment units within the hard microdomains. The intermediate temperature endotherm (T_2) observed at 287 °C is related to the melting of microcrystalline regions within hard microdomains. A higher melting temperature (T_3) was observed as a small peak and a broad peak at 342 and 394 °C, respectively. In PU3, the lowest endotherms (T_1) showed two small peaks at 139 and 163 °C due to local restructuring of hard segment units within the hard microdomains, while an intermediate temperature endotherm (T_2) displayed two peaks, one at 246 and another at 278 °C. The melting of microcrystalline regions within hard microdomains (T_3) is also observed at 332 °C. The three endothermic peaks are observed at 174, 236, and 321 °C, respectively.

Weight loss data from the TGA for all PUs are presented in Table II. These results suggest that zero weight loss occurs at 150 °C, while the curves show major weight loss between 150 and 435 °C. The residual weight remaining at 600 °C was about 1 to 25%.

TABLE I
Different Melting Endotherms from DSC

	T_1(°C)	T_2(°C)	T_3(°C)
PU1	174	236	321
PU2	230	287	342, 394
PU3	139, 163	246, 278	332
PU4	223	252	327
PU5	221	300	363
PU6	158	234	352

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

TABLE II
Thermal Properties of PUs

Polymer	Decomposition temperature (°C)		Major weight loss transition (°C)	Residual weight loss at 600°C (%)[c]
	$T_0{}^a$	$T_{50}{}^b$		
PU1	170	361	170–435	25
PU2	150	335	150–421	12
PU3	196	347	196–395	04
PU4	170	367	170–419	13
PU5	171	387	171–455	14
PU6	208	347	208–400	01

[a] Temperature at which 0% of weight loss is observed by TGA.
[b] Temperature at which 50% of weight loss occurred in TGA.
[c] Residual weight observed by TGA at 600°C in N_2.

This variation in weight loss is due to the differences in the structure of hard segments in PUs. In PU1, the weight loss begins at 170 °C but major weight loss occurs around 170–435 °C, respectively. In PU2, the weight loss begins at 150 °C and major weight loss occurred at 150–421 °C. In PU3, weight loss begins at 196 °C and major weight loss occurs at 196–395 °C, respectively. In PU4, the weight loss begins at 170 °C and the major weight loss occurs around 170–419 °C. In PU5, the weight loss begins at 171 °C, with a major weight loss occurring around 171–455 °C. In PU6, the weight loss begins at 208 °C, but the major weight loss occurs in the range 208–400 °C.

X-ray diffraction data

X-ray diffraction curves of the polymers are shown in Figure 7. All PUs are amorphous; this may be due to the presence of heterocyclics such as benzimidazole group and aromatic structures in the main chain, which limit the molecular mobility of all PUs.

The texture and anisotropic nature of all PUs were studied using a Euromax polarizing microscope equipped with a Linkem HFS91 heating stage and a TP-93 temperature programmer. The anisotropic be-havior observed by heating from ambient to 250 °C and cooled at a rate of 5 °C/min. None of the PUs studied exhibited any anisotropic behaviors.

CONCLUSIONS

Novel PUs based on [1,3-B[*HM*]B-2-O] and [1,3-B[*HM*]B-2-S] with MDI, 2,4-TDI, and HDI were synthesized. The structures of PUs were confirmed by FT-IR and ^{13}C-NMR CPMAS studies. All PUs were insoluble in almost all organic solvents due to the presence of intermolecular hydrogen bonding and alternative hard segments present in the main polymer chain. TGA studies indicate that all PUs were stable up to 150 °C, while the curves showed major weight loss between 150 and 435 °C. DSC displayed multiple endotherms that are in good agreement with the reported data. The amorphous nature of the PUs developed was confirmed by X-ray diffraction experiments. Research is now progress to develop soluble PUs.

References

1. Bengston, B.; Feger, C.; Macknight, W. J.; Schneider, N. S. Polymer 1985, 26, 895.
2. Arshady, R.; J Microencapsul 1989, 6, 13.
3. Bogdanov, B.; Toncheva, V.; Schacht, E.; Finelli, L.; Sarti, B.; Scandola, M. Polymer 1999, 40, 3171.
4. Skaja, G. A.; Woodhouse, K. A. J Appl Polym Sci 2000, 75, 1522.
5. PPG Industries, UK Pat. 2,157,702 (1985).
6. Frere, Y.; Danicher, L.; Germain, P. Eur Polym Mater 1998, 34, 193.
7. Chen, T. K.; Chi, J. Y.; Shieh, T. S. Macromolecules 1997, 30, 5068.
8. Xu, M.; Macknight, W. J.; Chen, C. H. Y.; Thomas, E. L. Polymer 1983, 24, 1327.
9. Paul, C. J.; Gopinathan Nair, M. R.; Neelakantan, N. R.; Koshy, P.; Idage, B. B.; Bhelhelear, A. A. Polymer 1998, 39, 6861.
10. Higgins, J.; Marvel, C. S. J Polym Sci A1 1970, 8, 171.
11. Frontini, M. F.; Pavan, A. J Appl Polym Sci 2003 1993, 48.
12. Koberstein, J. T.; Galambos, A. F. Macromolecules 1992, 25, 5618.
13. Phillips, R. A.; Cooper, S. L. J Polym Sci B Polym Phys 1996, 34, 737.
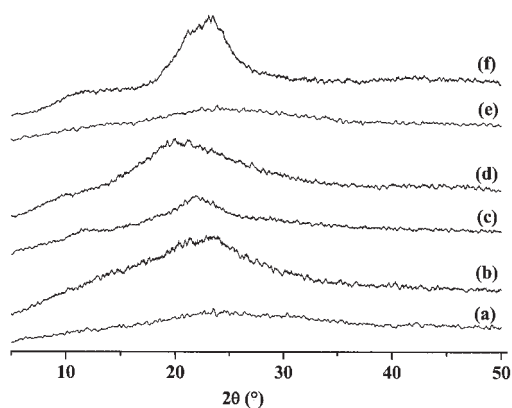
Figure 7 X-ray diffactograms of PU1 to PU6.

14. Saimot, A. G.; Cermieux, A. C.; Hay, J. M.; Meulemans, A.; Giovanangeli, M. D.; Delaitre, B.; Coulaud, F. P. Lancet 1983, 17, 652.

15. Niemegeers, C. J. E.; Awouters, F.; Janssen, P. A. J Agents Actions 1986, 18, 141.

16. Iemura, R.; Hori, M.; Ohtaka, H. Chem Pharm Bull 1989, 37, 962.

17. Cassidy, P. E. Thermally Stable Polymers; Dekker: New York, 1980.

18. Lyman, D. J. J Polym Sci 1960, 45, 49.

19. Jeffey, G. A.; Saenger, W. Hydrogen Bonding in Biological Structures; Springer-Verlag: New York, 1991.

20. Seymour, R. W.; Cooper, S. L. Macromolecules 1973, 6, 48.

21. Hesketh, T. R.; Van Bogart, J W. C.; Copper S. L. Polym Eng Sci 1980, 20, 190.

22. Jacques, C. H. M. In Polymer Alloys; Klempner, D. K.; Frisch, K. C., Eds.; Plenum Press: New York, 1977; p 287.

23. Martin, D. J.; Meijs, G.; Fgunatillake, P. A.; McCarthy, S. J.; Renvvick, G. M. J Appl Polym Sci 1997, 64, 803.

24. Van Bogart, J. W. C.; Bluemke, D. A.; Cooper, S. L. Polymer 1981, 22, 1428.

25. Blackwell, J.; Lee, C. D. J Polym Sci Polym Phys Ed 1984, 22, 769.

26. Mitsuhiro, S.; Masakatsu, S.; Shinichi, S.; Tomoyuki, Y.; Shunji, N. Macromolecules 1991, 24, 6254.