Synthesis and Characterization of Novel Polyurethanes Based on 2,6-Bis(4-hydroxybenzylidene) Cyclohexanone Hard Segments

A. V. Raghu, G. Anita, Y. M. Barigaddi, G. S. Gadaginamath, T. M. Aminabhavi

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

ABSTRACT: Four novel polyurethanes (PUs) containing 2,6-bis(4-hydroxybenzylidene) cyclohexanone hard segments with four diisocyanate, namely, 4,4′-diphenylmethane diisocyanate, toluene 2,4-diisocyanate, isophorone diisocyanate, and hexamethylene diisocyanate, were prepared. Structural elucidation and thermal characterization of these PUs were done by Fourier transform infrared, UV, and fluorescence spectroscopy, ^{1}H-NMR, ^{13}C-NMR, and differential thermal analysis/thermogravimetric analysis. All of the PUs contained domains of semicrystalline and amorphous structures as indicated by X-ray diffraction. PUs were soluble in polar aprotic solvents such as *N*-methyl-2-pyrrolidone, dimethylformamide, and dimethyl sulfoxide. Acoustic properties were calculated from the group contribution method. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 81–88, 2007

Key words: fluorescence; FT-IR; NMR; phase separation; polyurethanes

INTRODUCTION

Segmented polyurethane (PU) elastomers are used in a number of implantable medical devices.[1,2] However, the majority of PUs and polyureas are insoluble in common organic solvents due to their rigid backbone structures;[3,4] this prohibits their application due to difficulty in processing. To overcome these difficulties, the modification of their structures is necessary by the introduction of bulky or asymmetric groups on the pendant polymer backbone or the incorporation of noncoplanar structural units on the main polymer chain.[5–8] In our earlier studies,[9–11] we prepared Schiff-base PUs and azo-based diol-containing PUs with 2,2′-[ethane-1,2-diylbis(nitrilomethylylidene)] diphenol, 2,2′-[hexane-1,6-diylbis(nitrilomethylylidene)] diphenol, 4,4′-(ethane-1,2-diylidenedinitrilo) diphenol and 4,4′-(pentane-1,5-diylidene-dinitrilo) diphenol, 4, 4′-[1,4-phenylenedi-diazene-2,1-diyl] bis (2-carboxyphenol), and 4,4′-[1,4-phenylenedi-diazene-2,1-diyl] bis(2-chlorophenol) with different diisocyanates. In continuation of these studies, we now propose the synthesis of PUs based on chalcone groups containing diols such as 2,6-bis(4-hydroxybenzylidene) cyclohexanone (BHBC) as hard segments with 4,4′-diphenylmethane diisocyanate (MDI), toluene 2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI), and hexamethylene diisocyanate (HDI). Chalcones are an important class of natural/synthetic products belonging to the flavonoid family, and some of them possess a broad spectrum of biological activities.[12–17] Chalcones are nontoxic and become biologically compatible when they are incorporated into the PU structure as a chain extender. Such PUs are useful in drug delivery and biomedical applications. The chalcone diol was prepared as per the published report.[18] The structure of BHBC was established by Fourier transform infrared (FTIR) spectroscopy, ^{1}H-NMR and ^{13}C-NMR spectral data. The synthesized PUs were further characterized by ultraviolet–visible (UV–vis) spectroscopy, fluorescence, FTIR spectroscopy, ^{1}H-NMR, ^{13}C-NMR, differential thermal analysis (DTA)/thermogravimetric analysis (TGA), and X-ray diffraction techniques. The derived PUs were studied in terms of structure–morphology based considerations. Their acoustic properties were calculated from the group contribution method.

EXPERIMENTAL

Materials

MDI, TDI, IPDI, HDI, and dibutyltin diaurate were purchased from Aldrich (Milwaukee, WI) and were
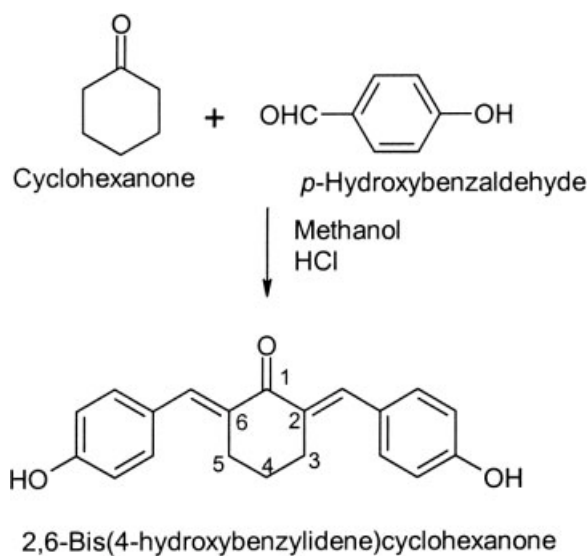
Scheme 1   Preparation of BHBC.

used without further purification. Cyclohexanone, *p*-hydroxybenzaldehyde, xylene, ethyl methyl ketone, toluene, *n*-hexane, chloroform, tetrahydrofuran, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone, dimethylacetamide, acetic acid, and hydrochloric acid were all are analytical-reagent-grade samples purchased from S. D. Fine Chemicals (Mumbai, India). All of the solvents were purified before use with standard procedures.

Preparation of BHBC

To a 500-mL, round-bottom flask containing methanol (160 mL) and fitted with a condensor and a mechanical stirrer, *p*-hydroxybenzaldehyde (24.4 g, 0.2 mol) and cyclohexanone (11.4 mL, 0.1 mol) were added. HCl gas was passed, and the reaction mixture was stirred at ambient temperature until the contents of the flask became dark pink. The contents of the flask were poured into a large quantity of distilled water, and the precipitate was filtered and dried *in vacuo* at 30°C. Recrystallization of the product was done in methanol.

The product yield was 20.6 g (57%; mp = 296–98°C). FTIR and NMR assignments of these compounds are given next:

FTIR (KBr, cm^{-1}): 3216, 2940, 2836,1652, 1571, 1541, 1508, 1434, 1376, 1303, 1242, 1162, 971, 922, 869, and 656. ^{1}H-NMR [DMSO-d_6, tetramethylsilane (TMS), δ]: 1.72 (t, J = 7.2 Hz, 2H, 4-CH$_2$), 2.86 (t, J = 7.2 Hz, 4H, 3-CH$_2$ and 5-CH$_2$), 6.85 (d, J = 8.5 Hz, 2H, *ortho*-ArH to phenolic OH), 7.41 (d, J = 8.5 Hz, 2H, *ortho*-ArH to —CH=), 7.55 (s, 2H, —CH=), and 9.93 (s, 2H, phenolic OH). ^{13}C-NMR (DMSO-d_6, δ): 22.97 (C$_4$ of cyclohexanone), 28.38 (C$_3$ and C$_5$ of cyclohexanone), 115.99 (*ortho*-Ar carbons to phenolic OH), 126.96 (Ar carbons

para to OH and linked to —CH=), 132.82 (C$_2$ and C$_6$ of cyclohexanone), 133.81 (Ar carbons ortho to —CH=), 136.19 (carbons of =CH—), 158.75 (Ar carbons linked to —OH), and 188.97 (carbons of —C=O).

Scheme 1 displays the formation of BHBC based on the previously cited spectral assignments.

Polymer synthesis

A typical general procedure used to synthesize PUs was carried out in a three-necked 100-mL, round-bottom flask equipped with a magnetic stirrer, condenser, and dropping funnel under a nitrogen atmosphere. BHBC was dissolved in dry DMF under a dry nitrogen atmosphere with constant stirring. Then, an equimolar quantity of diisocyanate (MDI, TDI, IPDI, or HDI) with respect to the previous diol taken in dry DMF was added to this solution over a period of 1 h. The reaction mixture was stirred continuously for 8 h at 80°C, cooled, poured into distilled water, and then filtered. The solid powder polymer obtained was washed with double-distilled water and dried under reduced pressure at 30°C. The chemical structures of the obtained PUs are shown in Scheme 2.

Preparation of poly[2,6-bis(benzyliden-4-yl) cyclohexanone 4,4′-methylene diphenylene diurethane] (PU-1)

We prepared PU-1 with MDI (2.0 g, 0.008 mol) and BHBC (2.4 g, 0.008 mol) to yield 4.09 g (95%). FTIR and NMR assignments are given next:
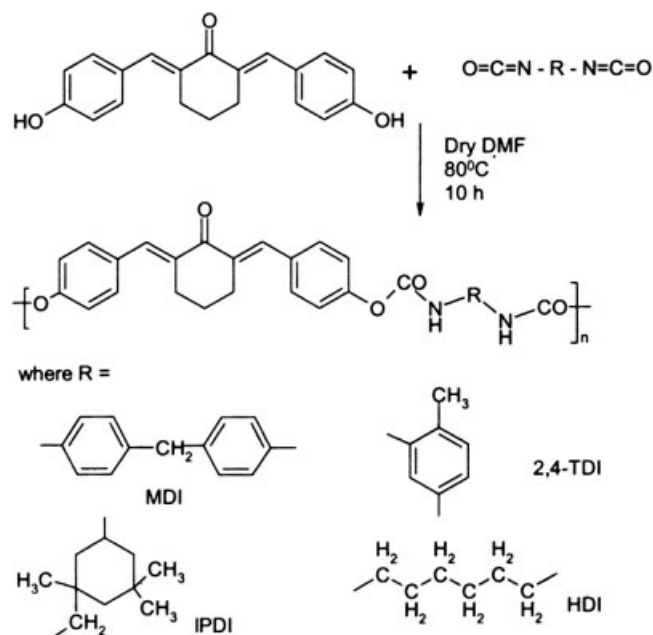
Scheme 2   Reaction schemes for the formation of PU-1 to PU-4.

FTIR (KBr, cm^{-1}): 3398, 3030, 2914, 1647, 1594, 1542, 1435, 1409, 1304, 1281, 1163, 1146, 972, 838, and 758. ^{1}H-NMR (DMSO-d_6, TMS, δ): 1.72 (m, C_4-CH$_2$), 2.86 (m, C_3 and C_5-CH$_2$), 3.81 (s, Ar—CH$_2$—Ar), 6.70–7.50 (m, ArH), 7.55 (s, —CH=), and 9.93 (br, —NH—COO—). ^{13}C-NMR (DMSO-d_6, δ): 22.55 (C_4 of cyclohexanone), 27.94 (C_3 and C_5 of cyclohexanone), 39.85 (Ar—CH$_2$—Ar carbon merged with DMSO-d_6 methyl carbon peaks), 115.57 (Ar carbons ortho to —O—), 118.39 (Ar carbons ortho to —NH—), 126.51 (Ar carbons para to —O— and linked to —CH=), 128.88 (Ar carbons ortho to —CH$_2$—), 132.39 (C_2 and C_6 of cyclohexanone), 133.41 (Ar carbons ortho to —CH=), 134.94 (Ar carbons linked to —CH$_2$—), 135.74 (=CH— carbons), 137.67 (Ar carbons linked to —NH—), 152.59 and 158.33 (Ar carbons linked to —O—), and 188.59 (carbonyl carbons of cyclohexanone and urethane carbonyl carbons).

Preparation of poly[2,6-bis(benzyliden-4-yl) cyclohexanone toluene 2,4-diurethane] (PU-2)

PU-2 was prepared with TDI (1.4 g, 0.008 mol) and BHBC (2.4 g, 0.008 mol) with a yield of 3.46 g (93%). FTIR and NMR assignments are given next:

FTIR (KBr, cm^{-1}): 3287, 2927, 2856, 1654, 1594, 1572, 1435, 1377, 1280, 1162, 971, 867, and 756. ^{1}H-NMR (DMSO-d_6, TMS, δ): 1.72 (t, J = 7.1 Hz, C_4-CH$_2$), 2.22 (s, —CH$_3$), 2.86 (m, C_3 and C_5-CH$_2$), 6.70–7.40 (m, Ar—H), 7.55 (s, —CH=), and 9.94 (br, urethane NH). ^{13}C-NMR (DMSO-d_6, TMS, δ): 17.41 (—CH$_3$ carbons), 22.55 (C_4 of cyclohexanone), 27.96 (C_3 and C_5 of cyclohexanone), 115.57 (Ar carbons ortho to —O— and —NH—), 126.49 (Ar carbons linked to —CH= and para to —O—), 132.41 (C_2 and C_6 of cyclohexanone and Ar carbons ortho to —CH$_3$), 133.36 (Ar carbons ortho to —CH=), 135.79 (=CH— carbons), 137.91 (Ar carbons linked to —NH—), 158.36 (Ar carbons linked to —O—), and 188.56 (cyclohexanone and urethane carbonyl carbons).

Preparation of poly[2,6-bis(benzyliden-4-yl) cyclohexanone isophorone diurethane] (PU-3)

PU-3 was prepared with IPDI (1.8 g, 0.008 mol) and BHBC (2.4 g, 0.008 mol) to yield 3.90 g (95%). FTIR and NMR assignments are given next:

FTIR (KBr, cm^{-1}): 3364, 2954, 1720, 1652, 1598, 1434, 1384, 1277, 1234, 1159, 1067, 970, 838, and 761. ^{1}H-NMR (DMSO-d_6, TMS, δ): 0.86 (s, —CH$_3$); 0.91 (s, —CH$_3$); 0.98 (s, —CH$_3$); 1.05, 1.48, 1.51, 1.70, 2.88 (isophorone methylene protons); 1.71 (m, C_4-CH$_2$ of cyclohexanone); 2.72 (s, —CO—NH—CH$_2$—); 2.84 (m, C_3 and C_5-CH$_2$ of cyclohexanone); 5.55 (br, ring urethane NH protons except those H-bonded); 6.82 (d, J = 8.5 Hz, ortho-ArH to —O—); 7.40 (d, J = 8.5 Hz, ortho-ArH to —CH=); 7.53 (s, —CH=); and 9.91 (br, urethane NH protons H-bonded). ^{13}C-NMR

(DMSO-d_6, TMS, δ): 22.54 (C_4 of cyclohexanone); 27.10 (—CH$_3$ carbons); 27.59 (—CH$_3$ carbons); 29.90 (—CH$_3$ carbons); 31.53, 35.02, 36.10, 39.18, 42.30, 47.11 (isophorone carbons); 46.64 (—NH—CH$_2$— carbons); 115.56 (Ar carbons ortho to —O—); 126.51 (Ar carbons para to —O— and linked to —CH=); 132.38 (C_2 and C_6 of cyclohexanone); 133.40 (Ar carbons ortho to —CH=); 135.75 (—CH= carbons); 158.32 (Ar carbons linked to —O—); and 188.59 (urethane carbonyl carbons and carbonyl carbons of cyclohexanone).

Preparation of poly[2,6-bis(benzyliden-4-yl) cyclohexanone hexamethylene 1,6-diurethane] (PU-4)

PU-4 was prepared with HDI (1.29 g, 0.008 mol) and BHBC (2.4 g, 0.008 mol) to yield 3.51 g (97%). FTIR and NMR assignments are given next:

FTIR (KBr, cm^{-1}): 3325, 2932, 2856, 1718, 1573, 1509, 1438, 1377, 1280, 1162, 1109, 1069, 971, 922, 837, and 763. ^{1}H-NMR (DMSO-d_6, TMS, δ): 1.24 (m, —NH—CH$_2$—$\underline{CH_2}$—), 1.35 (m, —NH—CH$_2$—CH$_2$—$\underline{CH_2}$—), 2.86 (m, C_3 and C_5-CH$_2$ of cyclohexanone), 2.96 (m, —NH—$\underline{CH_2}$—), 5.75 (br, urethane NH protons except those H-bonded), 6.84 (d, J = 8.5 Hz, ortho-ArH to —O—), 7.41 (d, J = 8.5 Hz, ortho-ArH to —CH=), 7.55 (s, —CH=), and 9.93 (br, urethane NH protons H-bonded). ^{13}C-NMR (DMSO-d_6, TMS, δ): 22.86 (C_4 of cyclohexanone), 25.90 (—NH—CH$_2$—$\underline{CH_2}$— carbons), 29.63 (C_3 and C_5 of cyclohexanone), 30.07 (—NH—CH$_2$—CH$_2$—$\underline{CH_2}$— carbons), 38.88 (—NH—CH$_2$— carbons), 116.02 (Ar carbons ortho to —O—), 126.94 (Ar carbons linked to —CH= and para to —O—), 132.85 (C_2 and C_6 of cyclohexanone), 133.89 (Ar carbons ortho to —CH=), 136.36 (=CH— carbons), 158.59 (Ar carbons linked to —O—), and 189.55 (urethane carbonyl carbons and carbonyl carbons of cyclohexanone).

Scheme 2 displays the chemical reactions for the formation of the different PUs.

Characterization

The melting temperatures (T_m's) of the monomers were determined in open capillary tubes. UV–vis spectra (Secomam, France) and fluorescence spectra (F-2000, Hitachi, Japan) were recorded for the monomer and the PUs in DMF. FTIR spectra were recorded on a PerkinElmer 881 spectrophotometer (Madison, WI). ^{1}H-NMR and ^{13}C-NMR spectra in CDCl$_3$ or DMSO-d_6 were recorded on a Bruker 300-MHz NMR spectrophotometer (Silberstreifen, Rheinstetten, Germany). Chemical shifts (δ) were taken with TMS as a reference liquid. TGA and DTA were recorded on a PerkinElmer diamond analyzer (Shelton, CT) from ambient temperature to 1000°C under a nitrogen gas flow rate of 100 mL/min. A sample weighing about 5–11 mg was placed in a platinum crucible, and

Name	Absorption λ_{max}* (nm)	Emission λ_{max} (nm)
BHBC	310, 369	466
PU-1	321, 386	464
PU-2	309, 368	465
PU-3	318, 389	462
PU-4	317, 364	466

*λ_{max} = absorption or emission maximum wavelength.

DTA/TGA runs were recorded with α-alumina at a heating rate of 10°C/min. X-ray diffractograms of the PUs were recorded with a Rigaku Geigerflex diffractometer (Tokyo) equipped with Ni-filtered Cu Kα radiation (λ = 1.5418 Å). Dried PUs were spread on a sample holder, and diffractograms were recorded in the 2θ angle range of 5–50° at a speed of 5°/min.

RESULTS AND DISCUSSION

The PUs of this study were novel, and all were obtained in quantitative yields. Because BHBC was incorporated, their physical, chemical, and thermal properties were substantially different than those containing aliphatic chains.
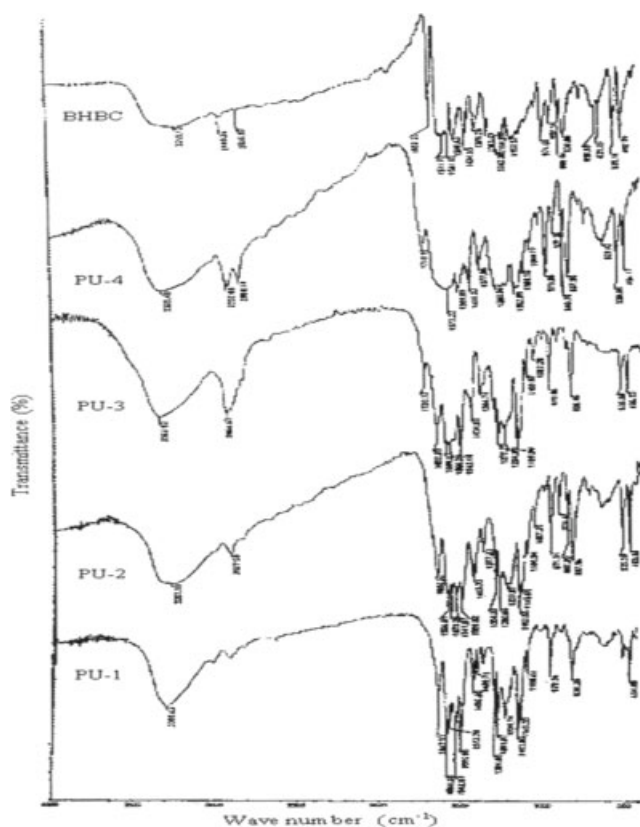
Solubility properties

All of the PUs were soluble in polar aprotic solvents such as N-methyl-2-pyrrolidone, dimethylacetamide, DMF, DMSO and acidic solvents such as m-cresol and concentrated H_2SO_4, but were insoluble in water, acetone, methanol, tetrahydrofuran, carbon tetrachloride, ethyl acetate, dioxane, xylene, ethyl methyl ketone, toluene, n-hexane, chloroform, and carbon disulfide.

Spectral data

UV–vis and fluorescence spectra of the chalcone-based monomer and PUs were determined with DMF solvent at ambient temperature. The absorption and emission spectral data of both the monomer and the PUs are listed in Table I. Both diol and the PUs showed two absorption bands in the regions 309–321 and 368–389 nm, which are attributed to the π–π* transitions of benzene and chalcone, respectively. Emissions from the monomer and the PUs were seen around 462–464 nm on excitation at 310 and 370 nm, respectively. From the absorption and emission spectra, we concluded that there was no significant difference in the monomer and the PUs.

Structures of both the monomer and PUs were characterized by NMR and FTIR; of these, the FTIR spectra showed the disappearance of both the phenolic hydroxyl group and the isocyanate group as well
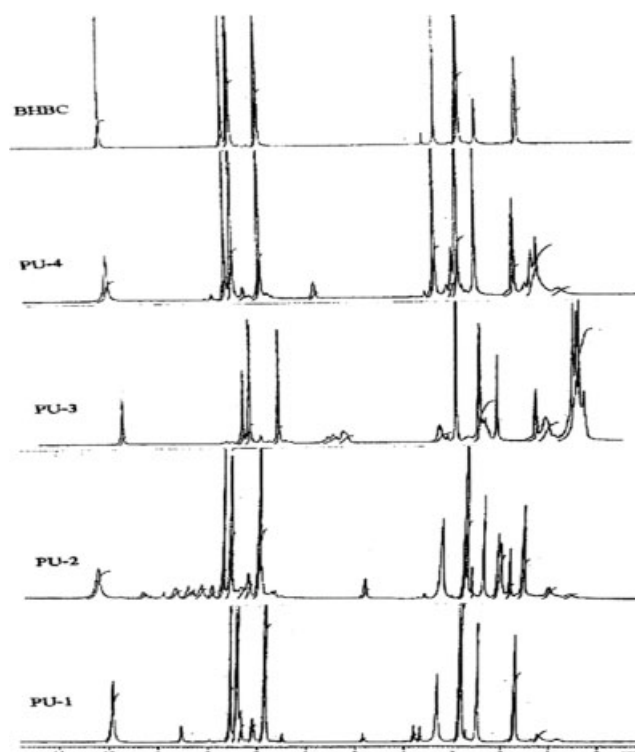

Figure 1 Representative FTIR spectra of the BHBC-based PUs (PU-1, PU-2, PU-3, and PU-4).

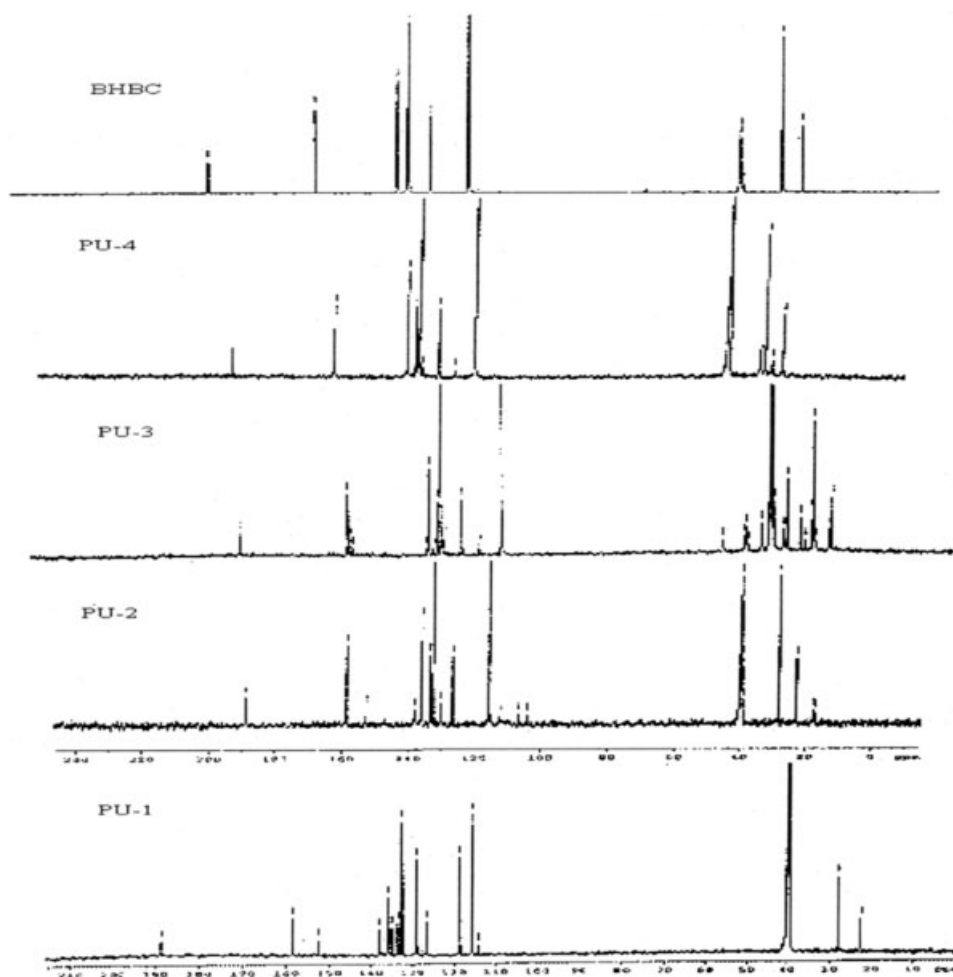**Figure 2** ^{1}H-NMR spectra of BHBC and PU-1 to PU-4.

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

as the formation of several characteristic stretching vibrations due to N—H, C=O and C—H bonds, all shown in Figure 1. In all the PUs, sharp bands appearing between 3287 and 3364 cm^{-1} are due to the presence of hydrogen-bonded N—H groups. However, the hydrogen-bonded broad carbonyl groups of urethane are evident in the region 1647–1720 cm^{-1}.

NMR analysis revealed the disappearance of —OH and —NCO groups and the formation of a urethane polymer chain. ^{1}H-NMR spectra of the PUs showed characteristic signals, as displayed in Figure 2. Resonance peaks observed in the region 0.86–3.81 ppm correspond to methyl/methylene/isophorone/cyclohexanone protons of the monomer and the PUs. The resonance peaks of the —NH—COO— protons of all of the PUs appeared in the region 9.91–9.94 ppm, except for those of IPDI and HDI-based polymers. In IPDI and HDI-based PUs, —NH—COO— protons are also observed around 5.55–5.75 ppm, which are in conformity with an earlier report,[19] but in the monomer, —OH protons are found around 9.93 ppm.

Aromatic protons show signals between 6.70 and 7.50 ppm.

^{13}C-NMR spectra of all of the PUs showed characteristic signals, as displayed in Figure 3. The chemical shifts ranging from $\delta = 17.41$ to $\delta = 47.11$ are due to aliphatic, cyclohexanone, and isophorone carbons. Resonance signals observed in the region between 115.56 and 158.75 ppm are due to aromatic carbons. Peaks observed in the region from 188.56 to 189.55 ppm are ascribed to urethane carbonyl carbons and carbonyl carbons of cyclohexanone.

Thermal properties

The thermal behavior of all of the PUs was studied in a nitrogen atmosphere with DTA/TGA. These data are presented in Tables II and III, whereas the curves are displayed in Figures 4 and 5, respectively. The existence of multiple endotherms has been documented on the thermal characteristics of the segmented PU block copolymers.[20–22] Koberstein and Galambos[23] suggested that the origin of multiple endotherms in

TABLE II
Different Melting Endotherms from DSC and the Group
Contribution Method for the PUs

Code	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_g from van Krevelen[27]	T_m from van Krevelen[27]
PU-1		283	364	142	360
PU-2	159	254	281	159	368
PU-3	184	260	326, 339	123	410
PU-4		240, 262	362	162	365

PUs is dependent on the specimen preparation procedure. Martin et al.[24] suggested that five endotherms observed were possibly due to the melting of various hard-segment-length populations. On the other hand, van Bogart et al.[25] identified three endothermic transitions associated with the ordering of MDI/BDO (1,4-butanediol) hard segments in materials subjected to the third thermal cycle. Blackwell and Lee[26] studied multiple melting in MDI-based PUs that were oriented and thermally annealed. Recently, Raghu and co-workers[9–11] observed two to five endothermic transitions associated with hard-segmented PUs and polyureas. In the light of these reports, it is obvious that the melting behavior of PUs is highly dependent on the procedure adopted for PU preparation. Indeed, the origin of multiple melting peaks are inherently different for materials prepared under varying conditions.

In this study, we observed multiple melting phenomena in identical PUs prepared from only hard segments in the main chain. In all of the PUs, the glass-transition temperature (T_g) was not clear due to the presence of alternative hard segments. Differential scanning calorimetry (DSC) of PU-1 showed two endothermic peaks, whereas PU-2 and PU-4 showed three endothermic peaks, and PU-3 showed four endothermic peaks. In the DSC of PU-1, the lowest endotherm (T_1) was not clear due to the restructuring of hard-segment units within the hard microdomains. An intermediate-temperature endotherm (T_2) was observed at 283°C, which was associated with the destruction of long-range order of an unspecified nature of the hard-segment part of the PUs. The higher temperature endotherm (T_3) observed at 364°C was ascribed to the melting of microcrystalline regions within the hard microdomains. In PU-2, T_1, observed at 159°C, was due to local restructuring of the hard-segment units within the hard microdomains. T_2, observed at 254°C, was related to the melting of microcrystalline regions within the hard microdomains. T_3 was observed at 281°C. In PU-3, T_1 had two small peaks at 184°C due to the local restructuring of hard-segment units within the hard microdomains, whereas T_2 displayed two peaks, one at 260°C and another at 326°C. The melting of microcrystalline regions within the hard microdomain (T_3) was also observed at 339°C. In PU-4, T_1 was not clear due to the restructuring of the hard-segment units within the hard microdomains. T_2 was observed at 262°C and was associated with the destruction of long-range order of an unspecified nature. T_3 observed at 362°C was ascribed to the melting of microcrystalline regions within the hard microdomains.

With procedures suggested by van Krevelen,[27] we calculated the T_g and T_m values of the PUs to correlate them with the experimental data shown in Table II. The calculated T_g and T_m values are in the ranges 132–162 and 360–410°C, respectively. We, therefore, concluded that the calculated T_g of the hard-segmented PUs is in a higher range than 132°C, and similarly, the calculated T_m of the hard-segmented PUs was observed in a range higher than 360°C.

TABLE III
Thermal Properties of the PUs as Obtained from TGA

Code	Decomposition temperature (°C)		Major weight loss transition (°C)	Residual weight loss at 700°C (%)[c]	Onset temperature (°C)
	T_{10}[a]	T_{50}[b]			
PU-1	298	380	273–383	24	269
PU-2	265	377	249–361	22	244
PU-3	280	364	268–456	11	264
PU-4	284	416	268–484	15	258

[a] Temperature at which 10% weight loss was observed by TGA.
[b] Temperature at which 50% weight loss was observed by TGA.
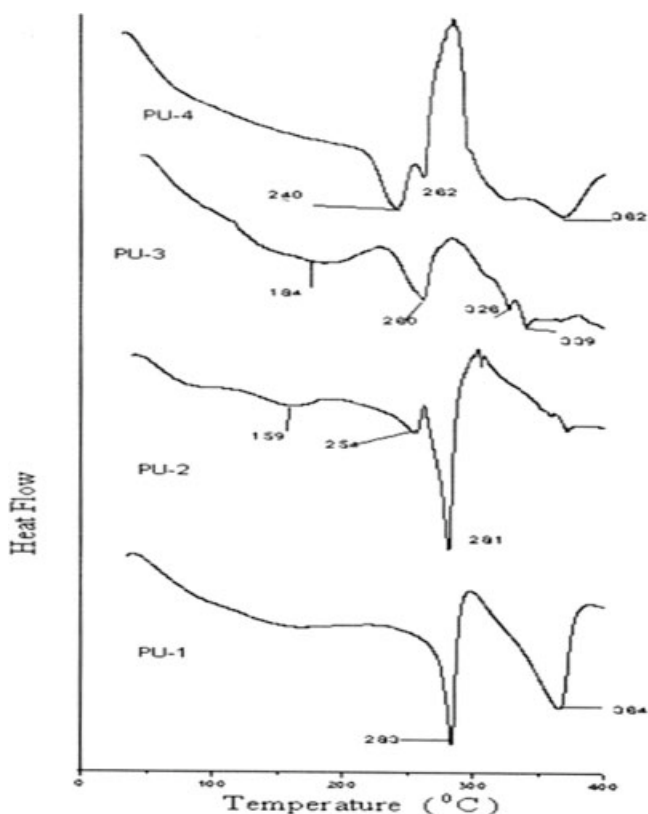[c] Residual weight loss observed by TGA at 700°C in N_2.

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

Weight loss data from TGA of all of the PUs are presented in Table III. These results suggest that 25 and 50% weight losses occurred in the temperature range 281–346 and 323–368°C, respectively. The PUs showed an onset temperature range from 260 to 327°C. The curves showed a major weight loss between 222 and 420°C, but the residual weight remain-
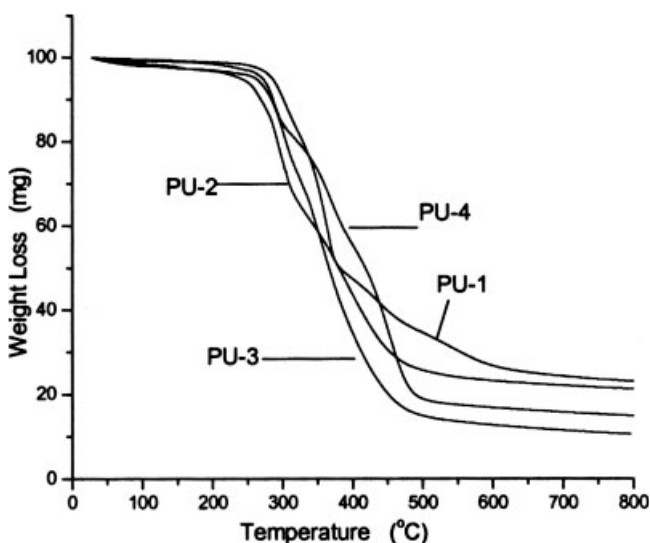
ing at 700°C was from 4 to 21%. This variation in weight loss is due to differences in the structures of the hard segments of the PUs. TGA data indicated that MDI-based PUs exhibited better thermal stability than the other discarnate-based PUs. This was attributed to the presence of a biphenyl ring on the main PU chains.

X-ray diffraction

X-ray diffraction curves of the PUs are shown in Figure 6. The semicrystalline form of the hard segments seem to depend on their structures and on the crystallization conditions. All the PUs displayed a semicrystalline nature, which followed the sequence PU-2 > PU-1 > PU-4 > PU-3. These results are in good agreement with our previous reports.[9–11] This could be due to variations in the unsaturated nature of the monomer.

Acoustic properties

The acoustic properties of PUs are important in the prediction of their properties in practical applications, particularly in applications as foam materials. The speeds of longitudinal and transverse (shear) ultrasonic waves can be predicted with two additive molar functions, namely, the Rao function (U_R) and the Hartmann function (U_H). From these, four important elastic parameters, namely, bulk modulus (K), shear
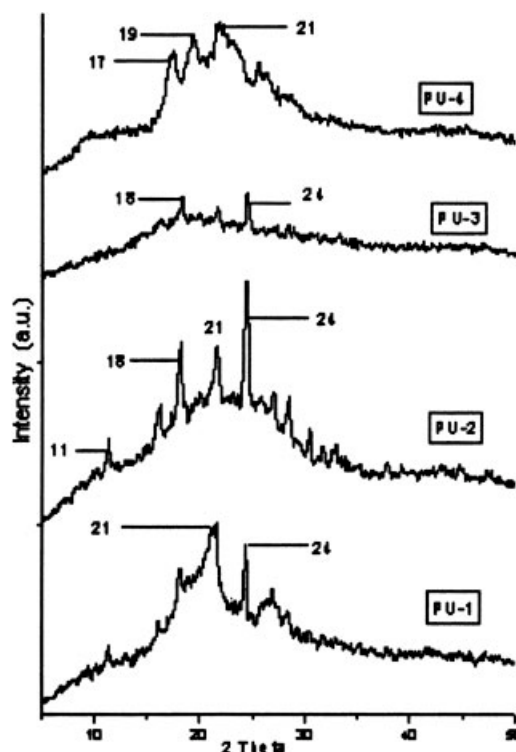

Figure 5 TGA tracings of PU-1 to PU-4.

Figure 6 X-ray diffractograms of PU-1 to PU-4.

TABLE IV
Elastic Parameters of the PUs Calculated from the Group Contribution Method[27]

Code	U_R	U_H	K ($\times 10^9$ N/m^2)	G ($\times 10^9$ N/m^2)	E ($\times 10^9$ N/m^2)	ν
PU-1	27,970	22,475	3.47	0.930	2.560	0.37
PU-2	26,790	21,490	6.44	1.715	4.725	0.37
PU-3	26,280	18,565	3.35	0.416	1.198	0.44
PU-4	24,170	19,250	3.76	0.960	2.655	0.38

modulus (G), Young's modulus (E), and the Poisson ratio (ν) were calculated[27] with eqs. (1)–(4):

$$K = \rho(U_R/V)^6 \tag{1}$$

$$G = \rho(U_H/V)^6 \tag{2}$$

$$E = 3G/(1 + G/3K) \tag{3}$$

$$\nu = (0.5 - G/3K)/(1 + G/3K) \tag{4}$$

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.[27] The calculated results are presented in Table IV. Both ρ and V were considered additive quantities.

CONCLUSIONS

Novel PUs based on BHBC with MDI, 2,4-TDI, IPDI, and HDI were synthesized. The structures of the monomer and the PUs were confirmed by UV–vis spectroscopy, fluorescence, and FTIR spectroscopy in addition to NMR studies. All of the PUs were soluble in polar aprotic solvents and exhibited fluorescent properties. TGA indicated that the onset temperature of all of the PUs was higher than 244°C, whereas the curves showed major weight losses between 249 and 484°C. DSC displayed multiple endotherms that were in good agreement with the reported data. The semi-crystalline and amorphous nature of the developed PUs was confirmed by X-ray diffraction. The acoustic properties of the PUs were in the range observed for other similar types of polymers. We believe that the novel types of PUs developed in this research may have applications in the production of membranes in separation science and drug delivery. Efforts in this direction are underway.

References

1. Lambda, N. M. K.; Woodhouse, K. A.; Cooper, S. L. Polyurethanes in Biomedical Applications; CRC: Boca Raton, FL, 1998.
2. Vermette, P.; Griesser, H. J.; Laroche, G.; Guidoin, R. Biomedical Applications of Polyurethanes; Eureka Com: Georgetown, TX, 2001.
3. Raghu, A. V.; Gadaginamath, G. S.; Aminabhavi, T. M. J Appl Polym Sci 2005, 96, 2236.
4. Raghu, A. V.; Gadaginamath, G. S.; Mallikarjuna, N. N.; Aminabhavi, T. M. J Appl Polym Sci 2006, 100, 576.
5. Yang, C. P.; Hsiao, S. H.; Lin, J. H. J Polym Sci Part A: Polym Chem 1993, 31, 2995.
6. Lee, H. J.; Lee, M. H.; Oh, M. C.; Han, S. G. Polym Bull 1999, 42, 403.
7. Chen, J. P.; Natansohn, A. Macromolecules 1999, 32, 3171.
8. Akimoto, S.; Jikei, M.; Kakimoto, M. High Perform Polym 2000, 12, 197.
9. Raghu, A. V.; Gadaginamath, G. S.; Halligudi, S. B.; Aminabhavi, T. M. J Polym Sci Part A: Polym Chem 2006, 44, 6032.
10. Raghu, A. V.; Gadaginamath, G. S.; Mathew, N. T.; Halligudi, S. B.; Aminabhavi, T. M. React Funct Polym, submitted.
11. Raghu, A. V.; Gadaginamath, G. S.; Mathew, N. T.; Halligudi, S. B.; Aminabhavi, T. M. React Funct Polym, submitted.
12. Dhar, D. N. The Chemistry of Chalcones and Related Compounds; Wiley-Interscience: New York, 1981.
13. Dimmock, J. R.; Elias, D. W.; Beazely, M. A.; Kandepu, N. M. Curr Med Chem 1999, 6, 1125.
14. Kidwai, M.; Sapra, P.; Misra, P.; Saxena, R. K.; Singh, M. Bioorg Med Chem 2001, 9, 217.
15. Ballesteros, J. F.; Sanz, M. J.; Ubeda, A.; Miranda, M. A.; Iborra, S.; Paya, M.; Alcaraz, M. J. J Med Chem 1995, 38, 2794.
16. Lin, Z.; Ming, C.; Jens, B.; Thor, T. G.; Soren, B. C.; Arlasan, K. J Antimicrob Chemother 1999, 43, 793.
17. Chen, M.; Christensen, S. B.; Zhai, L.; Rasmussen, M. H.; Theander, T. G.; Frokjaer, S. J Infect Dis 1997, 176, 1327.
18. Arun, A.; Reddy, B. S. R. J Appl Polym Sci 2004, 92, 2494.
19. Prabhakar, A.; Chattopadhyay, D. K.; Jagadeesh, B.; Raju, K. V. S. N. J Appl Polym Sci Part A: Polym Chem 2005, 43, 1196.
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: New York, 1977; p 287.
23. Koberstein, J. T.; Galambos, A. F. Macromolecules 1992, 25, 5618.
24. Martin, D. J.; Meijs, G.; Fgunatillake, P. A.; McCarthy, S. J.; Renvvick, G. M. J Appl Polym Sci 1997, 64, 803.
25. van Bogart, J. W. C.; Bluemke, D. A.; Cooper, S. L. Polymer 1981, 22, 1428.
26. Blackwell, J.; Lee, C. D. J Polym Sci Polym Phys Ed 1984, 22, 769.
27. van Krevelen, D. W. Properties of Polymers; Elsevier: New York, 1990.