

# Improvement of Thermal Stability of New Heteroaromatic Poly(azomethine urethane)s

A. M. Issam,<sup>1</sup> J. Ismail<sup>2</sup>

<sup>1</sup>School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia

<sup>2</sup>School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

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**ABSTRACT:** New poly(azomethine urethane)s were synthesized in the conventional literature manner by reacting a new bisphenol-containing azomethine group, *N,N'*-bis(4-hydroxyl-3-methoxy benzylidene)-2,6-diaminopyridine (**I**) with various diisocyanates, such as hexamethylene diisocyanate (HDI) (**a**), methylene-4,4'-diphenyl diisocyanate (MDI) (**b**), and toluene-2,4-diisocyanate (TDI) (**c**). The resulting polymers **I(a–c)** were confirmed by <sup>1</sup>H-NMR, FTIR, UV, and CHN analyses. Thermogravimetric analysis (TGA) revealed

that the polymers have high thermal stability. A semicrystalline behavior was noticed for polymers by wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1198–1204, 2006

**Key words:** thermal properties; polyurethanes; heteroatom-containing polymers; 2,6-diaminopyridine; synthesis

## INTRODUCTION

Polyurethane products have found extensive application in producing coatings, foams, and elastomers.<sup>1</sup> Several researches exist in the development of thermally stable polymers for a wide range of applications. Most conventional organic polymers have useful structural and mechanical properties, but are limited by their low thermo-oxidative stability and high flammability. A typical example is polyurethanes, many varieties of which are widely used in the aerospace and construction industries. However, polyurethanes are highly combustible.<sup>2</sup> As a result, their thermal stability has been studied extensively.<sup>3–5</sup> One attractive class of macromolecules is poly(azomethines), which contain azomethine (—CH=N—) linkages in the backbone, and are known to exhibit good thermal stability and many desirable properties due to the resonance stabilization of poly Schiff's base unit.<sup>6</sup> Several investigations are made on the development of heat-resistant polymers such as polyesters,<sup>7,8</sup> polyethers,<sup>9</sup> polysiloxanes,<sup>10</sup> etc., containing azomethine linkages in the polymer backbone. A number of interesting studies on synthesis of polyurethanes containing azomethine groups have been reported.<sup>11–15</sup> However, a few of them studied the effect of the azomethine linkages on thermal stability.<sup>11,12</sup> In this article, we report the synthesis of new bisphenol-containing

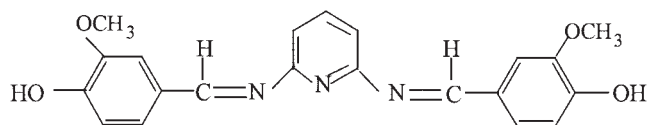
azomethine groups, with the expectation that they would result, on reaction with a various diisocyanates, in polyurethanes with considerably superior thermal properties.

## EXPERIMENTAL

### Materials

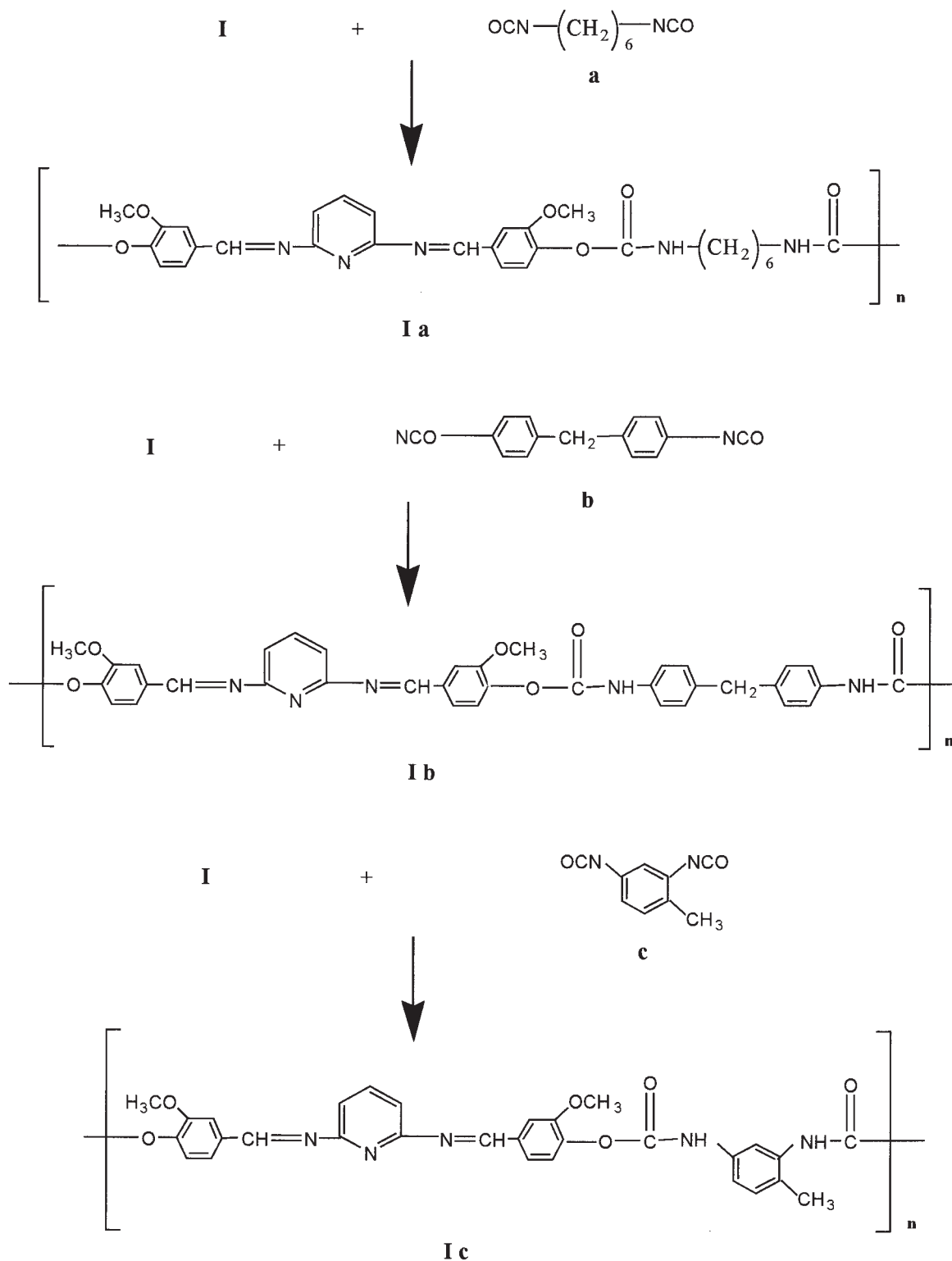
Methylene-4,4'-diphenyldiisocyanate (MDI), toluene-2,4-diisocyanate (TDI), and hexamethylene diisocyanate (HDI) from Aldrich Co. (Milwaukee, WI) were purified by distillation under reduced pressure. Dimethyl formamide (DMF) was distilled over calcium hydride (CaH<sub>2</sub>) before use. Vanillin and 2,6-diaminopyridine from Fluka Co. (Buchs, Switzerland) were used without further purification.

### Preparation of bisphenol *N,N'*-bis(4-hydroxyl-3-methoxy benzylidene)-2,6-diaminopyridine (**I**)



Vanillin (0.1 mol) was added dropwise to solution of 2,6-diaminopyridine (0.05 mol) in absolute ethanol. The mixture was refluxed for 6 h with stirring in a 500-mL flask during the reaction. The product was precipitated, filtered, washed several times with diethylether, and dried. Final purification was carried out by recrystallization from DMF/1-butanol (1 : 1) to give dark brown crystals, m.p. 300°C dec.

Correspondence to: A.M. Issam (issam@usm.my).  
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Scheme 1

Yield was 70%. FTIR (KBr disc):  $3377\text{ cm}^{-1}$  (OH stretch.),  $1613\text{ cm}^{-1}$  (C=N stretch.).  $^1\text{H-NMR}$  data (DMSO- $d_6$ ),  $-\text{CH}=\text{N}$ , 8.60 ppm ( $2 \times 1$ ) s. Elemental analysis: Found: C, 66.58; H, 5.33; N, 11.42,  $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_4$  Calc.: C, 66.84; H, 5.03; N, 11.14. Mass spectrum, Found: 377, Calc.: 377.

#### Preparation of polymers

General polymerization equations and structures are given in Scheme 1. Diisocyanate (0.011 mol) in 25 mL of DMF was added to a solution of bisphenol (0.01 mol) in DMF at  $60^\circ\text{C}$  for 1 h under constant stirring

TABLE I  
Yields, Inherent Viscosity, and Elemental Analysis of Polyurethanes I(a–c)

Polymer	Yield (%)	Inherent viscosity <sup>a</sup> (dL/g)	C (%)	H (%)	N (%)
Ia	61	0.185	64.51 (63.85)	5.55 (5.58)	11.89 (12.84)
Ib	65	0.162	68.11 (68.89)	5.48 (4.62)	11.18 (11.16)
Ic	59	0.208	64.49 (65.33)	4.80 (4.53)	12.62 (12.70)

<sup>a</sup> Measured in 97% sulfuric acid.

<sup>b</sup> Data in parentheses are calculated values.

under nitrogen. Subsequently, the temperature of the reaction mixture was increased to 140°C for 24 h. The polyurethanes I(a–c) thus prepared were precipitated in distilled water, filtered, and washed several times with distilled water, and finally with methanol. The purified sample was dried for 24 h in a vacuum oven at 75°C. The results are summarized in Table I.

### Instrumentation

FTIR spectrophotometric measurements measured in Perkin–Elmer 2000 using KBr pellet for polymers and monomers ranged from 4000 to 400 cm<sup>-1</sup>. <sup>1</sup>H-NMR spectra were obtained using Bruker 400 MHz NMR spectrometer, using DMSO-d<sub>6</sub> as the solvent and TMS as the internal reference. The UV–vis spectra of the polymers in concentrated 97% H<sub>2</sub>SO<sub>4</sub> were recorded with a Hitachi U-2000 spectrophotometer. The mass analysis was made on a LKB 9000 spectrometer; the energy of the electron beam was 70 eV and the source temperature was 290°C. Thermogravimetric analysis (TGA) was carried out in oxygen atmosphere with Perkin–Elmer TGA7 series at 20°C min<sup>-1</sup>. Differential scanning calorimetry (DSC) measurements were carried out with a Perkin–Elmer DSC7 series at heating rate of 20°C min<sup>-1</sup> in nitrogen. Inherent viscosities of polymers solutions (0.2 dL/g in 97% H<sub>2</sub>SO<sub>4</sub>) were determined at 30°C in an Ubbelohde viscometer. The X-ray diffractograms were recorded using Siemens Model D-5000 Diffractometer at room temperature with nickel-filtered Cu K $\alpha$  radiation.

## RESULTS AND DISCUSSION

### Structural characterization of bisphenol I

The structure of bisphenol (I) was confirmed by elemental analysis, FTIR, <sup>1</sup>H-NMR, UV, and mass spectroscopy. The characteristic FTIR absorption band of azomethine (—CH=N—) group is found at 1613 cm<sup>-1</sup>; other absorption bands are due to the aromatic ring at 1513 cm<sup>-1</sup> and phenolic hydroxyl (Ph—OH) group at 3377 cm<sup>-1</sup>. The chemical structure of bisphenol (I) in DMSO-d<sub>6</sub> was analyzed by <sup>1</sup>H-NMR spectrum is shown in Figure 1. Two characteristic broad peaks at  $\delta$  = 8.60 and 4.86 ppm are assigned to the proton in azomethine (—CH=N—) group and the

proton in the phenolic hydroxyl (Ph—OH) group, respectively. A singlet peak at 3.86 ppm is due to the protons in the methoxy (—OCH<sub>3</sub>) group. The two  $\beta$  protons of the pyridine ring resonated at 6.42 ppm as broad peaks and the  $\gamma$  proton resonated at 7.4 ppm. A multiplet at  $\delta$  = 6.97–7.42 ppm is attributed to the hydrogen atoms in the aromatic rings.

In the UV spectrum, three bands can be found for bisphenol (I) (298, 370, and 537). The value of  $\lambda_{\max}$  is 537. The results of elemental and spectroscopic analyses confirmed the structure of bisphenol.

### Structural characterization of polymers

The polymers were characterized by FTIR, <sup>1</sup>H-NMR, and elemental analysis. FTIR spectrum of polyurethane Ic in Figure 2 displayed band at 1668 cm<sup>-1</sup> attributed to the carbonyl group in the urethane linkage, and at 3345 cm<sup>-1</sup> due to the N—H stretching. In addition, the absorption bands at 1513 and 1610 cm<sup>-1</sup> are due to the aromatic and azomethine groups, respectively. The <sup>1</sup>H-NMR spectrum of polymer Ib in Figure 3 displayed two characteristic singlet peaks at 10.0 and 8.6 ppm, due to the protons in urethane —NHCOO— and —CH=N— groups, respectively. Two characteristic singlet peaks at 3.82 and 3.7 ppm are assigned to the protons in methoxy —OCH<sub>3</sub> and the protons in methyl Ph—CH<sub>2</sub>—Ph groups of the urethane linkage, respectively. A doublet at 6.48 ppm is due to the proton in  $\gamma$ -position of pyridine ring. A multiplet at 7.3–6.85 ppm is due to the protons of the benzene rings. The results of (CHN) elemental analysis of polyurethanes (Table I) are in good agreement with the structural formulas.

The UV spectra of polymers I(a–c) exhibit four absorption bands. The general chromophore units in the bisphenol I are extended by conjugation via the urethane linkage, —O—CO—NH—. The urethane linkage containing unpaired electrons on oxygen and nitrogen atoms enabled many resonance structures resulting in pseudoconjugation.

### Properties of polymers

Thermal stability and degradation of polyurethanes I(a–c) were analyzed based on the thermograms ob-

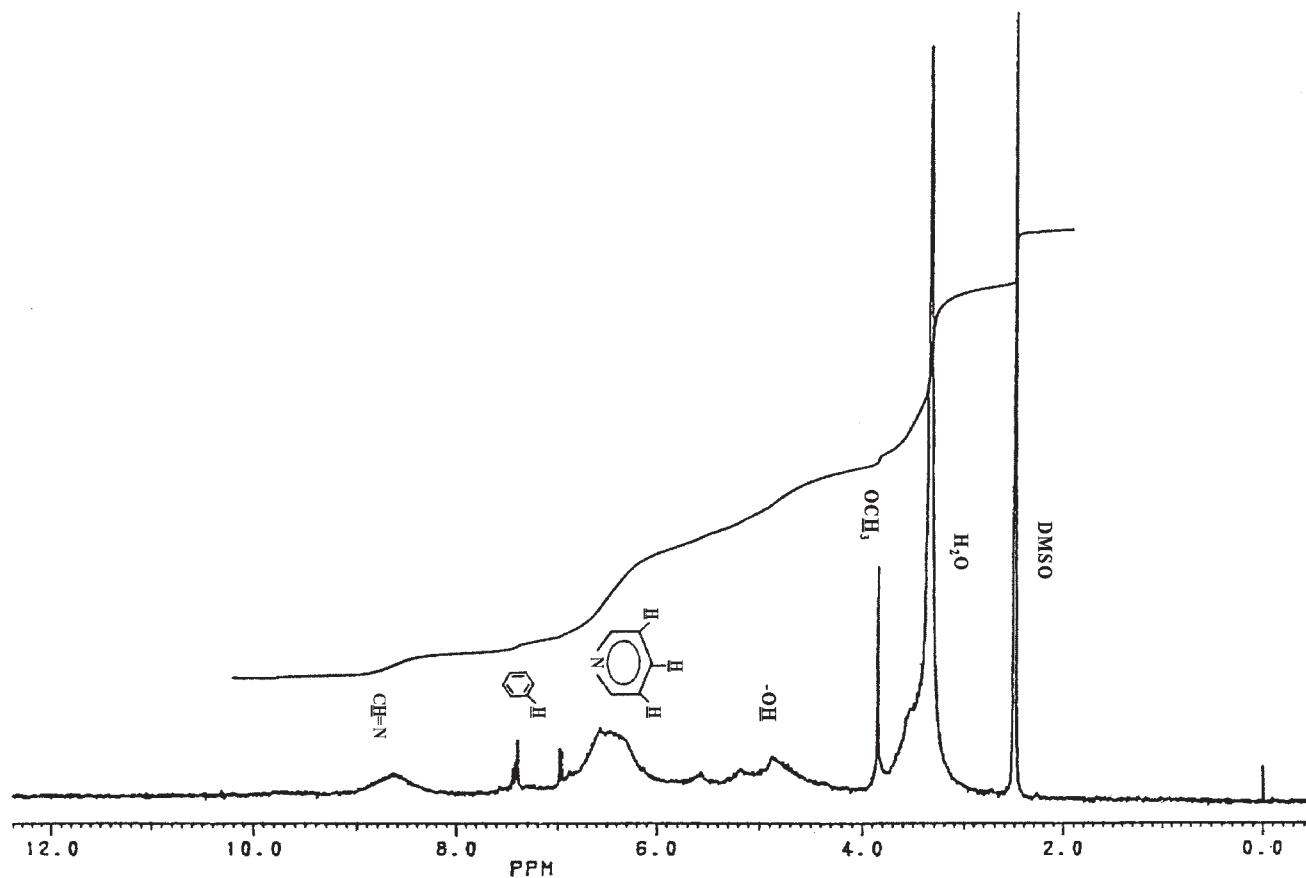


Figure 1  $^1\text{H-NMR}$  spectrum of bisphenol I in  $\text{DMSO-d}_6$ .

tained from TGA at a constant heating rate of  $20^\circ\text{C min}^{-1}$  in the temperature range of  $40^\circ\text{C}$  to  $600^\circ\text{C}$  under nitrogen and oxygen atmosphere. Equal weights were used in all experiments to eliminate the mass effects.

Enhancement of thermal stability of the polyurethanes observed in the present studies can be attributed to the delocalization characteristic of azomethine

linkage. This is similar to what has been reported by earlier investigation<sup>16</sup> on the effect of the presence of these groups conferring thermal stability in aromatic polyester. The results imply that the presence of azomethine linkage in the backbone of polyurethane is necessary to produce a high thermal stability and high yield of residue. The temperature required for 10% degradation ( $T_{10}$ ) and the amount of char formed at

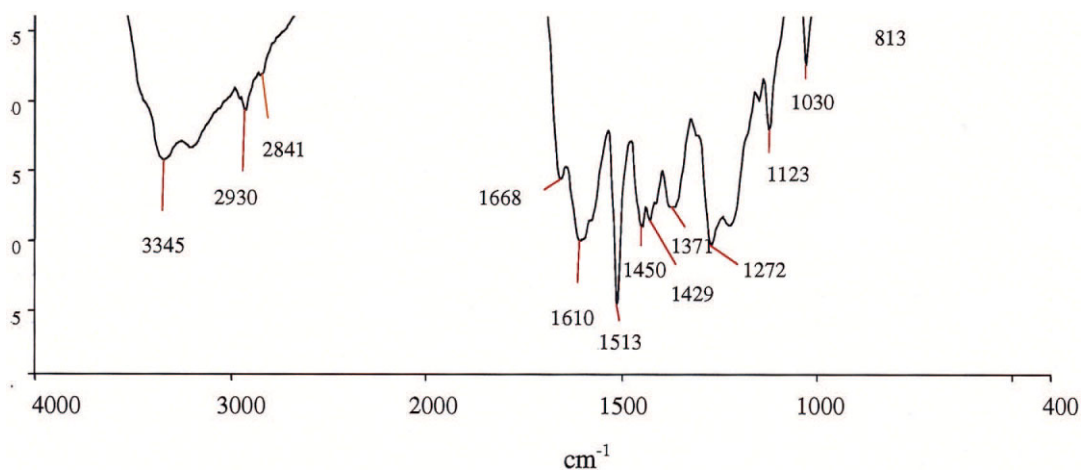


Figure 2 FTIR spectrum of polyurethane Ic. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

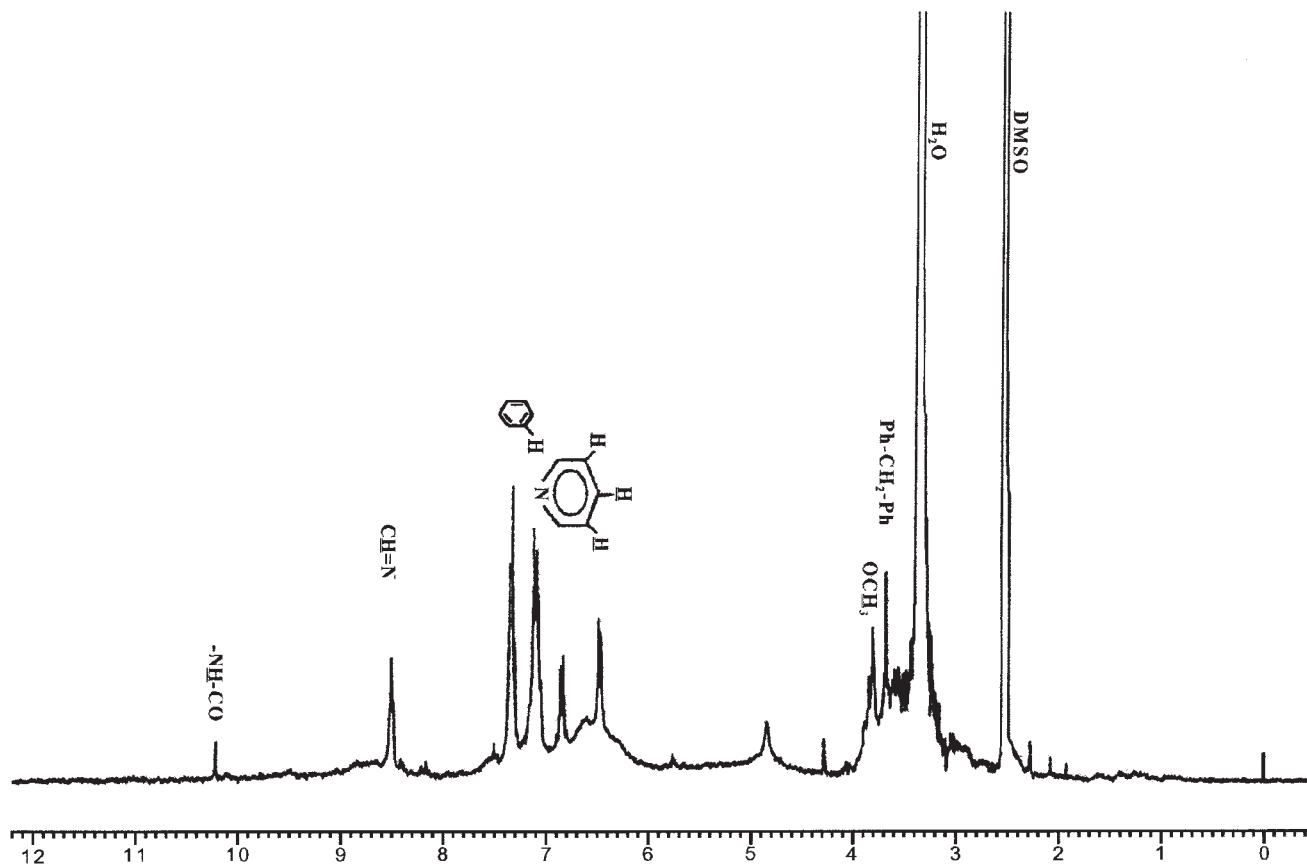


Figure 3  $^1\text{H-NMR}$  spectrum of polyurethane **Ib** in  $\text{DMSO-d}_6$ .

600°C are summarized in Table II and their decomposition behavior in nitrogen atmosphere are shown in Figure 4. The onset temperature of thermal degradation (OTD) of polyurethanes **I(a-c)** occurs at 220°C to 250°C and this is due to the cleavage of urethane linkage.<sup>17</sup> The maximum rate of degradation ranged from 320°C to 430°C, which is due to the oxidation of residual aromatic azomethine moiety, starting from 320°C to 332°C and continued up to 450°C.

With regard to the influence of the diisocyanates structure on the thermal stability based on  $T_{10}$  values, it has been observed that polyurethane based on MDI is the more stable than those based on TDI and HDI. This observation is attributed to the high symmetry of

the diphenyl methane unit in MDI (that means extended conjugation and strong intermolecular interactions) as compared to polyurethanes based on TDI and HDI. Similar observation has been reported previously.<sup>12</sup> A dramatic change in the structure leads to a dramatic enhancement in thermal stability. Such an enhancement is attributed to the effect of extended conjugation arising from aromatic and heteroaromatic (pyridine) with azomethine linkages. Poly(azomethine-urethane) is expected to have higher thermal stability than the corresponding polyurethanes without  $-\text{CH}=\text{N}-$  linkages. However, poly(azomethine-ester) and poly(azomethine-amide) analogues show

TABLE II  
Thermal Properties of Polyurethanes **I(a-c)**

Polymer	TGA, $T_d^a$ (°C)		Residue % at 600°C		DSC <sup>b</sup> (°C)		$T_g^c$
	In air	In nitrogen	In air	In nitrogen	First	Second	
<b>Ia</b>	322	325	33	56	205	n.d.	185
<b>Ib</b>	325	332	24	52	215	n.d.	n.d.
<b>Ic</b>	320	330	26	60	n.d.	n.d.	n.d.

<sup>a</sup> Decomposition temperature at 10% weight loss TGA.

<sup>b</sup> First and second heating run of DSC.

<sup>c</sup> Glass-transition temperature.

n.d., not detected.

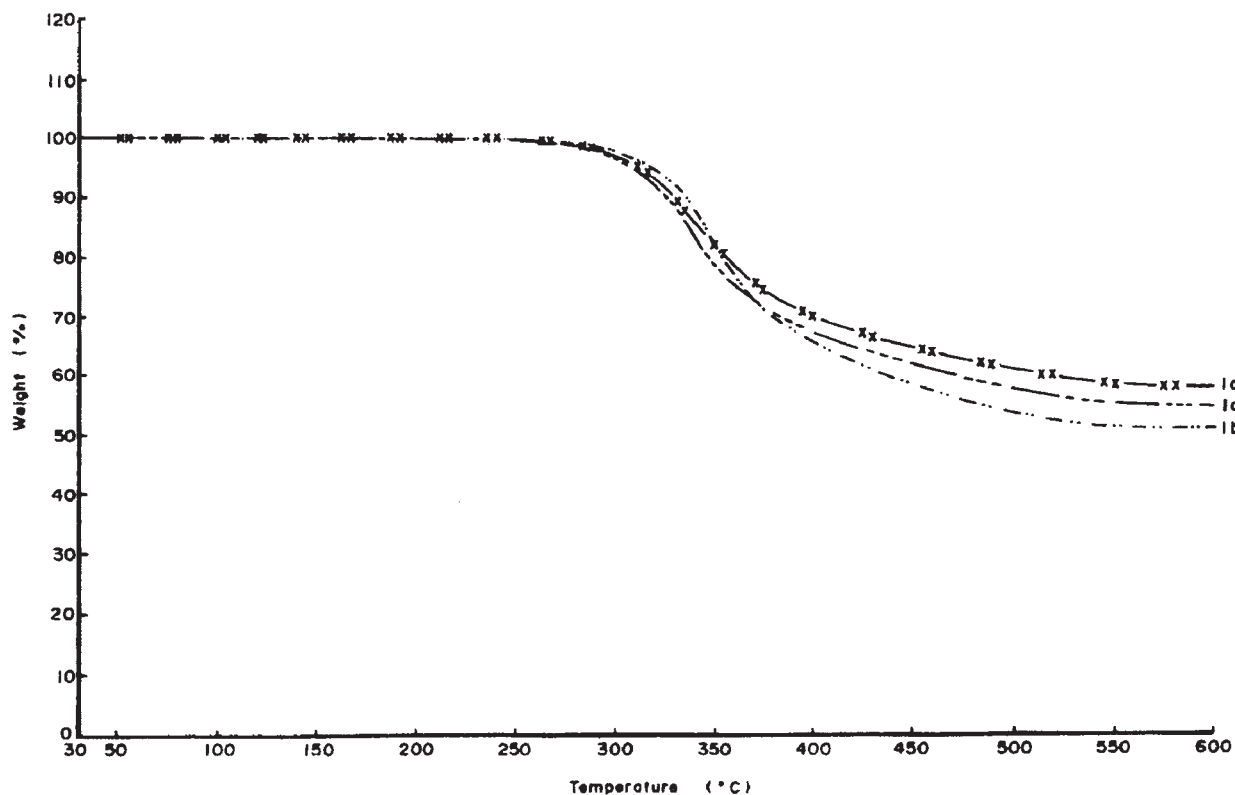


Figure 4 Thermogravimetric traces of polymers Ia-Ic.

higher thermal stability attributable to the additional groups of ester in the former and amide in the latter.

From DSC traces, single endothermic peak is observed during first heating in all polymers except Ic. No transition is observed during cooling or second heating. The glass-transition temperature,  $T_g$ , could not be detected probably due to the very small change in the specific heat. The phase behavior of polyurethanes investigated by optical microscopy revealed that all the polymers simply changes from solid to the isotropic fluid except Ic, which decomposed without prior melting.

The polyurethanes I(a-c) are soluble in 97%  $H_2SO_4$ , trifluoro acetic acid (TFA), and hot DMSO, whereas insoluble in common solvents such as methanol, methyl ethyl ketone, diethyl ether, and acetone. The solubility of these polymers, as compared to the completely insoluble poly(azomethine)s,<sup>18</sup> may be associated with the presence of only pseudoconjugation in the former as compared to the extended conjugation in the latter. The inherent viscosity values of polyurethanes I(a-c) (Table I) ranged between 0.15 and 0.31 dL/g, and were at least close to the reported values.<sup>12</sup>

The X-ray diffraction (WAXD) analyses of polyurethanes I(a-c) conducted at room temperature are shown in Figure 5. Apparent single or multiple diffraction peaks were observed in the range  $2\theta = 11^\circ$  to  $30^\circ$ , providing evidences of lateral distances between the neighboring chains. The results suggest a semic-

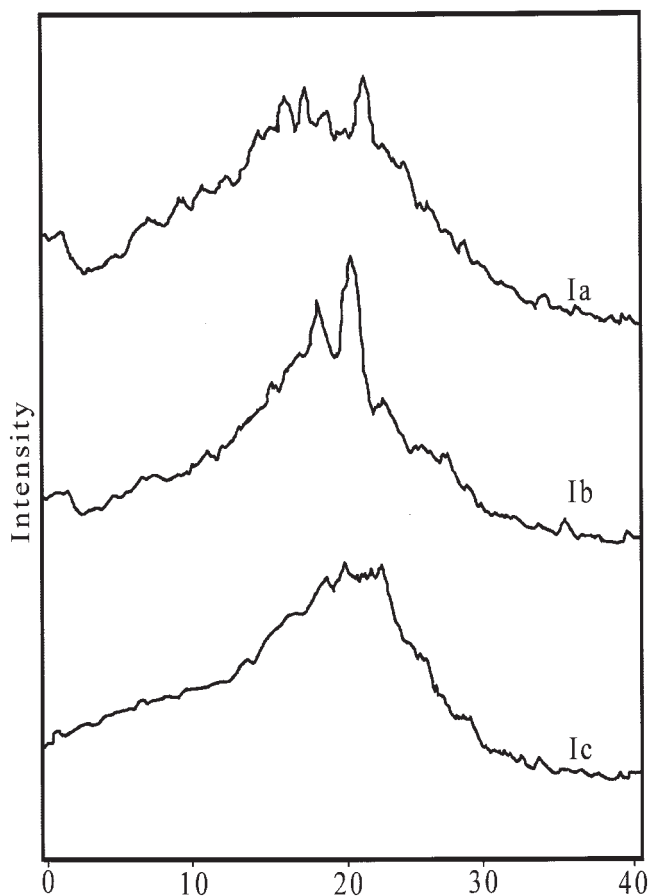


Figure 5 X-ray diffraction of polyurethanes Ia-Ic.

rystalline nature of polyurethanes **I(a,b)**. However, polyurethane **Ic** shows broad amorphous halo, indicating absence of crystallinity, probably an outcome of the strong hydrogen bonding in the polymers as has been explained elsewhere.<sup>19</sup>

### CONCLUSIONS

Three new polyurethanes have been successfully synthesized according to Scheme 1. Their structures were confirmed by CHN elemental analysis, FTIR, UV, and <sup>1</sup>H-NMR techniques. The results of TGA analysis showed that the polyurethanes possess good thermal stability under nitrogen and oxygen atmosphere. A semicrystalline nature is observed in all polyurethanes **I(a-c)**, as analyzed by X-ray diffraction, except for **Ic**.

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