

# Synthesis and Characterization of Novel Pyridine-Based Polyureas with Enhanced Solubility and High Thermal Stability

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Received 19 July 2011; accepted 24 November 2011

DOI 10.1002/app.36557

Published online in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** The main aim of this study was the preparation of modified polyureas with improved thermal stability and solubility. Accordingly, a series of aromatic/aliphatic pyridine-based polyureas was synthesized from the reaction of a novel diamine (DA) with different diisocyanates, including 4,4'-diphenylmethane diisocyanate, toluene diisocyanate, 1,5-naphthalene diisocyanate, and isophorone diisocyanate, by a solution polymerization route. The DA monomer was prepared via a two-step reaction. The nucleophilic substitution reaction of oxydianiline with 6-chloro-nicotinoylchloride led to the preparation of a diamide

dichloro compound, and the subsequent reaction of this compound with 4-aminophenol resulted in the preparation of the DA. After polymerization, the structural characterization and physical properties of the polymers were examined. The resulting polymers were soluble in common polar aprotic solvents, and they showed improved thermal stabilities in comparison with common polyureas. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** polymer synthesis and characterization; structure–property relations; thermal properties

## INTRODUCTION

Polyureas are one of the most important classes of high-performance polymers, and they have many uses in different industrial applications. They are unique polymers, with a broad range of physical and chemical properties, including abrasion resistance, water repellency, and leathery appearance. Polyureas are polyamides of carbonic acid, and like most conventional polyamides, they are suitable for elastomer and fiber applications because of their toughness and high melting point. Several methods have been reported for preparing polyureas, including the reaction of diamines (DAs) with phosgene, carbonate esters,<sup>1</sup> carbonate alkali metals,<sup>2</sup> carbon dioxides,<sup>3</sup> and ureas.<sup>4</sup> However, the best method includes the reaction of DAs with diisocyanates.

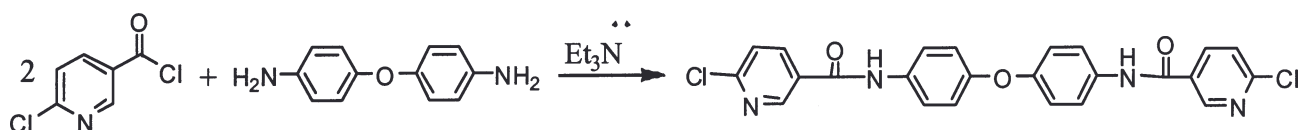
DAs are regularly used to cure diisocyanates, especially isocyanate prepolymers, to give polyureas; this is a step-growth addition reaction of amine across the carbon-nitrogen double bond.<sup>5–13</sup> The main advantages of this method are that polymerization can occur at a low temperature and that no byproducts are produced.

However, the uses of these polymers are limited by their poor solubility because of strong intermolecular hydrogen bonding. One approach for improving the solubility of the polymers without much sacrifice in their thermal properties is the introduction of bulky pendant groups; this reduces the molecular mobility so that the overall apparent effect is a simultaneous increase of the glass-transition temperature ( $T_g$ ) and improvement in the solubility.<sup>14–18</sup>

The introduction of polar and flexible groups, such as pyridine and ether linkages, along the polymer backbone is another important strategy for improving solubility. The objective for the selection of heterocyclic rings in the main chain of a synthetic polymer is to impart certain properties to the polymer. Among different heterocyclic rings, the advantage of using a pyridine nucleus is based on its high thermal stability, which is derived from its molecular symmetry and aromaticity. Also, the presence of nitrogen atoms in the structure produces a polarized bond, which improves the solubility of the prepared polymers because of increased dipole–dipole interactions in the polymer–solvent system. Therefore, the main advantage of using pyridine in the backbone of polymers is an increase in their solubility with the thermal stability maintained.<sup>19,20</sup>

In this article, we report and describe the preparation of a novel, pyridine-based, flexible DA containing ether and amide units and also resulting in new thermally stable polyureas with enhanced solubility.

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Scheme 1 Preparation of DC.

The physical properties of the polymers, including their inherent viscosity, solubility behavior, thermal properties, thermal stability, and crystallinity, were studied, and the structure–property relationships were investigated.

## EXPERIMENTAL

### Materials

All of the needed chemicals were purchased either from Merck or Aldrich Chemical Co (a local supplier in Tehran, Iran). *N*-Methyl-2-pyrrolidone (NMP) and toluene were dried over  $\text{CaH}_2$ , distilled under reduced pressure, and stored over a molecular sieve. Oxydianiline (ODA), 6-chloronicotinoylchloride, triethylamine ( $\text{Et}_3\text{N}$ ), 4-aminophenol (4-AP),  $\text{K}_2\text{CO}_3$ , and NaOH were used as received. *N,N*-Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N,N*-dimethyl acetamide (DMAC), *m*-cresol, tetrahydrofuran (THF), toluene diisocyanate (TDI), and isophorone diisocyanate (IPDI) were purified by distillation. 1,5-Naphthalene diisocyanate (NDI) was sublimed before use.

### Instruments

Infrared measurements were performed on a Bruker IFS 48 Fourier transform infrared (FTIR) spectrometer (Ettlingen, Germany). The  $^1\text{H-NMR}$  spectra were recorded in hexadeuterated dimethyl sulfoxide ( $\text{DMSO-}d_6$ ) solution with a Bruker Avance DPX 400-MHz instrument. The mass spectrum was recorded on a Shimadzu GCMS-QP 1100-EX (Tokyo, Japan). Elemental analyses were performed by a CHN—O—Rapid Heraeus elemental analyzer (Wellesley, MA). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780 (London, United Kingdom) from 25 to 300 and 25 to 600°C, respectively. The melting points were determined in open capilla-

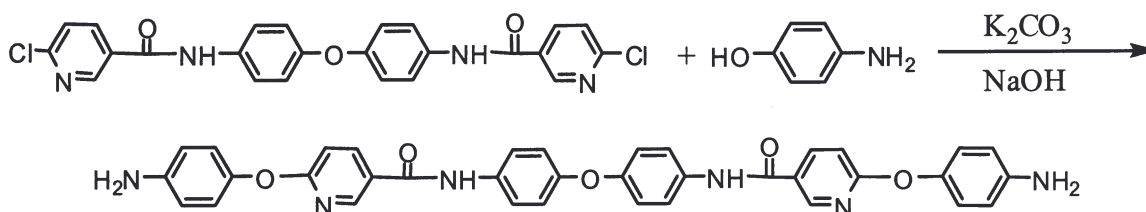
ries with a Buchi 535 instrument (Zurich, Switzerland). The inherent viscosities were measured at a concentration of 0.5 g/dL in DMF at 30°C with an Ubbelohde viscometer (a local supplier in Tehran, Iran). The weight-average molecular weight ( $M_w$ ) and the number-average molecular weight ( $M_n$ ) were determined by gel permeation chromatography (GPC). GPC was performed at 30°C on a Waters 150-C instrument with Styragel columns and a differential refractometer detector (Wellesley, MA). The molecular weight calibration was carried out with polystyrene standards. Calibration and measurements were made at a flow rate of 1 mL/min, and DMF was used as the solvent. Wide-angle X-ray diffraction patterns were obtained at room temperature on an X-ray diffractometer (Siemens, model D 5000, Karlsruhe, Germany) with Ni-filtered Cu  $K\alpha$  radiation (40 kV, 25 mA) at a scanning rate of 3°/min.

### Monomer synthesis

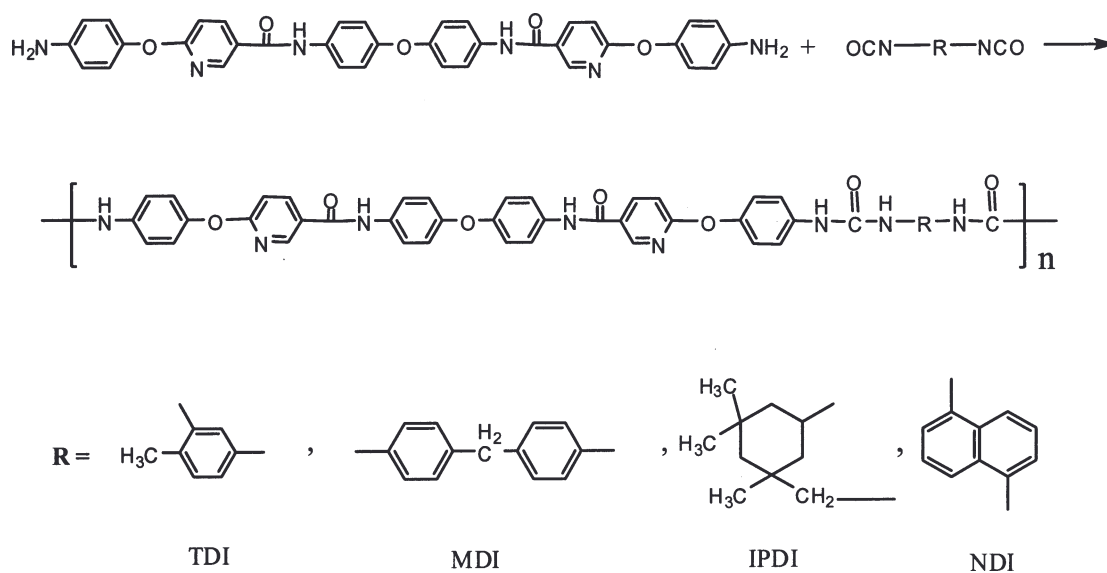
#### Synthesis of the dichloro compound (DC)

A two-necked, round-bottom flask equipped with a nitrogen inlet tube, magnetic stirrer, calcium chloride drying tube, and ice bath was charged with a solution of 3 mmol (0.62 g) of ODA and 30 mL of dry NMP. The mixture was stirred at 0°C for 0.5 h. Then, 19 mL of triethylamine ( $\text{Et}_3\text{N}$ ) and, after 3 min, 6.3 mmol (1.14 g) of 6-chloronicotinoylchloride were added, and the mixture was stirred at 0°C for 0.5 h. The temperature was raised to room temperature, and the solution was stirred for 8 h. Finally, we precipitated the product by pouring the flask contents into 300 mL of water. Then, it was filtered, washed with hot water and methanol, and dried overnight *in vacuo* at 80°C. The yield was 86%.

DC IR ( $\text{KBr}$ ,  $\text{cm}^{-1}$ ): 3237–3400 (N—H), 1645 (C=O), 1450–1600 (C=C), 1226 (—O—).  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ ,  $\delta$ , ppm): 7.03 (dd, 4H, benzene), 7.70 (d, 2H, py), 7.77 (dd, 4H, benzene), 8.36 (dd, 2H, py),



Scheme 2 Preparation of DA.



**Scheme 3** Preparation of the polyureas.

8.94 (d, 2H, py), 10.50 (s, 2H, amide). ANAL. Calcd for  $C_{24}H_{16}N_4O_3Cl_2$ : C, 60.12%; H, 3.34%; N, 11.69%. Found: C, 60.21%; H, 3.45%; N, 11.60%. Mass spectrum: Mass/charge ratio ( $m/e$ ) = 482. mp > 300°C.

#### Synthesis of the DA monomer

DC (2 mmol, 0.958 g), 4-AP (5.0 mmol, 0.558 g), 10 mL of NMP, 6 mL of dry toluene for azeotropic distillation, and 8.7 mmol (1.21 g) of  $K_2CO_3$  were placed into a 100 mL, two-necked, round-bottom flask equipped with a Dean-Stark trap, a condenser, a stirrer bar, a thermometer, an oil bath, and a nitrogen inlet tube. The mixture was heated at 140°C for 6 h, and then, the mixture was heated to 165°C and kept at this temperature for about 21 h. After this time, the product was precipitated in a mixture of water and 5% NaOH solution. Then, it was filtered and washed with hot water and methanol and dried overnight *in vacuo* at 80°C. The yield was 85%. DA IR (KBr,  $cm^{-1}$ ):  $\nu$  3358–3400 (N–H), 1658 (C=O), 1471–1599 (C=C), 1235, 1198 (–O–).  $^1H$ -NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 5.04 (s, 4H, amine), 6.58 (d, 4H, benzene), 6.81 (d, 4H, benzene), 6.95 (d, 2H, py), 6.99 (d, 4H, benzene), 7.72 (d, 4H, benzene), 8.26 (d, 2H, py), 8.66 (s, 2H, py), 10.25 (s, 2H, amide). ANAL. Calcd for  $C_{36}H_{28}N_6O_5$ : C, 69.23%; H, 4.49%; N, 13.46%. Found: C, 69.09%; H, 4.56%; N, 13.62%. Mass spectrum:  $m/e$  = 624. mp > 300°C.

#### Polyurea synthesis

The synthesis of the polyureas was typically carried out as follows: into a two-necked, round-bottom flask equipped with a nitrogen inlet tube, a thermometer, a condenser, and an oil bath, a solution of 5 mmol (3.12 g) of DA in 10 mL of dry NMP was

stirred for a few minutes. Subsequently, a solution of 5 mmol of diisocyanate (e.g., 0.87 g for TDI) in 10 mL of dry NMP was added to the mixture. The reaction mixture was stirred at room temperature for about 1 h, and then, the temperature was raised to 60°C for about 2 h. For precipitation of the polymer, the reaction mixture was poured into distilled water. It was then filtered and washed with hot water and methanol. Then, it was vacuum-dried at 100°C (yield > 78%).

## RESULTS AND DISCUSSION

The main goal of this study was the preparation of modified thermally stable polyureas with improved solubility. A new interesting class of pyridine-based polyureas containing diaryl ether and amide units in the polymer backbone was synthesized. In this way, the design and synthesis of a new monomer and the resulting polyureas with structural modifications were considered. These modifications included (1) the incorporation of flexible or kinked linkages in the backbone, (2) the introduction of a heterocyclic ring along the polymer backbone, and (3) the introduction of an amide group in the main chain.

A new DA was prepared through two successive reactions. In the first step, a DC was prepared by

**TABLE I**  
Elemental Analysis of the Polyureas

Polymer	Yield (%)	Calcd			Found		
		C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
DA–NDI	88	69.06	4.08	13.43	68.90	3.93	13.65
DA–MDI	85	70.03	4.35	12.81	69.89	4.52	12.66
DA–TDI	87	67.67	4.26	14.04	67.38	4.39	13.91
DA–IPDI	86	68.08	5.44	13.24	67.95	5.31	13.42

**TABLE II**  
Characterization Data of the Polymers

Polymer	IR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR (ppm)
DA-NDI	3180–3210 (NH, amide/NH, urea) 1652 (C=O, amide) 1648 (C=O, urea) 1596 (NH, CN) 1470–1497 (C=C, Ar) 1197 (C–O)	10.30 (NH, s, 2H), 8.73 (Py, s, 2H), 8.65 (NH, s, 2H) 8.58 (NH, s, 2H), 8.34 (Py, d, 2H), 7.77 (Bz, d, 4H), 7.59 (Na, d, 2H), 7.48 (Bz, d, 4H), 7.40 (Na, d, 2H), 7.10 (Bz, d, 4H), 7.06 (Bz, d, 4H), 6.99 (Na, d, 2H) 7.01 (Py, d, 2H)
DA-MDI	3307–3125 (NH, amide/NH, urea) 1652 (C=O, amide) 1648 (C=O, urea) 1596 (NH, CN) 1470–1497 (C=C, Ar) 1197 (C–O)	10.29 (NH, s, 2H), 8.72 (Py, s, 2H), 8.63 (NH, s, 2H) 8.57 (NH, s, 2H), 8.33 (Py, d, 2H), 7.76 (Bz, d, 4H) 7.58 (Bz, d, 4H), 7.47 (Bz, d, 4H), 7.23 (Bz, d, 4H), 7.08 (Bz, d, 4H), 7.06 (Bz, d, 4H) 7.01 (Py, d, 2H), 3.83 (CH <sub>2</sub> , s, 2H)
DA-TDI	3270–3400 (NH, amide/NH, urea) 1654 (C=O, amide) 1646 (C=O, urea) 1599 (NH, CN) 1471–1498 (C=C, Ar) 1198 (C–O)	10.27 (NH, s, 2H), 8.70 (Py, s, 2H), 8.60 (NH, s, 2H) 8.54 (NH, s, 2H), 8.31 (Py, d, 2H), 8.01 (Bz, s, 1H) 7.75 (Bz, d, 4H), 7.43 (Bz, d, 4H), 7.32 (Bz, d, 1H) 7.21 (Bz, d, 1H), 7.05 (Bz, d, 4H), 7.02 (Bz, d, 4H), 6.99 (Py, d, 2H), 2.12 (CH <sub>3</sub> , s, 3H)
DA-IPDI	3150–3368 (NH, amide/NH, urea), 1652 (C=O, amide), 1650 (C=O, urea) 1596 (NH, CN), 1471–1498 (C=C, Ar) 1198 (C–O)	10.26 (NH, s, 2H), 8.68 (Py, s, 2H), 8.58 (NH, s, 2H) 8.51 (NH, s, 2H), 8.29 (Py, d, 2H), 7.74 (Bz, d, 4H) 7.38 (Bz, d, 4H), 7.03 (Bz, d, 4H), 7.01 (Bz, d, 4H) 6.97 (Py, d, 2H), 3.56 (CH, q, 1H), 3.23 (CH <sub>2</sub> , s, 1H) 2.98 (CH <sub>2</sub> , s, 1H), 1.72 (CH, d, 2H), 1.47 (CH, d, 2H) 1.41 (CH <sub>2</sub> , s, 1H), 1.16 (CH <sub>2</sub> , s, 1H), 1.05 (CH <sub>3</sub> , s, 3H) 0.99 (CH <sub>3</sub> , s, 6H)

the nucleophilic reaction of ODA with 6-chloronicotinoylchloride (Scheme 1), and in the second step, the DC was reacted with 4-AP to prepare the DA (Scheme 2).

The novel, pyridine-based DA was prepared in such a way that it contained a diaryl ether unit to increase solubility of the polymers. In addition, the incorporation of rigid phenyl and amide groups were considered to increase the thermal stability properties of the final polyureas (Scheme 3). The structures of the DC and DA were characterized and confirmed by common spectroscopic methods, including FTIR, <sup>1</sup>H-NMR, and mass spectroscopy.

Polyaddition reactions of four different diisocyanates, including TDI, 4,4'-diphenylmethane diisocyanate (MDI), IPDI, and NDI, in dry NMP with the DA afforded the polyureas. As mentioned previously, the reaction of DA with diisocyanate is the best method for preparing polyureas because of the

**TABLE III**  
Solubilities of the Polyureas

Polymer	NMP	DMAC	DMF	DMSO	<i>m</i> -Cresol	THF	CHCl <sub>3</sub>
DA-NDI	+	+	+	+	±	–	–
DA-MDI	+	+	+	+	±	–	–
DA-TDI	+	+	+	+	+	±	–
DA-IPDI	+	+	+	+	+	±	±

+, Soluble by heating; ±, partially soluble by heating; –, insoluble.

**TABLE IV**  
Viscosity and Molecular Weight Values of the Polymers

Polymer	Inherent			
	viscosity (dL/g) <sup>a</sup>	<i>M<sub>w</sub></i> <sup>b</sup>	<i>M<sub>n</sub></i>	PDI <sup>c</sup>
DA-NDI	0.57	47,000	36,200	1.30
DA-MDI	0.61	49,800	40,500	1.23
DA-TDI	0.58	48,000	38,400	1.25
DA-IPDI	0.60	48,600	39,600	1.23

<sup>a</sup> Measured at a concentration of 0.5 g/dL in DMF at 30°C.

<sup>b</sup> According to GPC measurement (g/mol).

<sup>c</sup> PDI, polydispersity index.

**TABLE V**  
Thermal Properties of the Prepared Polyureas

Polymer	<i>T<sub>g</sub></i> <sup>a</sup> (°C)	<i>T<sub>0</sub></i> <sup>b</sup> (°C)	<i>T<sub>10</sub></i> <sup>c</sup> (°C)	<i>T<sub>max</sub></i> <sup>d</sup> (°C)	CY at 600°C <sup>e</sup>
DA-NDI	202	247	360	402	46
DA-MDI	196	242	351	395	44
DA-TDI	190	230	342	382	42
DA-IPDI	179	210	330	369	40

<sup>a</sup> Obtained from DSC.

<sup>b</sup> From TGA.

<sup>c</sup> Determined in an air atmosphere from TGA.

<sup>d</sup> *T<sub>max</sub>*, maximum decomposition temperature determined in an air atmosphere from TGA.

<sup>e</sup> CY, char yield calculated as the percentage of solid residue after heating from room temperature to 600°C in an air atmosphere from TGA.



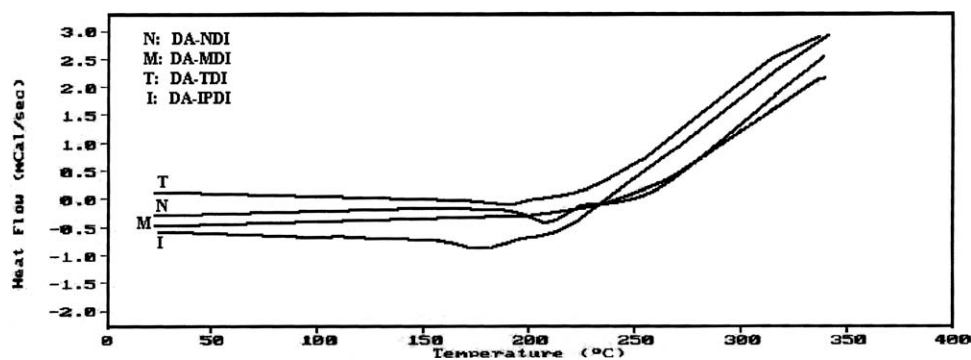


Figure 1 DSC curve of the polymers.

low-temperature polymerization reaction and the lack of byproducts.<sup>5–13</sup>

The structures of these polyureas were confirmed by elemental analysis (Table I). The CHN analysis of the polyureas was in good agreement with the calculated values. Their structures were also confirmed by spectral analysis, including FTIR and <sup>1</sup>H-NMR spectroscopy (Table II).

The solubility of all of the synthesized polyureas in various dipolar aprotic solvents, including DMF, DMSO, DMAC, and NMP, and even in less polar solvents, such as *m*-cresol, THF, and CHCl<sub>3</sub>, was examined. Their solubility in NMP, DMAC, DMF, DMSO, and *m*-cresol at 60°C were in the range 2.5–2.9 g/dL; this could be considered good solubility in dipolar aprotic solvents. The improved solubility was mainly attributed to the presence of flexible ether linkages and pyridine rings in the polymer backbone. It has been generally recognized that aromatic ether linkages inserted into aromatic main chains provide them with a significantly lower energy of internal rotation. Such a structural modification directs toward lower  $T_g$  and crystalline–melting temperatures as well as major improvements in the solubility and other processing characteristics of the polymers without great sacrifice of other valuable polymer properties. Also, the presence of nitrogen atoms (pyridine units) in the backbone of the polymer creates a polarized bond, which enhances the solubility of the prepared polymers because of increased dipole–dipole interactions in the polymer–solvent system.<sup>19–22</sup>

The presence of an alkyl group in the semiaromatic polyureas derived from aliphatic diisocyanate (IPDI) caused an increase in the solubility in comparison to the other aromatic polyureas. The solubility behaviors of the polymers in different solvents are summarized in Table III.

GPC and inherent viscosity measurements were used to estimate the molecular weights of the polymers, and according to the results, the polyureas showed reasonable molecular weights.  $M_n$  and  $M_w$  values of the polymers, on the basis of the GPC

method, were in the ranges 36,200–40,500 and 47,000–49,800, respectively. The inherent viscosity of the polymers in DMF at a concentration of 0.5 g/dL at 30°C was about 0.57–0.61 dL/g. These results are collected in Table IV.

The thermal behaviors and properties of the polymers were studied in air at a heating rate of 10°C/min with the DSC and TGA techniques. The thermal behavior data of these polymers are listed in Table V. The  $T_g$  values of the polymers were about 179 and 202°C according to DSC (the midpoint of the change in the slope of the baseline) techniques. TGA in air at a heating rate of 10°C/min was used to evaluate the thermal stability. The initial decomposition temperatures ( $T_0$ ) of the polyureas were about 210–247°C. The temperature for 10% gravimetric loss ( $T_{10}$ ), which is an important criterion for the evaluation of thermal stability, was in the range 330–360°C, and also, the char yields of the polymers at 600°C were about 40–46%. The high thermal stability could be related to the incorporation of preformed amide groups and the phenylation of the backbone. The symmetry of the structures and the avoidance of weak linkages, in addition to a stable pyridine heterocyclic ring, were the most important factors in

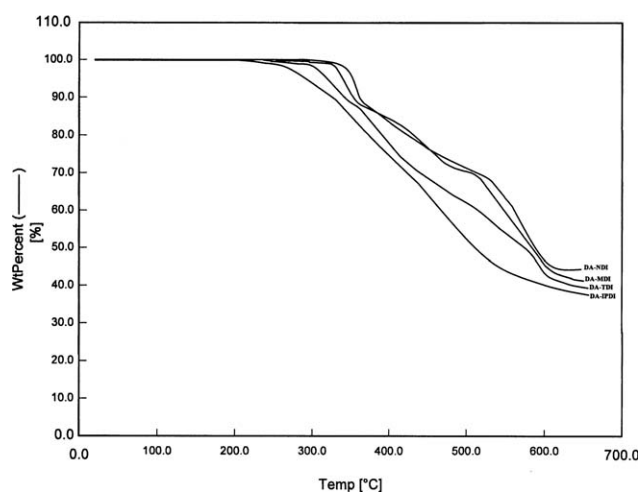


Figure 2 TGA curve of the polymers.

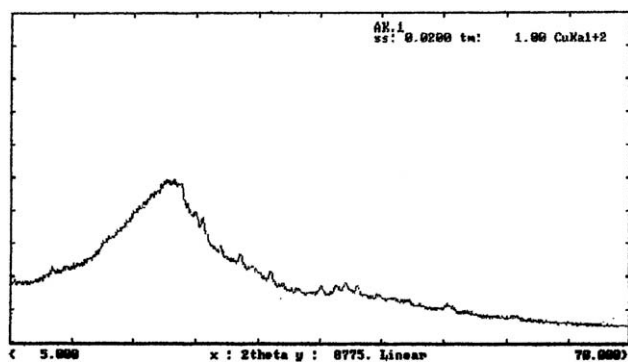


Figure 3 Wide-angle X-ray diffraction of DA-MDI.

improving the thermal properties. They caused an increase in the growth of the molecular weights, interactions, and close packing of the final polymer chains and, therefore, improved the thermal properties of the polymers.<sup>23–28</sup>

The IPDI-based polyurea showed the lowest thermal stability, and the NDI-based polyurea revealed the highest thermal stability among the prepared polymers. This was related to the higher rigidity of the NDI-based polyurea with respect to the other polyureas. The representative DSC and TGA curves of the polymers are shown in Figures 1 and 2, respectively.

Wide-angle X-ray diffraction patterns in the region  $2\theta = 5\text{--}70^\circ$  at room temperature were studied to estimate the crystallinity in the polyureas. Accordingly, the polymers were almost amorphous, and a representative wide-angle X-ray diffractogram of the polymers is shown in Figure 3.

## CONCLUSIONS

A novel DA was prepared and characterized via a two-step reaction. The reaction of ODA with 6-chloronicotinoylchloride resulted in the preparation of DC. The resulting pyridine-based DC was reacted with 4-AP to afford the novel DA. The solution polyaddition reaction with NMP as a solvent was successfully achieved to prepare new polyureas from the reactions of the new pyridine-based DA with four different diisocyanates. These polymers showed a nice balance of properties, including improved solubility and high thermal stability. The incorporation of ether, amide, pyridine, and bulky groups were

significant structural modifications in the preparation of these polyureas.

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