

Direct Synthesis of New Soluble and Thermally Stable Poly(urethane-imide)s from an Imide Ring-Containing Dicarboxylic Acid Using Diphenylphosphoryl Azide

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ABSTRACT: The direct preparation of various aromatic poly(urethane-imide)s from 4-*p*-biphenyl-2,6-bis(4-trimellitimidophenyl)pyridine (**1**) using diphenylphosphoryl azide (DPPA) was investigated. The polymers were mainly obtained by the conversion of imide ring-containing diacid **1** to corresponding di(carbonyl azide) **2** with DPPA and then to diisocyanate **3** through the Curtius rearrangement of compound **2** followed by polyaddition of **3** in different amounts with aromatic dihydroxy compounds. The molecular weights of the resulting poly(urethane-imide)s were evaluated viscometrically. All of the resulted polymers were thoroughly characterized by spectroscopic methods and elemental analyses. The poly(urethane-imide)s exhibited an excel-

lent solubility in a variety of polar solvents. Crystallinity nature of the polymers was estimated by means of WXR. The glass-transition temperatures of the polymers determined by DSC method were in the range of 191–202°C. The 10% weight loss temperatures of the poly(urethane-imide)s from their thermal gravimetric analysis curves were found to be in the range of 392–416°C in nitrogen. The films of the resulting polymers were also prepared by casting the solution. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 869–877, 2006

Key words: direct polycondensation; poly(urethane-imide)s; inherent viscosity; diphenylphosphoryl azide

INTRODUCTION

Diisocyanates are widely used as initial monomers for the preparation of various kinds of polymers.^{1–4} The commercial use of the most diisocyanates is often limited because of their poor stability, and in fact, these compounds are very susceptible to deterioration during storage.⁵ In the field of polymeric materials, one approach to solving this problem is to employ di(carbonyl azide) precursors as starting monomers in stead of diisocyanates for direct synthesis of them. In 1983, Ghatge and Jadhav reported the synthesis of *m*- and *p*-hydroxyethoxy benzoyl azides, and the direct polymerization of these monomers to homo- and random copolyurethanes. Because it was difficult to isolate monomers with reactive groups, these workers generated isocyanate groups in situ of the polymerization stage.⁶ Thereafter, in 1991, various kinds of polyurethanes were prepared by Nishi et al. through the reaction of a hydroxyl group with the isocyanate group that was formed by Curtius rearrangement of the carbonyl azide precursor.⁷ In general, the most

carbonyl azides are readily converted to corresponding isocyanates, which react in situ with hydroxylic compounds to form urethanes.^{8,9}

Moreover, it is mentionable that a major drawback of polyurethanes is their poor resistance toward mechanical strains and high temperatures. Generally, their acceptable mechanical properties vanish above 80°C and thermal degradation takes place above 200°C.¹⁰ Various attempts have been made to incorporate imide heterocyclic units into polyurethane backbone.^{11–17} On the other hand, the most heat resistant homopolyimides have almost poor processability because of their insolubility in common organic solvents. However, it is found that the synthesis of copolyimides by the introduction of other functional groups into the polymer backbone remarkably enhance their positive properties.^{18–21} Therefore, the presence of urethane linkages by the side of imide groups into a copolymer chain is useful both for polyurethane and polyimide. This putting together increases thermal stability and processability of polyurethane and polyimide, respectively.

In our previous studies, we successfully prepared a series of wholly aromatic poly(amide-imide)s, poly(ester-imide)s, and poly(urethane-imide)s from a number of new imide-containing dicarboxylic acids.^{22–27} Among them, a dicarboxylic acid bearing two imide rings 4-*p*-biphenyl-2,6-bis(4-trimellitimidophenyl)pyridine, **1**, was used for some polymerization purposes. The results

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clearly showed the polymers obtained from monomer **1** have both good solubility in a variety of organic solvents and high thermal stability. In addition to poly(amide-imide)s and poly(ester-imide)s, the imide ring-containing aromatic diacid **1** seems to be a good starting material for the preparation of various soluble and thermally stable poly(urethane-imide)s, using diphenylphosphoryl azide (DPPA) via a direct method. A disadvantage of this direct method is due to derangement in stoichiometric balance between the diisocyanate obtained from Curtius rearrangement and dihydroxylic compounds, which causes an obvious decrease in molecular weights of the final polymers. It seems that one approach to solving this problem is to employ an excess amount of the initial dicarboxylic acid against diol monomer. In the present study, compound **1** was polymerized directly with various aromatic diols in mole ratios of 1.5 COOH/1.0 OH and 1.0 COOH/1.0 OH to prepare a new family of poly(urethane-imide)s. The polymers obtained are thoroughly characterized by spectroscopic methods and elemental analyses. The structure effects on some properties of the resulting poly(urethane-imide)s including viscosity, crystallinity, solubility, and thermal stability could be easily clarified and compared with analogous poly(amide-imide)s resulted from our previous work.²⁵

EXPERIMENTAL

Materials

All chemicals were obtained either from Merck (Lindenplatz, Germany) or Fluka chemical Co. (Buchs, Switzerland). Diimide-dicarboxylic acid **1** was synthesized according to our previous work.²⁵ Resorcinol (**4a**) was used as obtained without further purification. 4,4'-Dihydroxybiphenyl (**4b**) and 2,2'-dihydroxybiphenyl (**4d**) were purified by recrystallization from ethanol. Bisphenol A (**4c**) was purified by recrystallization from acetic acid. 2,2'-Dihydroxy-1,1'-binaphthyl (**4e**) was synthesized from 2-naphthol as described previously.²⁸ *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), and pyridine (Py) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. The other solvents including chloroform, dichloromethane (DCM), tetrahydrofuran (THF), and acetone as well as triethylamine were used as obtained without further purification.

Synthesis of 4-*p*-biphenyl-2,6-bis(4-trimellitimidophenyl)pyridine (**1**)

The imide ring-containing diacid **1** was synthesized by the condensation of biphenyl-4-carboxaldehyde with 4-nitroacetophenone, then the reduction of the resulted dinitro compound, and finally by the conden-

sation of 4-*p*-biphenyl-2,6-bis(4-aminophenyl)pyridine with two mole equivalents of TMA in DMF/toluene, according to our previous work.²⁵

Synthesis of the poly(urethane-imide)s

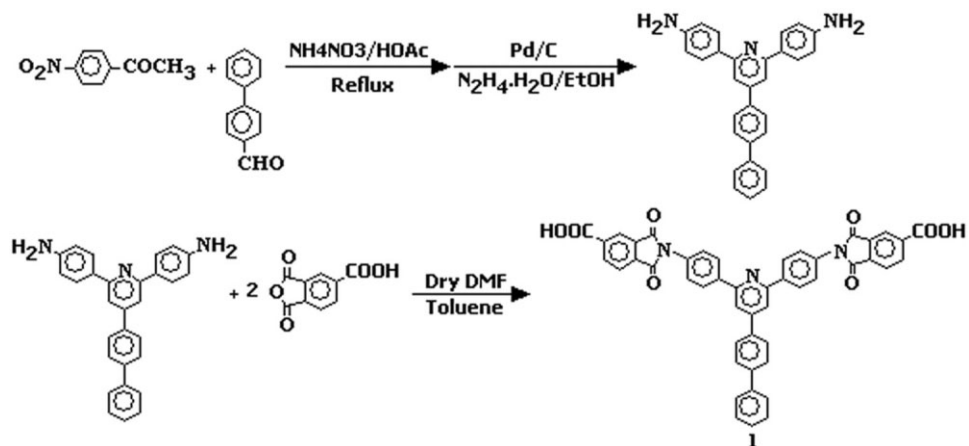
General procedure to prepare the poly(urethane-imide)s **5a–5e** is as follows: To a solution of diimide-dicarboxylic acid **1** and dihydroxylic compound (mole ratios of 1.5 : 1.0 or 1.0 : 1.0) in minimum amount of DMSO as reaction solvent were added DPPA (2.0 mol/mol COOH) and triethylamine (2.5 mol/mol COOH). The final mixture was stirred 1.5 h at about 10°C and 3 h at 120°C. The viscous polymer solution obtained was trickled on stirred water to give rise to a crude precipitate, which was collected by filtration, washed thoroughly with water, methanol, and ether, respectively, and dried under reduced pressure at 50°C. The total yield of the consecutive reactions including di(carbonyl azide) and diisocyanate formation and then polyaddition was about 60%.

Preparation of the polymeric films

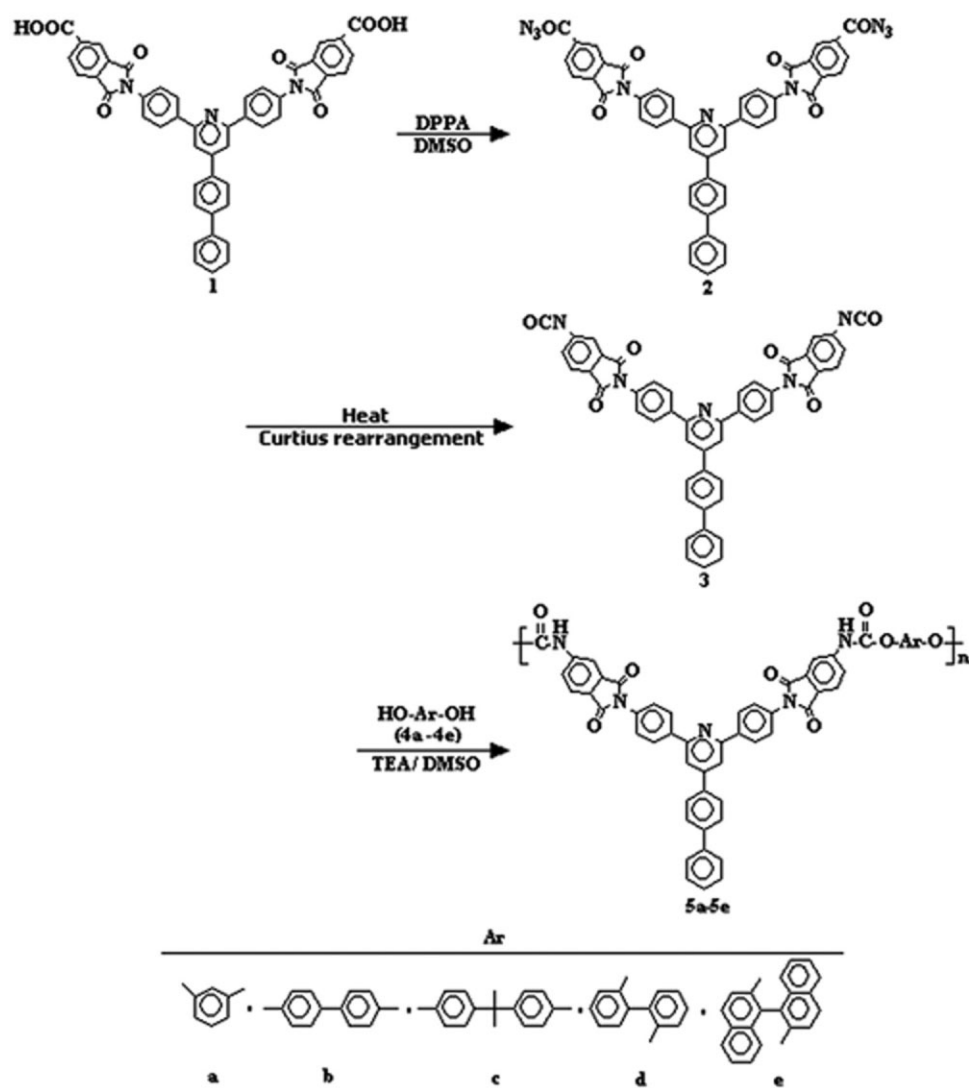
The films of the resulting poly(urethane-imide)s were prepared by casting the solution. To attain this object, all the polymers were dissolved in NMP as solvent on glass plates, separately to give 10% solutions. In all cases, the solvent was evaporated under reduced pressure at 40°C for 12 h, 50°C for 10 h, and 60°C for 5 h to obtain brownish films of the polymers, which had mostly a brittleness nature.

Measurements

Melting points were determined with a Buchi 535 melting point apparatus. Inherent viscosities were measured by a standard procedure, using a Cannon Fensk routine viscometer in DMAc at a concentration of 0.5 g dL⁻¹ at 30°C. Elemental analyses were performed with a Perkin-Elmer 2400 CHN analyzer. ¹H NMR spectra were recorded on a Bruker Advanced DPX-250 250 MHz spectrometer in DMSO-d₆ at 25°C with frequencies of 250.13 MHz. Tetramethylsilane was used as an internal standard. FT-IR spectra were recorded on a PERKIN ELMER RX I FT-IR spectrometer. The spectra of solids were obtained using KBr pellets. Wide-angle X-ray diffraction patterns were performed at room temperatures with film specimens on a D8 ADVANCE BRUKER X-ray diffractometer with Ni-filtered Cu K α radiation (30 kV, 25 mA). Differential scanning calorimetric (DSC) and thermal gravimetric analysis (TGA) were performed on a Mettler TA4000 System under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. The DSC traces were obtained from heating, rapidly cooling, and reheating



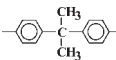




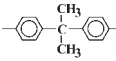




Scheme 1 Synthetic route used to obtain the imide-containing diacid 1.



Scheme 2 Synthetic route used to obtain the poly(urethane-imide)s.

TABLE I
Synthesis and Some Characteristics of the Resulting Poly(urethane-imide)s

Polymer code	Diol-Ar-	mol diacid/mol diol	Yield (%)	η_{inh}^a (dL g ⁻¹)	Color ^b
5a		1.0/1.0	58	0.10	PB
5b		1.0/1.0	61	0.11	B
5c		1.0/1.0	56	0.09	PB
5d		1.0/1.0	59	0.11	PB
5e		1.0/1.0	61	0.12	DB
5a		1.5/1.0	55	0.15	PB
5b		1.5/1.0	63	0.19	B
5c		1.5/1.0	59	0.13	PB
5d		1.5/1.0	62	0.17	B
5e		1.5/1.0	58	0.17	DB

^aMeasured in DMAc at a concentration of 0.5 g dL⁻¹ at 30°C.

^bB, brown; DB, dark brown; PB, pale brown.

of samples at a range of 50–400°C. The range FS of 20 mW for DSC and 10 mg for TGA were used.

RESULTS AND DISCUSSION

Synthesis

Scheme 1 shows the synthetic route used for the preparation of imide ring-containing diacid 1. First, 4-*p*-biphenyl-2,6-bis(4-nitrophenyl)pyridine was prepared with the use of biphenyl-4-carboxaldehyde and 4-nitroacetophenone. Second, the resulted dinitro compound was subjected to reduction using hydrazine hydrate as the source of hydrogen and palladium on charcoal (5%) as the catalyst. Third, a condensation reaction between the diamino compound and two mole equivalents of TMA in dry DMF and toluene as reaction solvents giving rise to the final monomer 1. The details of the synthesis route and the characterization data was reported in our previous work.²⁵

In general, when an acyl azide and alcohol are heated together in an organic solvent such as toluene,

dioxane, NMP, or DMF at about 80°C, the acyl azide will rearrange to form an isocyanate that then reacts with the alcohol to form a stable urethane.²⁹ This reality can be used to prepare polyurethanes as an important class of polymeric materials. The synthetic route chosen for the preparation of new poly(urethane-imide)s 5a–5e is shown in Scheme 2. Diimide-dicarboxylic acid 1 was converted to diimide-di(carbonyl azide) 2 using DPPA. The thermal decomposition of diimide-di(carbonyl azide) 2 via Curtius rearrangement gave the corresponding diisocyanate 3 in situ. In continuation of this reaction, compound 3 treated with a number of aromatic dihydroxylic compounds to prepare the final polymers. The reactions including diisocyanate formation and polyaddition readily proceeded in a brownish homogeneous solution for all polymers preparation. As listed in Table I, the poly(urethane-imide)s were prepared in total yields of about 60% with starting from triimide-dicarboxylic acid 1. These low yields are reasonable because the yields of the Curtius rearrangement reac-

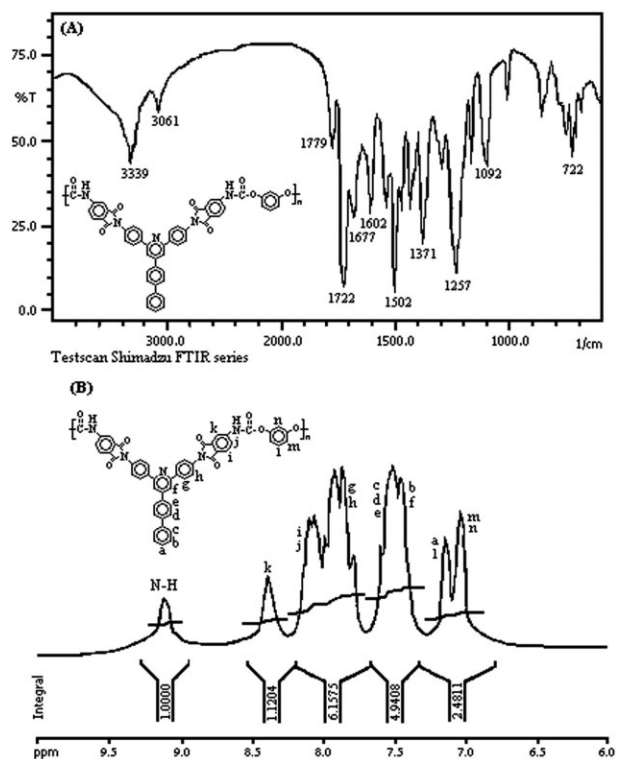


Figure 1 FTIR (A) and ^1H NMR (B) spectra of poly(urethane-imide) **5a**.

tions are known generally not to be very high.^{29–31} Also, as can be seen in Table I, the resulting poly(urethane-imide)s had inherent viscosities of 0.09–0.12 dL g^{-1} and 0.13–0.19 dL g^{-1} for mole ratios of 1.0 COOH/1.0 OH and 1.5 COOH/1.0 OH, respectively. These low viscosity values showed that the resulting polymers have relatively low molecular weight, which this reality is justifiable in spite of an inherent shortage of this direct method for polyurethanation. This disadvantage is due to derangement in stoichiometric balance between the diisocyanate obtained from Curtius rearrangement and the diols during the reaction progress. In fact, for the compensation of the diisocyanate shortage against the diols, an excess amount of initial dicarboxylic acid **1** (1.5 : 1.0) was also used for the preparation of polymers **5a–5e**, alternately. When the initial diimide-dicarboxylic **1** is used in excess

amount, the final polymers will possess relatively higher viscosity values than the polymers obtained from stoichiometrically balance conditions. The subsequent studies including characterization and properties were only performed on this block of poly(urethane-imide)s.

The structure of the poly(urethane-imide)s **5a–5e** was confirmed by FTIR and ^1H NMR spectroscopy methods and elemental analyses. As an example, a representative FTIR spectrum of poly(urethane-imide) **5a** is shown in Figure 1(A). The FTIR spectra of all polymers showed bands around 3300 cm^{-1} assigned to stretching vibration of the urethane N—H bonds. The characteristic absorptions of the carbonyl groups occurred around 1780, 1720 (asymmetric and symmetric imide C=O stretching, respectively), and 1680 (urethane C=O stretching) cm^{-1} . The ^1H NMR spectra of all the poly(urethane-imide)s showed —NH— proton signal in the range of 8.8–9.6 ppm. The aromatic ring protons appeared in the region of about 7.0–8.4 ppm. A typical ^1H NMR spectrum, for polymer **5a**, is presented in Figure 1(B). Finally, as shown in Table II, the elemental analyses of the polymers confirmed the proposed structures of them.

Properties of the poly(urethane-imide)s

The solubility behavior of poly(urethane-imide)s **5a–5e** is summarized in Table III. All polymers were soluble in polar aprotic solvents such as DMAc, DMF, DMSO, and NMP at room temperature. The polymers including **5a**, **5c**, **5d**, and **5e** exhibited a good solubility even in pyridine, chloroform, DCM, and THF. Furthermore, this block of copolyimides showed somewhat further solubility toward the above solvents compared with that of the poly(amide-imide)s with analogous structure.²⁵

To study the crystalline characteristics of the poly(urethane-imide)s, WXRd measurements at room temperature in the region of $2\theta = 5^\circ\text{--}50^\circ$ were performed. As shown in Figure 2, no crystal diffraction was detected for most of the polymers, except the poly(urethane-imide) **5b** bearing *p*-biphenylene moieties in its main chain. The polymer **5b** showed almost a semicrystalline pattern due to the existence of this

TABLE II
Elemental Analysis Data of the Resulting Poly(urethane-imide)s

Polymer code	Polymer formula	Calculated (%)				Found (%)		
		C	H	N	C	H	N	
5a	(C ₅₃ H ₃₁ N ₅ O ₈) _n (865) _n	73.53	3.58	8.09	73.06	3.62	8.05	
5b	(C ₅₉ H ₃₅ N ₅ O ₈) _n (941) _n	75.24	3.72	7.44	74.85	3.73	7.46	
5c	(C ₆₂ H ₄₁ N ₅ O ₈) _n (983) _n	75.69	4.17	7.12	75.12	4.22	7.08	
5d	(C ₅₉ H ₃₅ N ₅ O ₈) _n (941) _n	75.24	3.72	7.44	74.79	3.70	7.39	
5e	(C ₆₇ H ₃₉ N ₅ O ₈) _n (1041) _n	77.23	3.75	6.72	76.71	3.78	6.68	

TABLE III
Solubility of the Resulting Poly(urethane-imide)s

Polymer code	DMAc	DMF	DMSO	NMP	Py	Chloroform	DCM	THF	Acetone
5a	++	++	++	++	+	±	+	+	-
5b	++	++	++	++	±	±	±	±	-
5c	++	++	++	++	+	+	±	+	-
5d	++	++	++	++	+	+	±	+	-
5e	++	++	++	++	+	+	+	+	-

Concentration: 5 mg mL⁻¹.

Solubility: ++, soluble at room temperature; +, soluble on heating; ±, partially soluble on heating; -, insoluble.

DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; NMP, *N*-methyl-2-pyrrolidone; Py, pyridine; DCM, dichloromethane; THF, tetrahydrofuran.

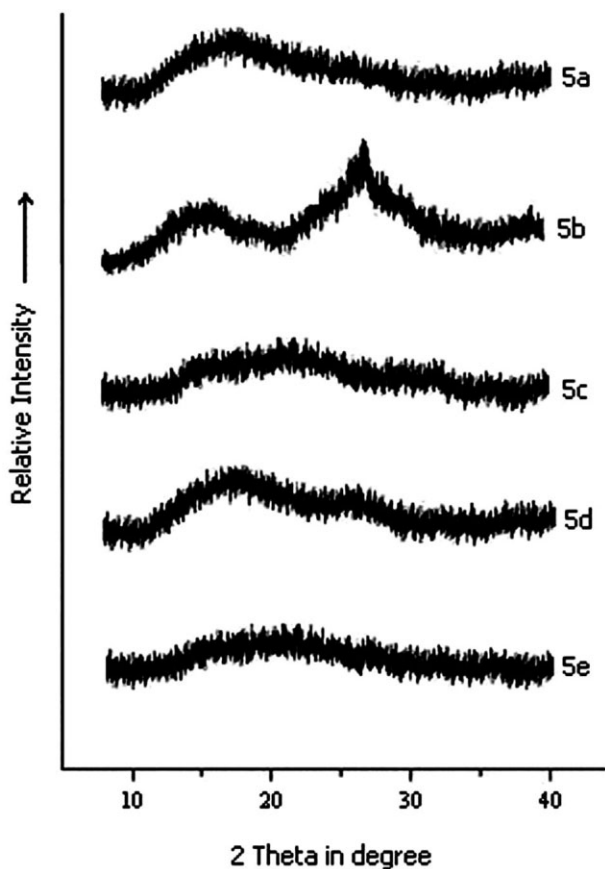


Figure 2 X-ray diffraction patterns of the resulting poly(urethane-imide)s.

symmetrical segment in its backbone that led to a better packing of the polymer chains. Moreover, isopropylidene- and binaphthylene-based polymers (5c and 5e) presented a significant decrease in crystallinity behavior that is reasonable because presence of the cranked units in a backbone induces looser chain packing. Consequently, the mentioned polymers showed almost amorphous diffraction patterns.

The thermal behavior of the resulting poly(urethane-imide)s was evaluated by differential scanning calorimetry (DSC) and TGA. The thermal properties data are summarized in Table IV. The DSC profiles were achieved at a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere. A rapidly quenching from the elevated temperatures to room temperature yields predominately amorphous samples so that discernible baseline shifts could be easily measured in the DSC charts of the second-heating trace. Nearly, high glass-transition temperatures were found for the polymers obtained because of their intractable wholly aromatic chains. According to the curves in Figure 3, the DSC thermograms of the poly(urethane-imide)s 5a–5e showed glass-transition temperatures (*T_g*'s) in the range between 191 and 202 °C depending on the structure of dihydroxylic components. Among the polymers obtained, polymer 5e showed higher *T_g* value than the other poly(urethane-imide)s. This could be attributed to the incorporation of rigid cardo binaphthylene segments along the polymers backbone, which

TABLE IV
Thermal Properties and Film Quality of the Resulting Poly(urethane-imide)s

Polymer Code	<i>T_g</i> ^a (°C)	<i>T</i> _{10%} ^b (°C)	Char yield ^c (%)	Film quality ^d	
5a	193	398	33	Brittle	Transparent brown
5b	198	410	38	Brittle	Opaque brown
5c	191	406	31	Slightly flexible	Transparent brown
5d	195	392	35	Brittle	Opaque brown
5e	202	416	37	Brittle	Opaque brown

^aFrom the second heating traces of DSC measurements with a heating rate of 10 °C min⁻¹ in N₂.

^bTemperature at which 10% weight loss was recorded by TGA at a heating rate of 10 °C min⁻¹.

^cResidual wt % at 800 °C in nitrogen.

^dFilms were cast from a 10% NMP solution on glass plates.

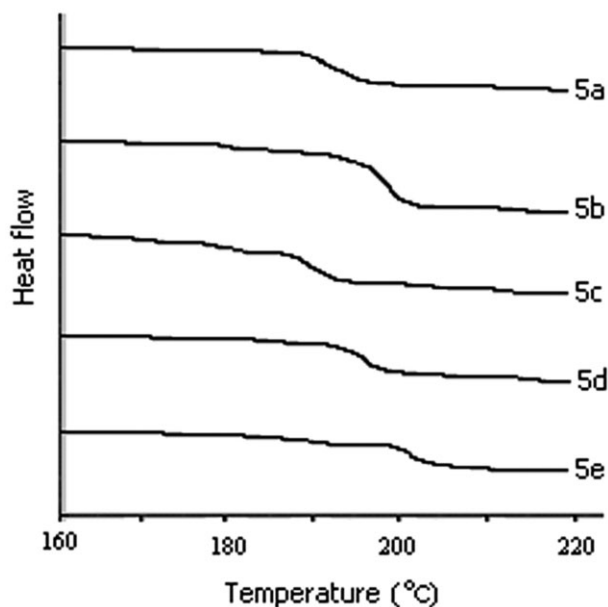


Figure 3 DSC plots of the poly(urethane-imide)s.

restricted the free rotation of the macromolecular chains leading to an enhanced T_g value. To compare the thermal properties, some homo- and copolymers including polyimide, polyurethane, poly(ether-imide), and poly(amide-imide) with the structures shown in Scheme 3 were considered. The thermal properties of these reference polymers are also listed in Table V. All

TABLE V
Thermal Properties of Some Reference Polymers^a

Polymer code	Polymer class	T_g (°C)	$T_{10\%}$ (°C)	Char yield (%)
R1	Polyimide	412	600	58 ^b
R2	Poly(ether-imide)	428	528 ^c	– ^d
R3	Polyurethane	110	248	–
R4	Poly(amide-imide)	290	540	–
R5	Poly(amide-imide)	–	495	55 ^e

^aData from Refs. 32–34.

^bResidual wt % at 700°C in nitrogen.

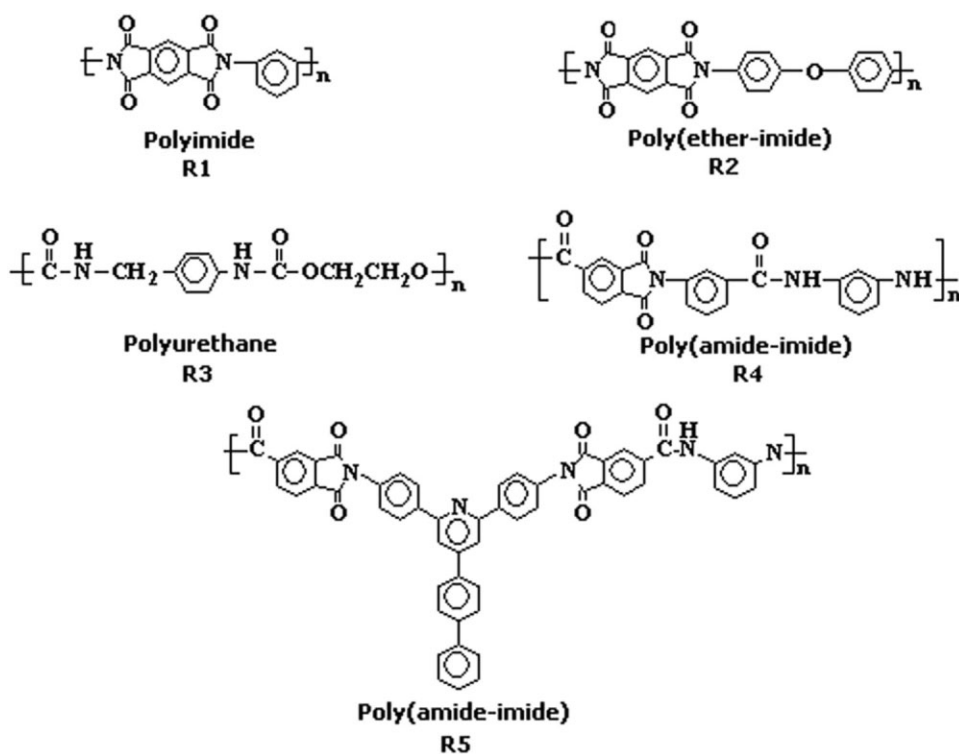
^cTemperature at which 5% weight loss.

^dNot reported.

^eResidual wt % at 800°C in nitrogen.

the poly(urethane-imide)s exhibited lower T_g 's than the fully aromatic homopolyimide R1,³² the commercially available poly(ether-imide) Kapton H, R2,³³ the poly(amide-imide)s R4³³ and R5²⁵ because of higher flexibility of the urethane linkages than those of imide and amide bonds. However, they showed higher T_g values than the homopolyurethane R3.³⁴

Thermal stability evaluation of the polymers was carried out by TGA in nitrogen at a heating rate of 10 °C min⁻¹. The TGA curves of the resulting polymers are shown in Figure 4. The poly(urethane-imide)s obtained were stable up to 400°C and lost 10% of their total weight between 392 and 416°C, which showed a



Scheme 3 The chemical structure of some reference polymers.

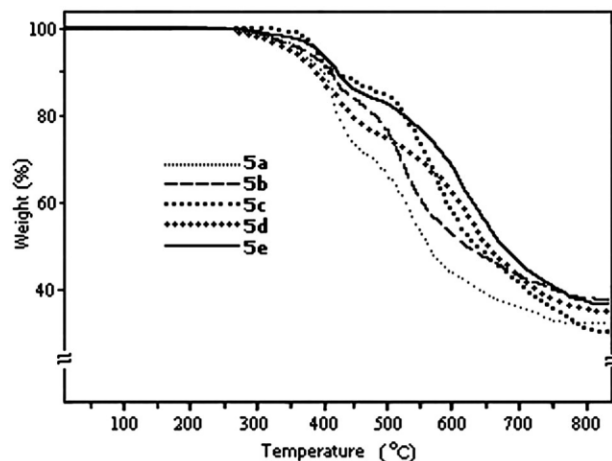


Figure 4 TGA thermograms of the poly(urethane-imide)s, obtained at a heating rate of $10^{\circ}\text{C min}^{-1}$ in a nitrogen atmosphere.

remarkably improvement of decomposition temperature in comparison with common homopolyurethanes.^{35–37} The desirable thermal stability of the resulting polymers is ascribed to their wholly aromatic structures. All thermograms of the polymers obtained were almost similar with each other. In fact, all the poly(urethane-imide)s showed an obviously two-stage decomposition at elevated temperatures. Assuming a different stability of the urethane units and the imide units, the first stage of weight losses might be attributed to the early degradation of the urethane linkages. Therefore, the 10% weight loss temperatures are mainly caused by the decomposition of urethane units. Since the dipoles present at the urethane groups are the weakest sites in terms of thermal stability, the rupture of the urethane bonds occurs first. Furthermore, The poly(urethane-imide)s **5a–5e** exhibited less thermal stability than those of the homopolyimide **R1**, the poly(ether-imide) Kapton H, **R2**, and the poly(amide-imide)s **R4** and **R5** (Table V). However, they showed higher $T_{10\%}$ values than the homopolyurethane **R3**. These observations might be attributed to the early degradation of the urethane linkages than those of the imide, amide, and even ester groups against high temperatures.

Finally, owing to the study of flexibility or brittleness properties, the films of the polymers were prepared by casting the solution. As could be predicted from the fully aromatic and highly imidized rigid structure of the polymers, no flexibility behavior was observed, and the resulting transparent films had a brittle nature in all cases except polymer **5c**, which had somewhat flexibility. This brittleness behavior of the polymers could be attributed to the low molecular weight of the polymers because of an imbalance in stoichiometric amounts between the in situ-formed diisocyanates and the dihydroxylic compounds. Fur-

thermore, the relatively perceptible flexibility in polymer **5c** might be attributed to the presence of flexible isopropylidene units in the polymer backbone. The films quality for all the poly(urethane-imide)s are summarized in Table IV.

CONCLUSIONS

Dicarboxylic acid **1** with preformed two imide rings and fully aromatic structure was synthesized and used for polymerization purpose. The direct polyaddition reaction of compound **1** with a number of aromatic dihydroxylic compounds resulted in preparation of some fully aromatic poly(urethane-imide)s, **5a–5e**. For the compensation of the diisocyanate shortage against the diols, an excess amount of initial dicarboxylic acid **1** (1.5 : 1.0) was used for the preparation of the polymers. When the initial diimide-dicarboxylic **1** is used in excess amount, the final polymers will possess higher viscosity values than the stoichiometric conditions. In this direct polyurethanation, separately synthesis and purification of the intermediates including di(carbonyl azide) **2** and diisocyanate **3** were not necessary, and the polyaddition readily proceeded as one-pot reaction starting from imide ring-containing dicarboxylic acid **1**. The resulting poly(urethane-imide)s showed a better solubility in common organic solvents than the polyimides, and poly(amide-imide)s with the same aromatic structure. Furthermore, the amorphous polymers obtained exhibited a desirable heat resistance in comparison with aromatic polyurethanes because of the presence of thermally stable imide rings into the fully aromatic structures.

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