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Direct synthesis of soluble and thermally stable poly(urethane-imide)s from a new triimide–dicarbonylazide

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Abstract

A new aromatic dicarbonylazide (**3**) bearing three preformed imide rings was synthesized by treating *N*-[3,5-bis(trimellitimido)phenyl]phthalimide (**1**) with thionyl chloride followed by a nucleophilic reaction with sodium azide. A novel family of fully aromatic poly(urethane-imide)s with inherent viscosities of 0.19–0.24 dl g^{-1} were prepared from triimide–dicarbonylazide **3** and various aromatic diols. The polyaddition reactions readily proceeded in desirable yields as one-pot reactions starting from **3** without separately synthesis of the corresponding diisocyanate. All of the resulted polymers were thoroughly characterized by spectroscopic methods and elemental analyses. The poly(urethane-imide)s exhibited an excellent solubility in a variety of polar solvents. Crystallinity nature of the polymers was estimated by means of WXRD. The glass transition temperatures of the polymers determined by DSC method were in the range of 197–219 °C. The 10% weight loss temperatures of the poly(urethane-imide)s from their TGA/DTG curves were found to be in the range of 391–412 °C in nitrogen. The films of the polymers were also prepared by casting the solution.
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Keywords: Triimide–dicarbonylazide; Curtius rearrangement; Poly(urethane-imide)s

1. Introduction

Diisocyanates are widely used as initial monomers for the preparation of various kinds of polymers [1–4]. The high interest in diisocyanates is attributed to their unique ability to undergo polymerization reactions with numerous comonomers such as dianhydrides, diamines, and diols to prepare polyimides, polyureas, and polyurethanes, respectively. However, 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 dicarbonylazide 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 co-polyurethanes. 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, a number 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 carbonylazide precursor [7]. In general, the most carbonylazides 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 towards mechanical strains and high temperatures. Generally, their acceptable mechanical properties vanish above 80 °C and thermal degradation takes place above 200 °C [10]. Attempts to improve the thermal stability of polyurethanes have been made over a long period, and this property can be improved by chemical modification of their structure by blending or copolymerization with more thermally stable polymers such as polyimides. 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.

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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 and poly(ester-imide)s from a number of new imide-containing dicarboxylic acids [22–27]. Among them, a dicarboxylic acid bearing three imide rings *N*-[3,5-bis(trimellitimido)phenyl]phthalimide, **1**, was used for some polymerization purposes. The results 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 synthesized fully aromatic and highly imidized diacid **1** seems to be a good starting material for the preparation of various soluble and thermally stable aromatic poly(urethane-imide)s after its conversion to the corresponding acid azide. In the present study, a new imide ring-containing aromatic dicarbonylazide by the name of *N*-[3,5-bis(trimellitimidoylazido)phenyl]phthalimide (**3**) was synthesized from *N*-[3,5-bis(trimellitimidoylchlorido)phenyl]phthalimide (**2**), and then polymerized directly with various aromatic dihydroxylic compounds to prepare a new family of poly(urethane-imide)s by the source-based names of {*N*-[3,5-bis(4-isocyanatophthalimido)phenyl]phthalimide-*alt*-resorcinol} **6a**, {*N*-[3,5-bis(4-isocyanatophthalimido)phenyl]phthalimide-*alt*-hydroquinone} **6b**, {*N*-[3,5-bis(4-isocyanatophthalimido)phenyl]phthalimide-*alt*-4,4′-dihydroxybiphenyl} **6c**, {*N*-[3,5-bis(4-isocyanatophthalimido)phenyl]phthalimide-*alt*-2,2′-dihydroxybiphenyl} **6d**, {*N*-[3,5-bis(4-isocyanatophthalimido)phenyl]phthalimide-*alt*-bisphenol A} **6e**, and {*N*-[3,5-bis(4-isocyanatophthalimido)phenyl]phthalimide-*alt*-2,2′-dihydroxy-1,1′-binaphthyl} **6f**. 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 and poly(ester-imide)s resulted from our previous works [22,23].

2. Experimental

2.1. Materials

All chemicals were purchased either from Merck or Fluka Chemical Co. Triimide–dicarboxylic acid **1** and triimide–dicarboxylic acid chloride **2** were synthesized according to our previous works [22,23]. 4,4′-Dihydroxybiphenyl (**5c**) and 2,2′-dihydroxybiphenyl (**5d**) were purified by recrystallization from ethanol. Bisphenol A (**5e**) were purified by recrystallization from acetic acid. 2,2′-Dihydroxy-1,1′-binaphthyl (**5f**) was synthesized from 2-naphthol as described previously [28]. The other aromatic dihydroxylic compounds were used as obtained without further purification. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and pyridine (Py) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Sodium azide was activated by the addition of hydrazine hydrate. After being kept overnight, it was dissolved in a minimum amount of water, precipitated in acetone, and dried. Dibutyltin dilaurate (DBTD) was used as obtained without further purification.

2.2. Monomer synthesis: N-[3,5-bis(trimellitimidoylazido)phenyl]phthalimide (3)

A three-necked round-bottomed flask equipped with a magnetic stirrer, a dropping funnel, and a nitrogen gas inlet tube was charged with an ice-cold solution of activated sodium azide (25 mmol) in water (20 mL). A solution of triimide–diacid chloride **2** (6.384 g, 10 mmol) in DMF (20 mL) was added dropwise to the initial solution at 0 °C under N_2, while stirring. Next, the final mixture was further stirred, vigorously at the same temperature in a stream of nitrogen until compound **2** disappeared (track by TLC, about 3 h). Then, the reaction mixture obtained was trickled on 300 mL stirred mixture of ice water and methanol to give rise to a crude precipitate, which was collected by filtration, washed three times by water, 10% sodium carbonate solution, and water, respectively, and dried under reduced pressure to afford triimide–dicarbonylazide **3** as tiny pale yellow crystals.

Yield 89%. Mp > 130 °C (dec.). FT IR (KBr, cm^{-1}): 3054 (m), 2412 (w), 2115 (m), 1778 (m), 1722 (s,), 1685 (s), 1597 (m), 1499 (s), 1363 (s), 1288 (w), 1231 (m), 1099 (m), 868 (w), 727 (m), 685 (w). ^{1}H NMR (δ, ppm, DMSO-d_6): 8.37 (s, 2H), 8.18 (d, 2H), 8.06 (d, 2H), 7.86 (d, 2H), 7.55 (s, 3H), 7.26 (m, 2H). ^{13}C NMR (δ, ppm, DMSO-d_6): 170.15, 166.84, 143.61, 139.11, 138.56, 137.41, 135.12, 134.91, 134.57, 134.09, 129.78, 126.53, 126.07, 120.94, 119.47. Anal. Calcd for $C_{32}H_{13}N_9O_8$ (651.54): C, 58.99%; H, 2.01%; N, 19.35%. Found: C, 58.95%; H, 2.04%; N, 19.29%.

2.3. Preparation of poly(urethane-imide)s 6a–6f

Into a three-necked round-bottomed flask equipped with a magnetic stirrer, a dropping funnel, and a nitrogen gas inlet tube, there was placed a solution of triimide–dicarbonylazide **3** (1.302 g, 2 mmol) in dry NMP (5 mL). A solution of dihydroxylic compound (2 mmol) in dry NMP (5 mL) was added in small quantities to the initial solution over a period of 30 min at room temperature. Then, three

drops of DBTD were added to the stirred solution. The temperature was slowly raised to 80–100 °C, and maintained for 5 h. During the course of reaction, a mild stream of nitrogen was passed over the reaction. After the chain-extending reaction, the resulting polymer was precipitated by being poured into excess methanol. It was then filtered, washed several times with hot water, and dried under reduced pressure at 50 °C. The total yield of reactions including diisocyanate formation and then polyaddition was about 70% for all cases.

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

2.4. 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. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advanced DPX-250 250 MHz spectrometer in DMSO-d_6 at 25 °C with frequencies of 250.13 and 62.89 MHz for the ^{1}H and ^{13}C spectra, respectively. 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. Average molecular weights were determined by gel permeation chromatography (GPC). Waters chromatography instrument connected to a differential refractometer using Styragel columns was used for GPC analysis with DMF (1 mL min^{-1}) as the eluent. The molecular weight calibration was carried out using polystyrene standards. 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$_\alpha$ 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 of samples at a range of 50–400 °C. The range FS of 20 mW for DSC and 10 mG for TGA were used.

3. Results and discussion

3.1. Synthesis of the triimide–dicarbonylazide 3

The triimide–dicarboxylic acid **1** was synthesized by the condensation of *N*-(3,5-diaminophenyl)phthalimide and 2 mol equiv. of trimellitic anhydride in refluxing glacial acetic acid as described in our previous work [22]. The new aromatic dicarbonylazide **3** bearing three preformed imide rings was synthesized by treating compound **1** with thionyl chloride for synthesis of triimide–diacid chloride **2** followed by a nucleophilic reaction with sodium azide. Scheme 1 outlines the synthesis route of the new monomer. The chemical structure and purity of the resulting triimide–dicarbonylazide were confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR and elemental analysis. The FT-IR spectrum of compound **3** showed absorption peaks at about 2115, 1230 (asymmetric and symmetric azido group stretching), 1780, 1720 (asymmetric and symmetric imide C=O stretching), 1685 (carbonyl azide C=O stretching) and 1360 cm^{-1} (imide ring vibration, axial) confirming the structure of the monomer. The ^{1}H NMR spectroscopic data are nearly in the range of 7.0–8.4 ppm, which protons of the trimellitimido aromatic rings create resonance signals around downfield regions, above 8 ppm. Also, the ^{13}C NMR spectrum of **3** exhibited 13 peaks of various absorptions for every aromatic carbon. Carbonyl carbons of acid azide and imide heterocyclic ring resonate in the downfield region at about 170 and 167 ppm, respectively. Furthermore, as another reason confirming the structure of **3**, the elemental analysis data are in agreement with the predicted structure of this monomer.

3.2. Preparation of the poly(urethane-imide)s

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]. The synthetic route chosen for preparation of new poly(urethane-imide)s **6a–6f** is shown in Scheme 2. The thermal decomposition of triimide–dicarbonylazide **3** via Curtius rearrangement gave the corresponding diisocyanate **4** in situ. In continuation of this reaction, compound **4** treated with a number of aromatic dihydroxylic compounds to prepare the final polymers. The reactions including diisocyanate formation and polyaddition readily
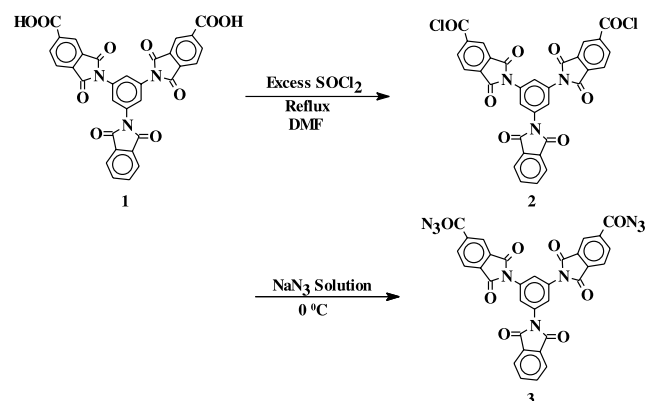
Scheme 1. Synthesis route of triimide–dicarbonylazide **3**.
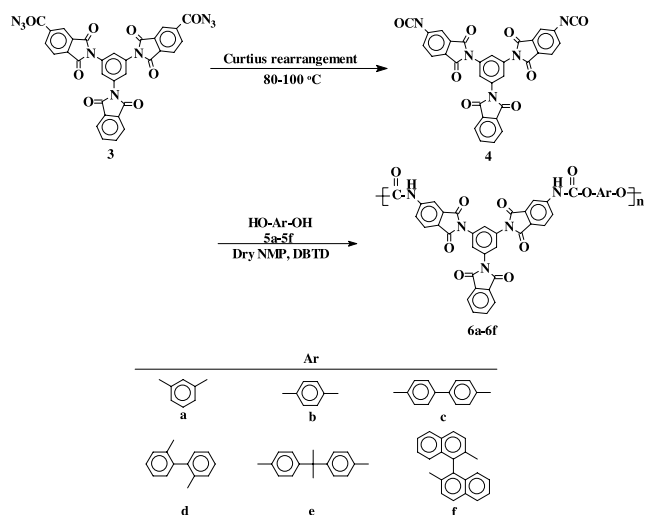
Scheme 2. Preparation of the poly(urethane-imide)s **6a–6f**.

proceeded in a brownish homogeneous solution for all polymers preparation. The polymerization reaction rate is accelerated by using two to three drops of the metal salt DBTD as a useful catalyst. As listed in Table 1, the poly(urethane-imide)s were prepared in total yields of about 70% with starting from triimide–dicarbonylazide **3**. These low yields are reasonable because the yields of the Curtius rearrangement reactions are known generally not to be very high [29]. The resulting poly(urethane-imide)s had inherent viscosities of 0.19–0.24 dl g^{-1} in DMAc. The GPC measurements demonstrated that these polymers exhibited number-average molecular weight (M_n) and weight-average molecular weight (M_w) values of 8400–10,700 and 27,900–32,800, respectively. Inherent viscosities, molecular weights, and polydispersities (M_w/M_n) are presented in Table 2. GPC results 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

diisocyanates obtained from Curtius rearrangement and the diols, during the reaction progress. The structure of the poly(urethane-imide)s **6a–6f** was confirmed by FT-IR and ^{1}H NMR spectroscopy methods and elemental analyses. As an example, a representative FT-IR spectrum of poly (urethane-imide) **6a** is shown in Figure 1(A). The FT–IR 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 1690 (urethane C=O stretching) cm^{-1}. The ^{1}H NMR spectra of all the poly(urethane-imide)s showed a –NH– proton signal in the range of 8.8–9.7 ppm. The aromatic ring protons appeared in the region of about 7.3–8.6 ppm. A typical ^{1}H NMR spectrum, for polymer **6a**, is presented in Figure 1(B). Finally, as shown in Table 2, the elemental analyses of the polymers confirmed the proposed structures of them.

3.3. Properties of polymers

The solubility behavior of all poly(urethane-imide)s is summarized in Table 3. All of the polymers were soluble in polar aprotic solvents such as DMAc, DMF, DMSO, and NMP at room temperature. A number of them including **6a**, **6d**, **6e**, and **6f** 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 [22] and poly(ester-imide)s [23] with analogous structure. Also, the poly(urethane-imide)s **6e** and **6f** showed a better solubility in less polar solvents compared with the polymers **6a–6d** owing to the presence of the isopropylidene segments and bulky binaphthylene units into the polymers backbones, respectively. A highly chain packing of the polymers is probably disturbed by the mentioned groups.

To study the crystalline characteristics of the poly-(urethane-imide)s, WXRD measurements at room temperature in the region of $2\theta = 5°–50°$ were performed. According

Table 1
Synthesis and some characteristics of the resulting poly(urethane-imide)s

Polymer code	Dihydroxylic compound		Yield (%)	Polymer appearance	Color[a]
	Code	Ar			
6a	**5a**		74	String	B
6b	**5b**		76	Powder	B
6c	**5c**		72	Powder	DB
6d	**5d**		69	Powder	B
6e	**5e**		71	String	PB
6f	**5f**		63	String	B

Polymerizations were carried out using 2.0 mmol of triimide–dicarbonylazide **3** and dihydroxylic compounds **5a–5f** with three drops of DBTD as a reaction catalyst in 10 mL dry NMP at 80–100 °C.

[a] B, brown; DB, dark brown; PB, pale brown.

Table 2
Inherent viscosity, molecular weights, and elemental analysis data of the resulting poly(urethane-imide)s

Polymer code	Formula	η_{inh}^{a} (dl g^{-1})	M_n^{b} ($\times 10^{-3}$)	M_w^{b} ($\times 10^{-3}$)	PDI	Elemental analysis (%)			
							C	H	N
6a	$(C_{38}H_{19}N_5O_{10})_n$	0.19	8.9	27.9	3.1	Calcd.	64.68	2.70	9.93
	$(705)_n$					Found	64.54	2.73	10.09
6b	$(C_{38}H_{19}N_5O_{10})_n$	0.20	8.4	29.6	3.5	Calcd.	64.68	2.70	9.93
	$(705)_n$					Found	64.61	2.74	10.07
6c	$(C_{44}H_{23}N_5O_{10})_n$	0.23	10.2	32.4	3.2	Calcd.	67.61	2.94	8.96
	$(781)_n$					Found	67.48	3.05	8.89
6d	$(C_{44}H_{23}N_5O_{10})_n$	0.22	9.9	31.4	3.2	Calcd.	67.61	2.94	8.96
	$(781)_n$					Found	67.52	2.89	8.91
6e	$(C_{47}H_{29}N_5O_{10})_n$	0.24	10.7	32.8	3.0	Calcd.	68.53	3.52	8.51
	$(823)_n$					Found	68.12	3.57	8.46
6f	$(C_{52}H_{27}N_5O_{10})_n$	0.22	9.8	28.5	2.9	Calcd.	70.83	3.06	7.95
	$(881)_n$					Found	70.67	3.11	8.01

[a] Measured in DMAc at a concentration of 1.0 g dl^{-1} at 30 °C.
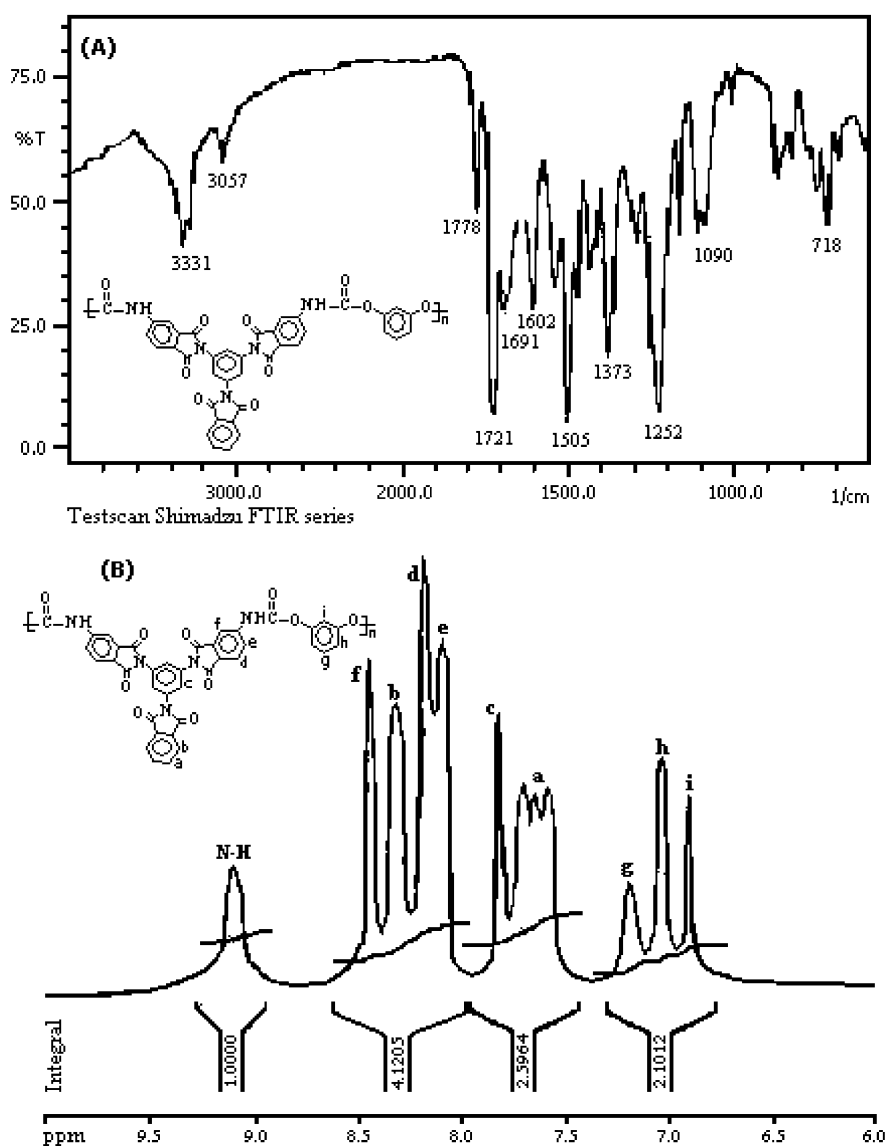[b] Measured by GPC in DMF with polystyrene as a standard.

Fig. 1. FT IR (A) and ^{1}H NMR (B) spectra of poly(urethane–imide) **6a**.

Table 3
Solubility of the resulting poly(urethane-imide)s

Polymer code	DMAc	DMF	DMSO	NMP	Py	Chloroform	DCM	THF	Acetone
6a	++	++	++	++	+	±	+	+	−
6b	++	++	++	++	±	±	±	±	−
6c	++	++	++	++	±	±	±	±	−
6d	++	++	++	++	+	+	±	+	−
6e	++	++	++	++	+	+	+	+	−
6f	++	++	++	++	+	+	+	+	−

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.

to the results, no crystal diffraction was detected for most of the polymers, except poly(urethane-imide)s **6b** and **6c** bearing *p*-phenylene and *p*-biphenylene moieties, respectively. The polymers **6b** and **6c** showed about 10% crystalline patterns due to the existence of the rigid and symmetrical segments in their backbones that led to a better packing of the polymer chains. Moreover, isopropylidene- and binaphthylene-based polymers (**6e** and **6f**) 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 thermogravimetric analysis (TGA/DTG). The thermal properties data are summarized in Table 4. The DSC profiles were achieved at a heating rate of 20 °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 due to their intractable wholly aromatic chains. The DSC thermograms of the poly(urethane-imide)s **6a–6f** showed glass-transition temperatures (T_g's) in the range between 197 and 219 °C depending on the structure of dihydroxylic components. Among the polymers obtained, polymer **6f** 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 restricted the free rotation of the macromolecular chains leading to an enhanced T_g value. In order to compare the thermal properties, some homo- and co-polymers, including poly-imide, polyurethane, poly(amide-imide), poly(ether-imide), and poly(ester-imide) with the structures shown in Scheme 3 were considered. The thermal properties of these reference polymers are also listed in Table 5. All the poly(urethane-imide)s exhibited lower T_g's than the fully aromatic homopolyimide **R1** [30], the commercially available poly(ether-imide) Kapton H, **R2** [31], the poly(amide-imide)s **R3** [31] and **R4** [22], and the poly(ester-imide) **R5** [23] due to higher flexibility of the urethane linkages than those of imide, amide, and ester bonds. However, they showed higher T_g values than the homopolyurethane **R6** [32].

Thermal stability evaluation of the polymers was carried out by TGA/DTG in nitrogen at a heating rate of 10 °C min^{-1}. The representative TGA/DTG curves of polymers **6a** and **6f** are shown in Figures 2 and 3, respectively. The poly(urethane-imide)s obtained were stable up to 400 °C and lost 10% of their total weight between 385 and 412 °C, which showed a remarkably improvement of decomposition temperature in comparison with common homopolyurethanes [33–35]. The desirable thermal stability of the resulting polymers is ascribed to their wholly aromatic structures. All thermograms of the

Table 4
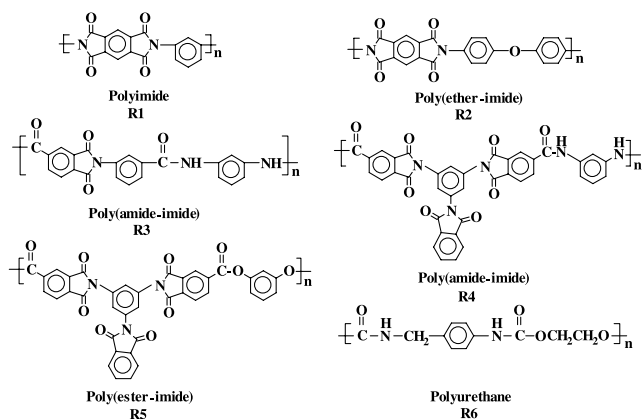Thermal properties and film quality of the resulting poly(urethane-imide)s

Polymer code	T_g[a] (°C)	$T_{10\%}$[b] (°C)	Char yield[c] (%)	Film quality[d]	
6a	204	391	31	Brittle	Transparent brown
6b	198	399	28	Brittle	Transparent brown
6c	209	404	37	Brittle	Transparent brown
6d	197	403	33	Brittle	Opaque brown
6e	211	385	29	Slightly flexible	Transparent brown
6f	219	412	38	Brittle	Opaque brown

[a] From the second heating traces of DSC measurements with a heating rate of 10 °C min^{-1} in N$_2$.
[b] Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10 °C min^{-1}.
[c] Residual wt% at 800 °C in nitrogen.
[d] Films were cast from a 10% NMP solution on a glass plates.

Scheme 3. The chemical structure of some reference polymers.

Table 5
Thermal properties of some reference polymers

Polymer code	T_g (°C)	$T_{10\%}$ (°C)	Char yield (%)
R1	412	600	58[a]
R2	428	528[b]	–[c]
R3	290	540	–
R4	372	541	61[d]
R5	264	455	32[d]
R6	110	248	–

Data from Refs. [30–32].
[a] Residual wt% at 700 °C in nitrogen.
[b] Temperature at which 5% weight loss.
[c] Was not reported.
[d] Residual wt% at 800 °C in nitrogen.

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 **6a–6f** exhibited less thermal stability than those of the homopolyimide **R1**, the poly(ether-imide) Kapton H, **R2**, the poly(amide-

imide)s **R3** and **R4**, and the poly(ester-imide) **R5** (Table 5). However, they showed higher $T_{10\%}$ values than the homopolyurethane **R6**. 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 **6e** which had somewhat flexibility. This brittleness behavior of the polymers could be attributed to the low molecular weight of the polymers due to an
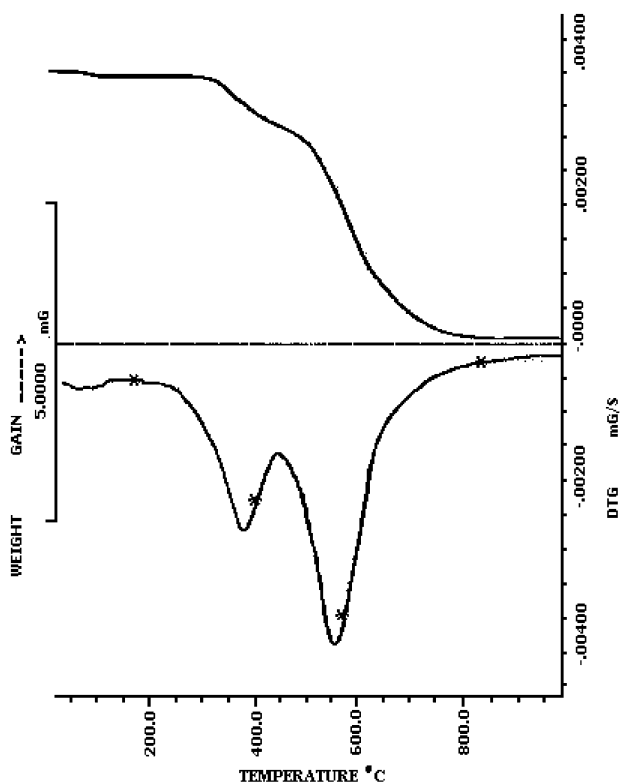
Fig. 2. TGA/DTG curves of poly(urethane-imide) **6a**.
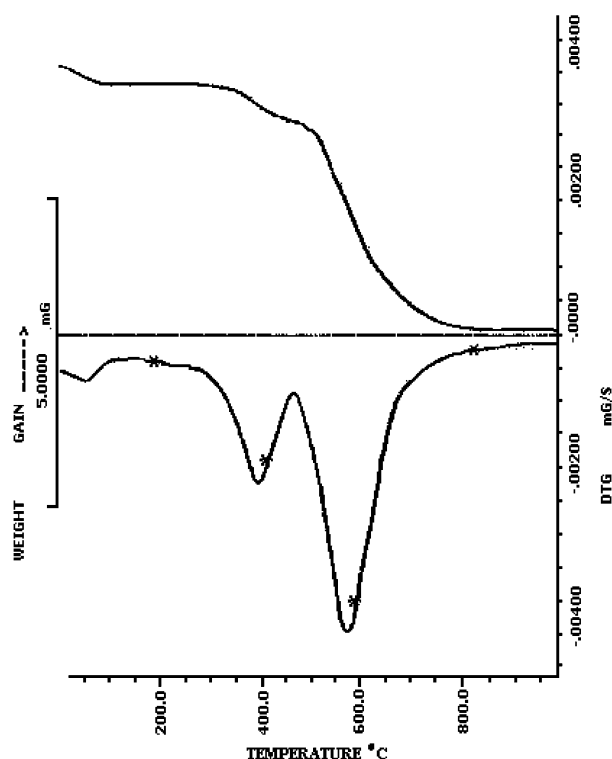
Fig. 3. TGA/DTG curves of poly(urethane-imide) **6f**.

imbalance in stoichiometric amounts between the in situ-formed diisocyanates and the dihydroxylic compounds. Furthermore, the relatively perceptible flexibility in polymer **6e** containing isopropylidene might be attributed to the moderate inherent viscosity of this polymer (0.24 dl g^{-1}), which caused by its chain-extended conformations in solution state. The films quality for all the poly(urethane-imide)s are summarized in Table 4.

4. Conclusion

New dicarbonylazide **3** with preformed three imide units and fully aromatic structures was synthesized and characterized. The direct polyaddition reaction of compound **3** with a number of aromatic dihydroxylic compounds resulted in preparation of wholly aromatic poly(urethane-imide)s, **6a–6f**. In fact, separately synthesis and purification of the intermediate diisocyanate was not necessary, and the polyaddition readily proceeded as a one-pot reaction starting from triimide–dicarbonylazide **3**. The main objectives of this study were to improve the solubility of homopolyimides as well as the thermal stability of homopolyurethanes by the introduction of both imide and urethane linkages into the macromolecular chains. The resulting poly(urethane-imide)s showed a better solubility in common organic solvents than the polyimides, poly-(amide-imide)s, and even poly(ester-imide)s with the same aromatic structure. Furthermore, the amorphous polymers obtained exhibited a desirable heat resistance in comparison with aromatic polyurethanes due to the presence of thermally stable imide groups into the fully aromatic structures.

Acknowledgements

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