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### A Facile Route for the One-Step Synthesis of New Fully Aromatic Poly(urea-imide)s

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## A Facile Route for the One-Step Synthesis of New Fully Aromatic Poly(urea-imide)s

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*The direct preparation of various aromatic poly(urea-imide)s (5a<sub>1</sub>–5b<sub>4</sub>) from N-[3,5-bis(trimellitimido)phenyl]phthalimide (1) using diphenylphosphoryl azide (DPPA) was investigated. The polymers were 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. This was followed by poly-addition of 3 with two aromatic diamines (4a and 4b). In order to compensate the diisocyanate shortage against the diamines, some excess amounts of the initial triimide-dicarboxylic acid 1 were used. The molecular weights of the resulting poly(urea-imide)s were evaluated viscometrically. The poly(urea-imide)s exhibited an excellent solubility in a variety of polar solvents. The crystallinity nature of the polymers was estimated by means of WXR. The glass transition temperatures and the 10% wt loss temperatures of the polymers 5a<sub>3</sub> and 5b<sub>3</sub> were determined by DSC and TGA/DTG methods in nitrogen atmosphere, respectively. The transparent films of the resulting polymers were also prepared by casting the solution.*

**Keywords** direct polycondensation, poly(urea-imide)s, diphenylphosphoryl azide, thermal stability

### Introduction

Most carbonyl azides are readily converted to corresponding isocyanates via a Curtius rearrangement, and these latter compounds react *in situ* with amino or hydroxylic groups to form ureas or urethanes linkages, respectively (1, 2). In 1991, various kinds of polyureas and polyurethanes were prepared by Nishi et al. through the reaction of amino and hydroxyl groups with the isocyanates that were formed by Curtius rearrangement of the carbonyl azide precursors. These precursors themselves were prepared from the corresponding carboxylic acids using diphenylphosphoryl azide (3).

Polyureas are among the most advanced resins on the market. Its versatility, strength, and longevity make them suitable for many applications. In fact, this block of polymers give fire-proofing polycoats, elastomers, fibers and adhesives (4). Polymerizations of this type have been investigated (5–10). In order to increase

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thermal and mechanical properties of such a polymer, various attempts have been made to incorporate amide linkages and imide heterocyclic units into polyurea 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 solubility (18–22). Therefore, it appears that the presence of urea linkages by the side of imide heterocyclic rings into a polymer chain is useful for presentation of positive properties. It means that this putting together increases thermal stability and processability of polyurea and polyimide, respectively.

In our previous studies, we successfully prepared a series of wholly aromatic poly(amide-imide)s (23), poly(ester-imide)s (24), and poly(urethane-imide)s (25) from a new dicarboxylic acid bearing three imide heterocyclic rings N-[3,5-bis(trimellitimidophenyl)]phthalimide, **1**. The results clearly showed the polymers obtained from monomer **1** have both good solubility in common organic solvents and high thermal stability. In this paper, in continuation of the above-mentioned works, owing to comparison between the characterization and property data of the polymers obtained, and in order to study a one-step route for polyurylation, we will discuss the detailed synthetic procedure for the preparation of poly(urea-imide)s based on a fully aromatic triimide-dicarboxylic acid (**1**) and two aromatic diamines (**4a** and **4b**) via Curtius rearrangement.

Yields of the Curtius rearrangement reactions are known generally not to be very high (26, 27). Hence, a disadvantage of this direct method is due to derangement in stoichiometric balance between the diisocyanate obtained from Curtius rearrangement and diamine 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 diamine monomer. In the present study, compound **1** was polymerized directly with various aromatic diamines in mole ratios of 1.8 COOH/1.0 NH<sub>2</sub>, 1.5 COOH/1.0 NH<sub>2</sub>, 1.2 COOH/1.0 NH<sub>2</sub>, and 1.0 COOH/1.0 NH<sub>2</sub> to prepare a new family of poly(urea-imide)s. The polymers obtained are thoroughly characterized by spectroscopic methods and elemental analyses. The structure effects on some properties of the resulting poly(urea-imide)s including viscosity, crystallinity, solubility, and thermal stability could be easily clarified and compared with analogous poly(amide-imide)s, poly(ester-imide)s, and poly(urethane-imide)s resulted from our previous works (23–25).

## Experimental

### Materials

All initial chemicals were purchased either from Merck or Fluka Chemical Co., except DPPA (97%) that was prepared from Sigma-Aldrich Chemical Co. and used as obtained without further purification. The diamines compounds including N-(3,5-diaminophenyl)-phthalimide (**4a**) and 4-*p*-biphenyl-2,6-bis(4-aminophenyl)pyridine (**4b**) were synthesized as described previously (23, 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 N-[3,5-bis(trimellitimido)phenyl]phthalimide (1)*

N-(3,5-Diaminophenyl)phthalimide was synthesized via condensation between 3,5-dinitroaniline and phthalic anhydride in dry DMF and a subsequent reduction with powdered tin and concentrated hydrochloric acid similar to that as reported in the literature (29). Then, imide ring-containing diacid **1** was synthesized by the condensation of the resulting N-(3,5-diaminophenyl)phthalimide with two mole equivalents of TMA in glacial acetic acid according to our previous work (23).

#### *Synthesis of the Poly(urea-imide)s*

The general procedure to prepare the poly(urea-imide)s **5a<sub>1</sub>–5b<sub>4</sub>** is as follows: To a mixture of triimide-dicarboxylic acid **1** (1.0, 1.2, 1.5 or 1.8 mmol) in DMSO as reaction solvent (3.0 mL) were added DPPA (1.2 mL) and triethylamine (1.5 mL). The final mixture was stirred 2 h at about 10°C and then for 3 h at 70°C until evolution of nitrogen gas stopped. After both steps, the reaction progress was checked by TLC plates. The diamine compound N-(3,5-diaminophenyl)phthalimide (**4a**) or 4-*p*-biphenyl-2,6-bis(4-aminophenyl)pyridine (**4b**) (1.0 mmol) in DMSO (2 mL) was added dropwise to the initial reaction mixture, and the final mixture was heated for 12 h at 90°C. The viscous polymer solution obtained was trickled on stirred methanol to give rise to a crude precipitate, which was collected by filtration, washed thoroughly with methanol, hot water, 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%. Elemental analysis for **5a<sub>3</sub>**, C<sub>46</sub>H<sub>24</sub>N<sub>8</sub>O<sub>10</sub> (848)<sub>n</sub>: C, 65.09%; H, 2.83%; N, 13.21%. Found: C, 64.21%; H, 2.91%; N, 13.25%. **5b<sub>3</sub>**, C<sub>61</sub>H<sub>36</sub>N<sub>8</sub>O<sub>8</sub> (1008)<sub>n</sub>: C, 72.62%; H, 3.57%; N, 11.11%. Found: C, 71.83%; H, 3.61%; N, 11.15%.

The films of the resulting poly(urea-imide)s were prepared by casting the solution. In order to attain this objective, 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.

#### *Determination of the Diisocyanate Content*

Owing to a study of the Curtius rearrangement content, a reaction flask was quenched after diisocyanate **3** formation. The Curtius rearranged diisocyanate solution obtained was trickled on stirred dry toluene to give rise to a crude precipitate, which was collected by filtration. Recrystallization of the product obtained from DMF-benzene mixture gave the corresponding white diisocyanate in pure form in 74% yield, mp > 95°C (dec.). The diisocyanate content of compound **3** was determined by the treatment of di-*n*-butylamine solution (25 ml of 0.1 M) with a solution of compound **3** (0.595 g, 1 mmol) in DMF followed by the titration of the resulting solution against hydrochloric acid (0.02 M) to bromocresol green end point. Elemental analysis for diisocyanate **3**, C<sub>32</sub>H<sub>13</sub>N<sub>5</sub>O<sub>8</sub>: C, 64.54%; H, 2.18%; N, 11.76%. Found: C, 64.13%; H, 2.24%; N, 11.81%.

### Measurements

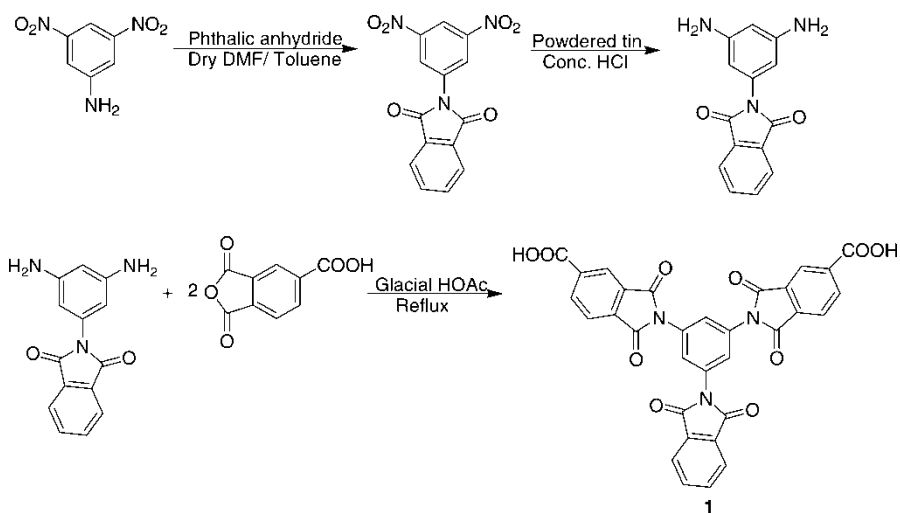
Melting points were determined with a Buchi 535 melting point apparatus. Inherent viscosities were measured by a standard procedure using a Cannon Fensk routine viscometer in DMAc at a concentration of  $0.5 \text{ g} \cdot \text{dL}^{-1}$  at  $30^\circ\text{C}$ . Elemental analyses were performed with a Perkin-Elmer 2400 CHN analyzer.  $^1\text{H-NMR}$  spectra were recorded on a Bruker Advanced DPX-250 250 MHz spectrometer in  $\text{DMSO-d}_6$  at  $25^\circ\text{C}$  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  $\text{Cu-K}_\alpha$  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  $10^\circ\text{C min}^{-1}$ . The DSC traces were obtained from heating, rapidly cooling, and reheating of samples at a range of  $50\text{--}400^\circ\text{C}$ . The range FS of 20 mW for DSC and 10 mG for TGA were used.

## Results and Discussion

### Synthesis

Scheme 1 Shows the synthesis route of imide ring-containing diacid **1**.

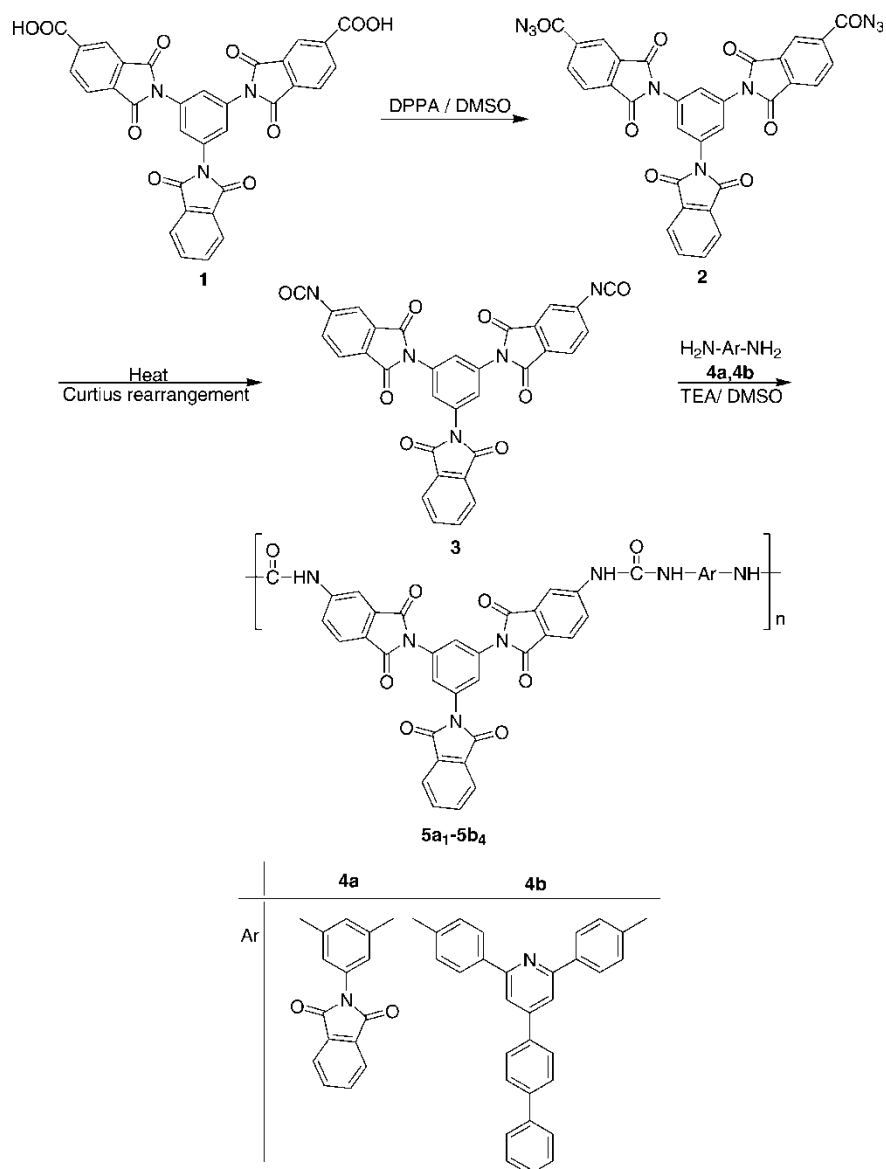
A condensation reaction between *N*-(3,5-diaminophenyl)phthalimide and two mole equivalents of TMA in glacial acetic acid gave rise to the final monomer **1**. The details of the synthesis procedure and the characterization data was reported in our previous work (23). The monomer **1**, with different molar ratios against two aromatic diamines (**4a** and **4b**), was directly used to prepare some poly(urea-imide)s by means of DPPA in DMSO as polymerization solvent. In this procedure, for avoidance of polyamidation as the side polymerization reaction, the acyl azide, which is derived from the carboxyl component, has to be converted to isocyanate prior to the addition of the amino



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

component. By employing this procedure, polymers with urea bonds could only be prepared from dicarboxylic acids and diamines. The synthetic route chosen for the preparation of new poly(urea-imide)s **5a<sub>1</sub>–5b<sub>4</sub>** is shown in Scheme 2.

Triimide-dicarboxylic acid **1** was converted to triimide-di(carbonyl azide) **2** using DPPA in DMSO. The thermal decomposition of triimide-di(carbonyl azide) **2** via Curtius rearrangement gave the corresponding diisocyanate **3**. In continuation of this reaction, compound **3** was treated with two aromatic diamines (**4a** and **4b**) to prepare the final poly(urea-imide)s. The reactions including diisocyanate formation and polyaddition proceeded readily in a yellowish and brownish homogeneous solution for all polymers



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

preparation. The poly(urea-imide)s were prepared in total yields of about 60% starting from triimide-dicarboxylic acid **1**. These low yields are reasonable because of the *in situ* initial Curtius rearrangement reaction. In order to further study this particular Curtius rearrangement, a reaction system was stopped before polyurylation reactions. In fact, in this study the diamine was not added to the reaction flask, and 3 h heat and stirred under  $N_2$  at  $70^\circ C$  was the end of the reaction (track by TLC). The Curtius rearranged diisocyanate was obtained in 74% yield. The impurities in this test reaction could contain unfunctionalized or only monofunctionalized species, which their presence in the polymerization flask unfortunately causes not only a significantly decrease in molecular weight of final products, but also a loss in polyurylation reactions yields. The identity of diisocyanate synthesized was confirmed by FT-IR and  $^{13}C$ -NMR spectroscopy and elemental analysis. The FT-IR spectrum of diisocyanate **3** showed the

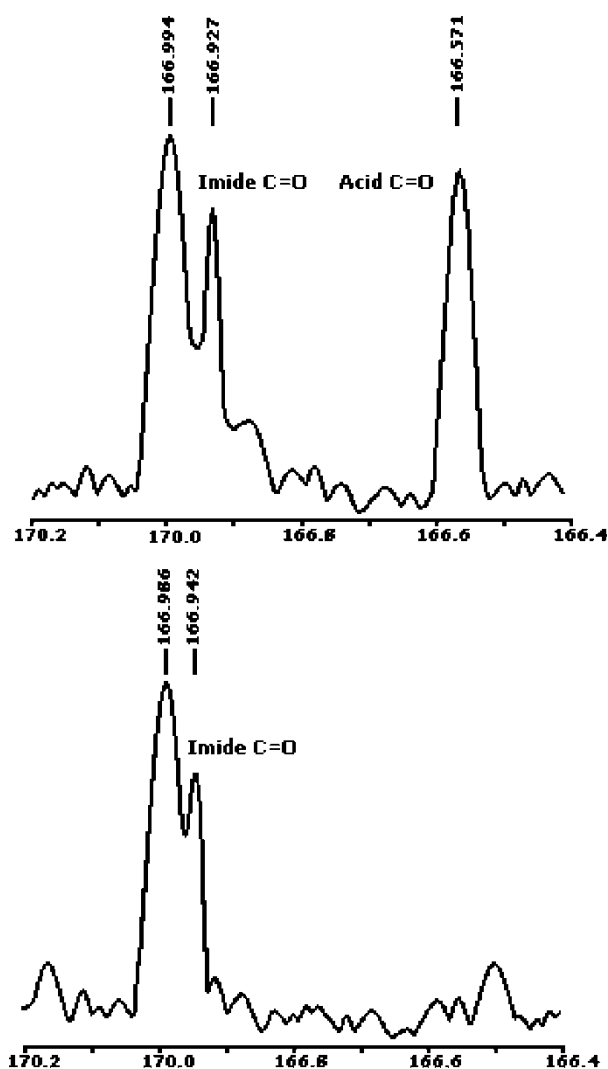


Figure 1.  $^{13}C$ -NMR of initial diacid **1** and diisocyanate **3**.

characteristic absorption band at  $2255\text{ cm}^{-1}$  assigned isocyanate group. Furthermore, in this spectrum the outstanding signals attributed to COO-H stretching of the initial diacid and  $-\text{N}=\text{N}^+=\text{N}^-$  stretching of the intermediate di(carbonyl azide) disappeared, completely. The successful thermal Curtius rearrangement is also justifiable by  $^{13}\text{C}$ -NMR spectra. Figure 1 shows extended  $^{13}\text{C}$ -NMR spectra of the initial diacid **1** and the diisocyanate **3** in a region of 166.4–167.2 ppm.

The signal attributed to acid carbon resonance in  $^{13}\text{C}$ -NMR spectrum of initial diacid **1** at about 166.6 ppm disappeared in diisocyanate **3** spectrum. Instead, the resonance of isocyanate carbon appeared at about 124 ppm. Moreover, according to the analytical measurement used, the isocyanate content of compound **3** based on di-*n*-butylamine method (30) is 1.964 equivalents. On the other hand, as can be seen in Table 1, the resulting poly(urea-imide)s had different inherent viscosities depending on COOH/NH<sub>2</sub> mole ratios of the initial monomers. These viscosity values were measured in DMAc at a concentration of  $0.5\text{ g}\cdot\text{dL}^{-1}$  at  $30^\circ\text{C}$ . Furthermore, these low data showed that the resulting polymers have relatively low molecular weight, and this reality is justifiable in spite of an inherent shortage of this direct method for polyurylation. This disadvantage is due to derangement in stoichiometric balance between the diisocyanate obtained from the Curtius rearrangement and the diamines during the reaction progress. In fact, for the compensation of the diisocyanate shortage against the diamines, excess amounts of initial dicarboxylic acid **1** (1.8:1.0, 1.5:1.0, and 1.2:1.0) were also used alternately for the preparation of polymers **5a<sub>1</sub>–5b<sub>4</sub>**. When the initial triimide-dicarboxylic **1** is used in the 1.5:1.0 mole ratio of COOH/NH<sub>2</sub>, the final polymers possess relatively higher viscosity values than the polymers obtained from other conditions, and when a stoichiometrically balance condition is used, the final polymers will possess the lowest viscosities. Therefore, most of the subsequent studies, including characterization and properties, were only performed for poly(urea-imide)s **5a<sub>3</sub>** and **5b<sub>3</sub>** with the highest viscosity values. Consequently, the observed low yields and, in particular, low molecular weights in this easy direct polyurylation are reasonable because the polymerization reactions are very sensitive to the reaction medium.

The structure of the above-mentioned poly(urea-imide)s were confirmed by FT-IR and  $^1\text{H}$ -NMR spectroscopy methods and elemental analyses. As an example, a representative FT-IR spectrum of poly(urea-imide) **5a<sub>3</sub>** is shown in Figure 2(A). The FT-IR spectra

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

Polymer code	Diamine code	Mol ratio of COOH/OH	Yield (%)	$\eta_{\text{inh}}^a$ (dL · g <sup>-1</sup> )	Color
<b>5a<sub>1</sub></b>	<b>4a</b>	1.0/1.0	58	0.10	Yellow
<b>5a<sub>2</sub></b>	<b>4a</b>	1.2/1.0	61	0.14	Yellow
<b>5a<sub>3</sub></b>	<b>4a</b>	1.5/1.0	59	0.19	Yellow
<b>5a<sub>4</sub></b>	<b>4a</b>	1.8/1.0	57	0.15	Yellow
<b>5b<sub>1</sub></b>	<b>4b</b>	1.0/1.0	62	0.11	Pale brown
<b>5b<sub>2</sub></b>	<b>4b</b>	1.2/1.0	59	0.13	Pale brown
<b>5b<sub>3</sub></b>	<b>4b</b>	1.5/1.0	61	0.21	Pale brown
<b>5b<sub>4</sub></b>	<b>4b</b>	1.8/1.0	61	0.17	Pale brown

<sup>a</sup>Measured in DMAc at a concentration of  $0.5\text{ g}\cdot\text{dL}^{-1}$  at  $30^\circ\text{C}$ .



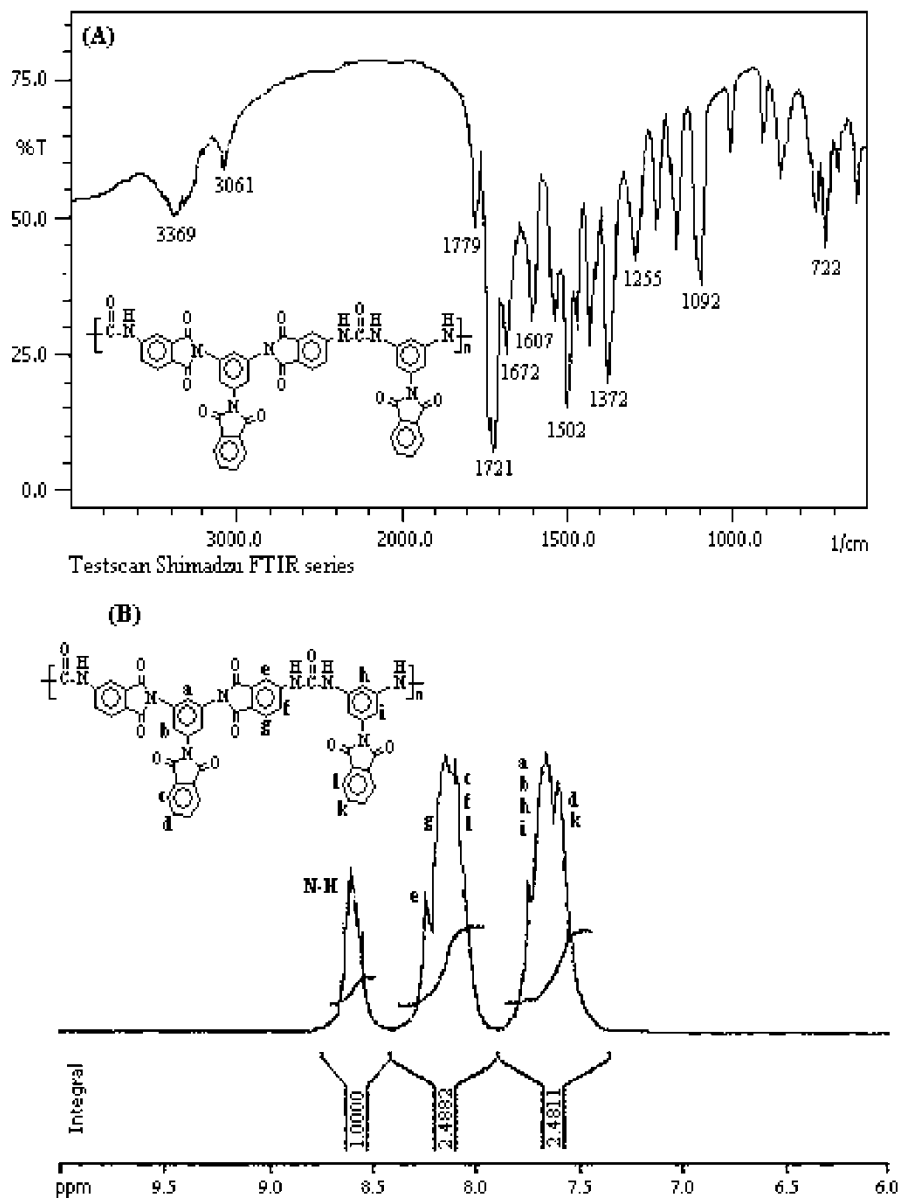


Figure 2. FT-IR (A) and <sup>1</sup>H NMR (B) spectra of poly(urea-imide) **5a<sub>3</sub>**.

of the polymers showed bands around  $3340\text{ cm}^{-1}$  assigned to stretching vibration of the urea N-H bonds. The characteristic absorptions of the carbonyl groups occurred around 1780, 1720 (asymmetric and symmetric imide C=O stretching, respectively), and 1670 (urea C=O stretching)  $\text{cm}^{-1}$ . The <sup>1</sup>H-NMR spectra of both poly(urea-imide)s **5a<sub>3</sub>** and **5b<sub>3</sub>** showed -NH- proton signal in about 8.60 ppm. The aromatic ring protons appeared in the region of about 7.40–8.40 ppm. A typical <sup>1</sup>H-NMR spectrum, for polymer **5a<sub>3</sub>** is presented in Figure 2(B). Finally, the elemental analyses of the polymers **5a<sub>3</sub>** and **5b<sub>3</sub>** confirmed their proposed structures.

**Properties of the Poly(urea-imide)s**

The solubility behavior of poly(urea-imide)s **5a<sub>3</sub>** and **5b<sub>3</sub>** in a variety of common organic solvents such as DMAc, DMF, DMSO, NMP, pyridine, chloroform, DCM, THF and acetone was studied in a concentration of 5 mg · mL<sup>-1</sup>. These polymers easily could be dissolved in polar aprotic solvents such as N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), pyridine at room temperature, and all of them were soluble in weakly polar solvents such as chloroform, dichloromethane (DCM), and tetrahydrofuran (THF) upon heating at about 60°C. In general, the flexible amide, ester, urethane, and urea linkages affect the solubility of a copolyimide to a great extent due to a solvation effect. Besides the solvation effects related to enthalpy factor, the good solubility of these polymers is also caused, mainly by the entropy advantage which resulted from bulky pendant groups in the polymer structures that lead to expansion of the macromolecular chains in their solution state. Furthermore, this block of copolyimides showed somewhat further solubility toward the above solvents compared with that of the other copolyimides with analogous structure (23–25). This organosoluble behavior of these polymers could also be attributed to the introduction of bulky phthalimido and biphenyl pendant groups related to diamines components that inhibited the close packing of the polymer chains.

The crystallinity nature of the poly(urea-imide)s **5a<sub>3</sub>** and **5b<sub>3</sub>**, was measured by wide-angle X-ray diffraction scans at room temperature. Diffraction patterns of the above poly(urea-imide)s were obtained with 2θ ranging from 5° to 50°. According to the results, no crystal diffraction was detected for these polymers. This amorphous diffraction patterns is reasonable because the presence of the bulky and disorderly phthalimido pendant group decreases the intermolecular forces between the polymer chains causing a decrease in crystallinity. Moreover, poly(urea-imide) **5b<sub>3</sub>** presented a significant decrease in crystallinity behavior that is reasonable because presence of the bulky biphenylene pendant groups attached to the backbone induces looser chain packing.

The thermal behavior of the poly(urea-imide)s **5a<sub>1</sub>**, **5b<sub>1</sub>**, **5a<sub>3</sub>**, and **5b<sub>3</sub>** was evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA/DTG). The thermal properties data are summarized in Table 2.

As shown in Figure 3, high glass transition temperatures were found due to their intractable wholly aromatic chains.

**Table 2**  
Thermal properties and film quality of the resulting poly(urea-imide)s

Polymer code	T <sub>g</sub> <sup>a</sup> (°C)	T <sub>10%</sub> <sup>b</sup> (°C)	Char yield <sup>c</sup> (%)	Film quality <sup>d</sup>	
<b>5a<sub>1</sub></b>	241	409	44	Brittle	Transparent yellow
<b>5b<sub>1</sub></b>	237	359	48	Slightly flexible	Transparent brown
<b>5a<sub>3</sub></b>	254	413	47	Slightly flexible	Transparent yellow
<b>5b<sub>3</sub></b>	239	402	53	Slightly flexible	Brown

<sup>a</sup>From the second heating traces of DSC measurements with a heating rate of 10°C min<sup>-1</sup> in N<sub>2</sub>.

<sup>b</sup>Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C min<sup>-1</sup>.

<sup>c</sup>Residual wt% at 800°C in nitrogen.

<sup>d</sup>Films were cast from a 10% NMP solution on a glass plates.

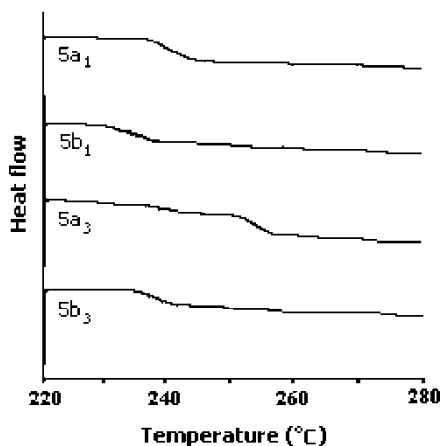
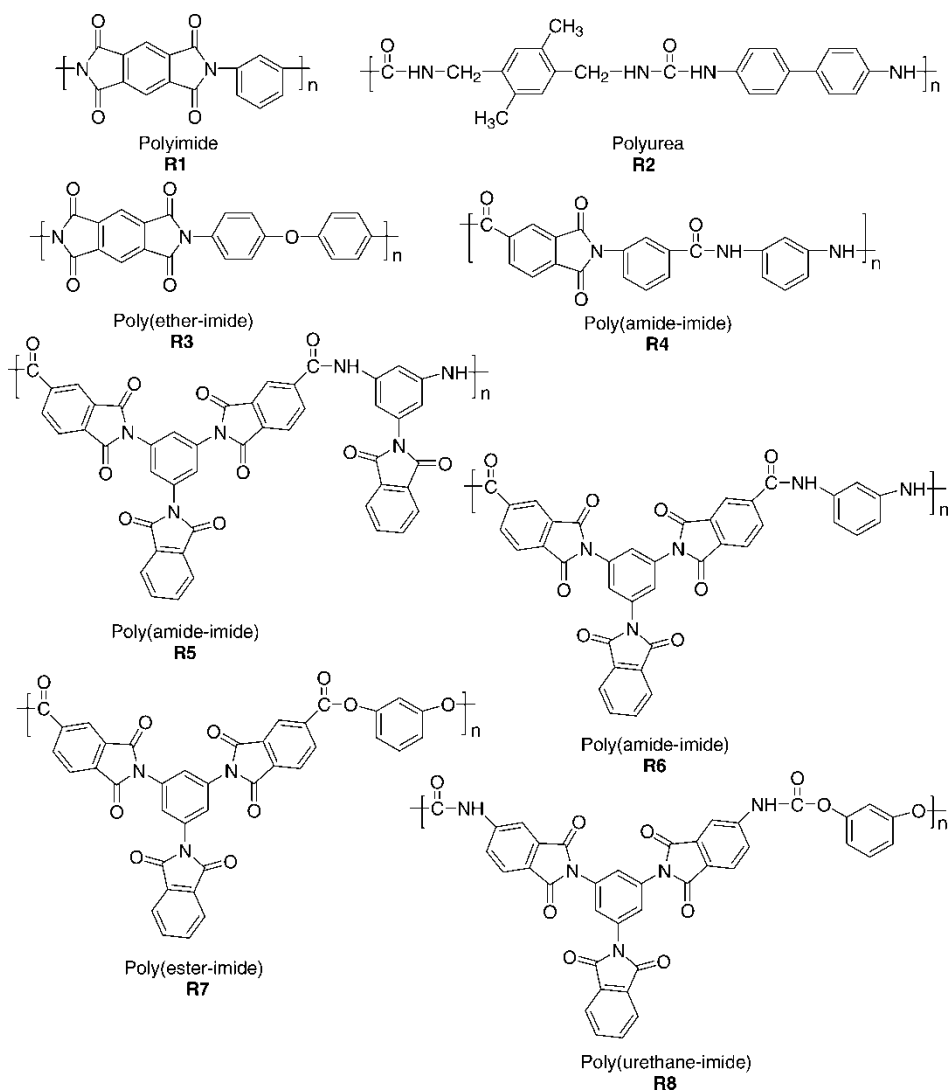


Figure 3. DSC plots of the poly(urea-imide)s **5a<sub>1</sub>**, **5b<sub>1</sub>**, **5a<sub>3</sub>**, and **5b<sub>3</sub>**.

The DSC investigations were achieved at a heating rate of  $10^{\circ}\text{C min}^{-1}$  in a nitrogen atmosphere. The influence of residual water or reaction solvent was observed in the first scanning of DSC measurements. However, the study of these first heating traces in DSC curves didn't show obvious peaks indicating phase transitions because of their amorphous nature, which easily could have resulted from wide-angle x-ray diffractograms. A rapid 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. The DSC thermograms of the mentioned poly(urea-imide)s showed glass-transition temperatures ( $T_g$ 's) at about  $240^{\circ}\text{C}$  depending on the structure of aromatic diamine component and the mole ratios of dicarboxylic acid **1**. Among the polymers **5a<sub>3</sub>** and **5b<sub>3</sub>**, polymer **5a<sub>3</sub>** showed a higher  $T_g$  value than the other. This could be attributed to the incorporation of rigid imide ring-containing pendant group 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 polyimide, polyurea, poly(ether-imide), poly(amide-imide), poly(ester-imide), and poly(urethane-imide) with the structures shown in Scheme 3 were considered.

The thermal properties of these reference polymers are also listed in Table 3. The resulting poly(urea-imide)s exhibited remarkably lower  $T_g$ 's than the fully aromatic homopolyimide **R1**, the commercially available poly(ether-imide) Kapton H, **R3**, the poly(amide-imide)s **R4**, **R5**, and **R6** due to higher flexibility of the urea linkages than those of imide and amide bonds. However, they showed higher  $T_g$  values than the poly(urethane-imide) **R8**.

Thermal stability evaluation of the polymers **5a<sub>1</sub>**, **5b<sub>1</sub>**, **5a<sub>3</sub>**, and **5b<sub>3</sub>** was carried out by TGA/DTG in nitrogen at a heating rate of  $10^{\circ}\text{C} \cdot \text{min}^{-1}$ . The above-mentioned poly(urea-imide)s were stable up to  $400^{\circ}\text{C}$  and lost 10% of their total weight at  $413^{\circ}\text{C}$  and  $402^{\circ}\text{C}$  for polymers **5a<sub>3</sub>** and **5b<sub>3</sub>**, respectively, which showed a remarkable improvement of decomposition temperature in comparison with common homopolyurea **R2**. The desirable thermal stability of the resulting polymers is ascribed to their wholly aromatic structures. The representative TGA/DTG curves of polymers **5a<sub>3</sub>** and **5b<sub>3</sub>** are shown in Figures 4 and 5, respectively.



**Scheme 3.** The chemical structure of some reference polymers.

As can be seen, the two thermograms of these polymers were almost similar to each other. In fact, all the poly(urea-imide)s showed an obviously two-stage decomposition at elevated temperatures. Assuming a different stability of the urea and the imide units, the first stage of weight losses might be attributed to the early degradation of the urea linkages. Therefore, the 10% wt loss temperatures are mainly caused by the decomposition of urea linkages. Since the dipoles present at the urea groups are the weakest sites in terms of thermal stability, the rupture of the urea bonds occurs first. Furthermore, The poly(urea-imide)s **5a<sub>3</sub>** and **5b<sub>3</sub>** exhibited less thermal stability than those of the homopolyimide **R1**, the poly(ether-imide) Kapton H, **R3**, the poly(amide-imide)s **R4**, **R5**, and **R6**, and the poly(ester-imide) **R7** (Table 3). However, they showed higher  $T_{10\%}$  values than the homopolyurea **R2** and

**Table 3**  
Thermal properties of some reference polymers

Polymer code	Polymer class	T <sub>g</sub> (°C)	T <sub>10%</sub> (°C)	Char yield (%)
R1	Polyimide	412	600	58 <sup>a</sup>
R2	Polyurea	— <sup>b</sup>	340	—
R3	Poly(ether-imide)	428	528 <sup>c</sup>	—
R4	Poly(amide-imide)	290	540	—
R5	Poly(amide-imide)	403	554	63 <sup>d</sup>
R6	Poly(amide-imide)	372	541	61 <sup>d</sup>
R7	Poly(ester-imide)	264	455	32 <sup>d</sup>
R8	Poly(urethane-imide)	204	391	31 <sup>d</sup>

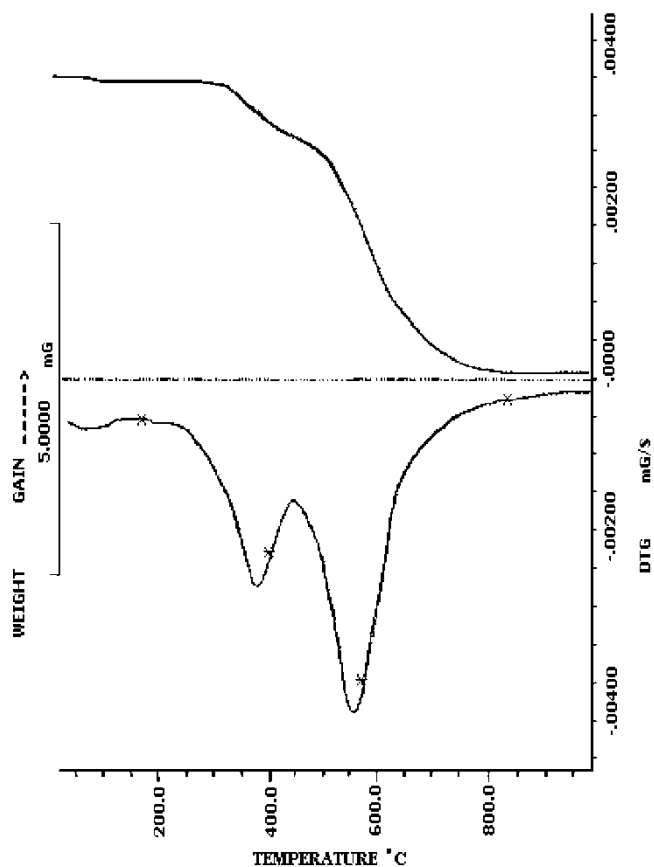
Data from Refs. (23–25) and (31–34).

<sup>a</sup>Residual wt% at 700°C in nitrogen.

<sup>b</sup>Was not reported.

<sup>c</sup>Temperature at which 5% wt loss.

<sup>d</sup>Residual wt% at 800°C in nitrogen.



**Figure 4.** TGA/DTG curves of poly(urea-imide) **5a<sub>3</sub>**.

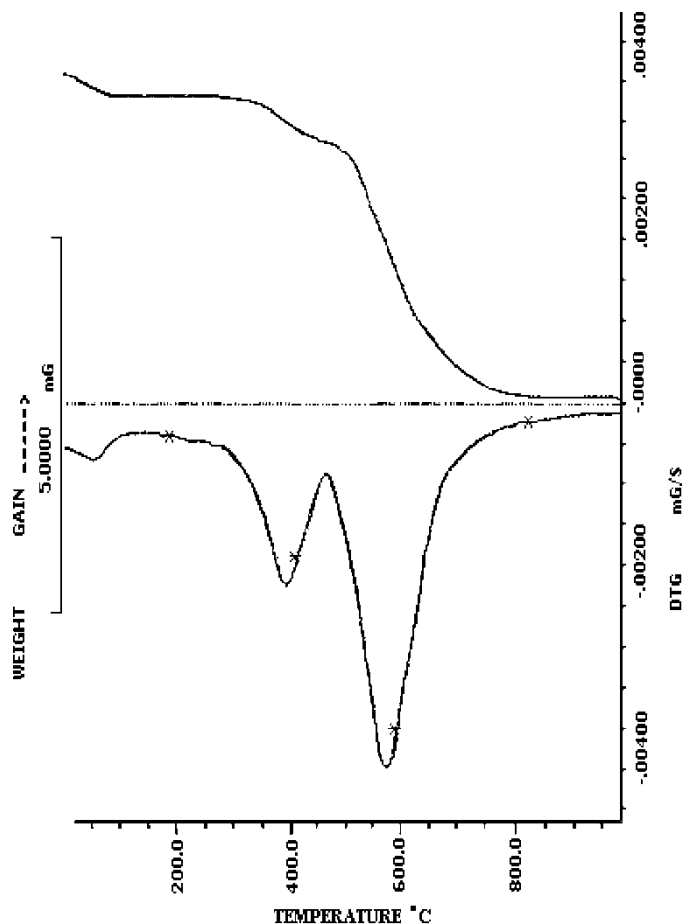


Figure 5. TGA/DTG curves of poly(urea-imide) **5b<sub>3</sub>**.

copoly(urethane-imide) **R8**. These observations might be attributed to the early degradation of the urea 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 obvious flexibility behavior was observed, and the resulting transparent films had a somewhat brittle nature. Although excess mole fractions of triimide-dicarboxylic acid **1** were used (1.8, 1.5, and 1.2) for polyurylation purposes, and in this manner we tried somewhat to compensate the shortage of *in situ*-formed diisocyanate **3** against diamines **4a** or **4b**, but this brittleness behavior of the poly(urea-imide)s could be attributed to both the macromolecular chains with a high degree of rigidity and the low molecular weight of the polymers due to a relative imbalance in stoichiometric amounts between the *insitu*-formed diisocyanates and the aromatic diamine compounds. The films quality for poly(urea-imide)s **5a<sub>1</sub>**, **5b<sub>1</sub>**, **5a<sub>3</sub>**, and **5b<sub>3</sub>** are summarized in Table 2.

## Conclusions

Dicarboxylic acid **1** with preformed three imide rings and fully aromatic structure was synthesized and used for the purpose of polymerization. The direct polyurylation reaction of compound **1** with a number of aromatic diamines resulted in preparation of some fully aromatic poly(urea-imide)s, **5a<sub>3</sub>–5b<sub>4</sub>**. In addition to 1.0:1.0 molar ratio of the initial monomers, for the compensation of the diisocyanate shortage against the diamines used, excess amounts of initial triimide-dicarboxylic acid **1** (1.8:1.0, 1.5:1.0, and 1.2:1.0) were also used for the preparation of the final polymers. It was found that when the initial dicarboxylic **1** is used in excess amount, in particular, for the case of 1.5:1.0 molar ratios, the final polymers possess higher viscosity values than the stoichiometric conditions. In this direct polyurylation, separate synthesis and purification of the intermediates including di(carbonyl azide) **2** and diisocyanate **3** were not necessary, and the polymerization reaction readily proceeded as one-pot reaction starting from imide ring-containing dicarboxylic acid **1**. The resulting poly(urea-imide)s showed 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 homopolyureas due to the presence of thermally stable imide rings into the fully aromatic structures.

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