

# Synthesis and Characterization of New Aromatic Polyamides, Polyimides, and Polyureas Containing 1,3,5-Triazine Rings

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## Synopsis

Novel aromatic polyamides, polyimides, and polyureas containing 1,3,5-triazine rings were prepared by the reaction of 2-anilino-4-aminoanilino-6-aminophenyl-1,3,5-triazines with aromatic dicarboxylic acid chlorides, pyromellitic dianhydride, and diisocyanates, respectively. All polymers were soluble in polar aprotic solvents such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, dimethyl sulfoxide, and pyridine. The glass transition temperatures of polymers were in the range of 220–260°C. The thermal stabilities of polymers were evaluated by thermogravimetric analysis in air. These polymers were stable up to 420°C for polyamides, 470°C for polyimides, and 300°C for polyureas.

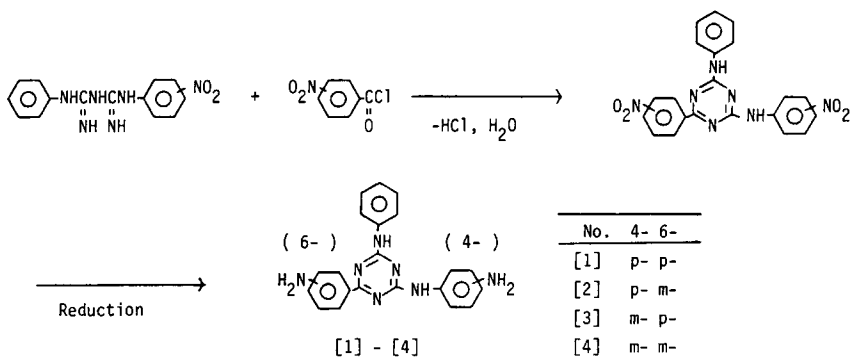
## INTRODUCTION

Aromatic polyamides and polyimides have been exploited for their excellent thermal and mechanical properties, some of them are commercially available.<sup>1-3</sup> Among the studies for preparing thermally stable polymers, many aromatic polyamides and polyimides containing heterocyclic units in the main chain have been shown to possess excellent thermal stability.<sup>4-7</sup>

In our previous articles,<sup>8-10</sup> we have demonstrated that the aromatic polymers containing triazine rings have good thermal stabilities. For example, the aromatic polyamides and polyimides prepared from 2-amino-4-aminoanilino-6-aminophenyl-1,3,5-triazines were stable up to 450°C for polyamides and 500°C for polyimides. However, the solubilities of these polymers in organic solvents were limited. It is well known that aromatic polymers are difficult to process due to their limited solubilities, thus improvement of their solubilities has become an important problem. Several articles<sup>11-13</sup> reported that the solubility of aromatic polymer could be increased by the introduction of a suitable substituent, but this modification often decreased the thermal stability of polymer. Recently, Imai et al.<sup>14</sup> and de Abajo et al.<sup>15</sup> reported that the aromatic polyamides containing bulky pendant groups are soluble in a wide range of organic solvents and the bulky groups have almost no effect on thermal stability.

In this work, we prepared several polyamides, polyimides, and polyureas containing anilino pendant groups on the triazine rings by the use of four new diamines of 2-anilino-4-aminoanilino-6-aminophenyl-1,3,5-triazines. The thermal behavior and solubility of these polymers will be presented.

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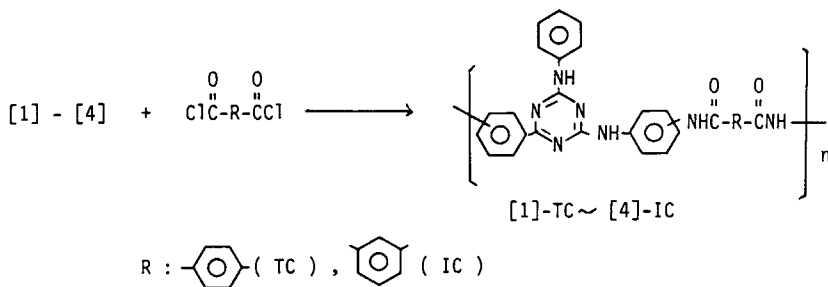
Scheme 1

## EXPERIMENTAL

### Materials

The 1-(*p*- or *m*-nitrophenyl)-5-phenylbiguanides were prepared by the reaction of phenyldicyanodiamide<sup>16</sup> with *p*- or *m*-nitroaniline hydrochlorides according to the method reported elsewhere.<sup>10</sup> Solvents used for the reactions such as *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), and *N,N*-dimethylacetamide (DMAc) were purified by distillation and drying. Terephthaloyl chloride (TC), isophthaloyl chloride (IC), pyromellitic dianhydride (PA), 4,4'-diphenylmethane diisocyanate (MI), and toluene 2,4-diisocyanate (TI) were used as obtained.

2-Anilino-4-(*p*-nitroanilino)-6-(*p*-nitrophenyl)-1,3,5-triazine [5]: 18.5 g (0.1 mol) of *p*-nitrobenzoyl chloride in 50 mL of acetone was added dropwise to a solution of 60 g (0.2 mol) of 1-(*p*-nitrophenyl)-5-phenylbiguanide in 350 mL of acetone and 50 mL of DMSO for 30 min at 0–5°C. After 1 h of stirring, 8 g (0.2 mol) of sodium hydroxide in water (50 mL) was added to this solution. After 30 min, 18.5 g (0.1 mol) of *p*-nitrobenzoyl chloride was added dropwise to this mixture again at 0–5°C for 30 min. The reaction was continued for 8 h at room temperature. The precipitated product was separated and washed with hot water.



Scheme 2

TABLE I  
 Preparation of Polyamides<sup>a</sup>

Polymer no.	Yield (%)	$\eta$ sp/C <sup>b</sup> (dL/g)
[1]-TC	94	0.40
[2]-TC	94	0.35
[3]-TC	96	0.33
[4]-TC	92	0.32
[1]-IC	99	0.35
[2]-IC	98	0.31
[3]-IC	95	0.32
[4]-IC	96	0.33

<sup>a</sup> Polymerization was carried out with 1.35 mmol of [1]–[4] and 1.35 mmol of diacid chlorides in 10 mL of NMP/HMPA (7/3) at room temperature for 24 h.

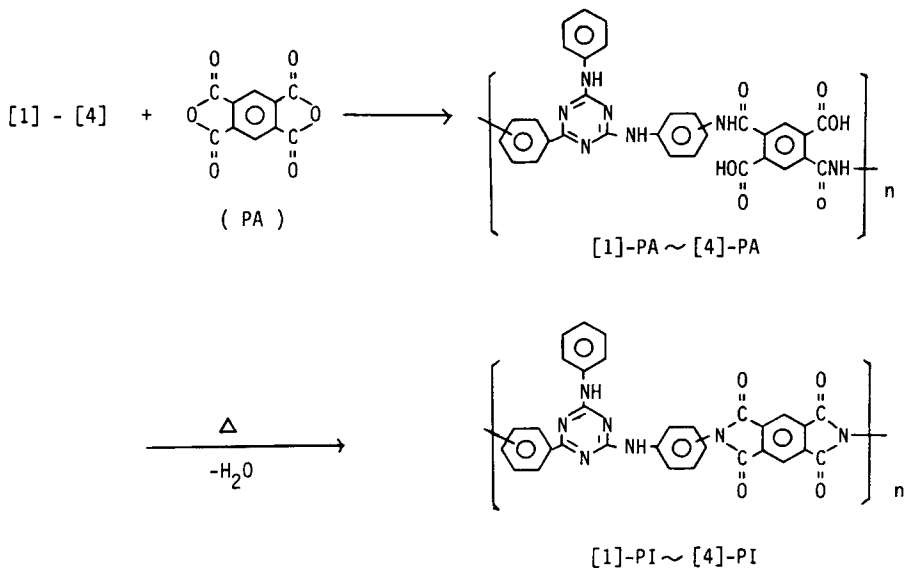
<sup>b</sup> Measured at a concentration of 0.2 g/dL in DMAc at 30°C.

The yield was 61 g (70%), recrystallized from *N,N*-dimethylformamide (DMF) and water, mp 283°C.

ANAL. Calcd: C<sub>21</sub>H<sub>15</sub>N<sub>7</sub>O<sub>4</sub>: C, 58.47%; H, 3.52%; N, 22.83%. Found: C, 58.81%; H, 3.33%; N, 22.43%.

Other dinitro-compounds [6]–[8] were also prepared by the reaction of 1-(*p*- or *m*-nitrophenyl)-5-phenylbiguanides with *p*- or *m*-nitrobenzoyl chlorides in a similar method above.

2-Anilino-4-(*p*-nitroanilino)-6-(*m*-nitrophenyl)-1,3,5-triazine [6]: Yield 65%, mp 282°C. (Found: C, 58.66%; H, 3.37%; N, 22.72%). 2-Anilino-4-(*m*-nitroanilino)-6-(*p*-nitrophenyl)-1,3,5-triazine [7]: Yield 71%, mp 270°C. (Found: C, 58.77%; H, 3.46%; N, 23.05%). 2-Anilino-4-(*m*-nitroanilino)-6-



Scheme 3

TABLE II  
Preparation of Polyamic Acids<sup>a</sup>

Polymer no.	Yield (%)	$\eta$ sp/C <sup>b</sup> (dL/g)	Water loss (%)	
			By desorp. <sup>c</sup>	By cyclo. <sup>d</sup>
[1]-PA	92	0.28	4.63	6.25
[2]-PA	94	0.25	4.55	6.64
[3]-PA	98	0.24	5.04	6.19
[4]-PA	95	0.26	4.33	6.28

<sup>a</sup> Polymerization was carried out with 1.35 mmol of [1]–[4] and 1.35 mmol of pyromellitic dianhydride in 10 mL of NMP/HMPA (7/3) at room temperature for 24 h.

<sup>b</sup> Measured at a concentration of 0.2 g/dL in DMAc at 30°C.

<sup>c</sup> Estimated values; 4.40% (1.5 H<sub>2</sub>O) from elemental analysis.

<sup>d</sup> Calculated values; 6.13%.

(*m*-nitrophenyl)-1,3,5-triazine [8]: Yield 80%, mp 155°C. (Found: C, 58.31%; H, 4.03%; N, 22.53%).

### Monomer Preparation

2-Anilino-4-(*p*-aminoanilino)-6-(*p*-aminophenyl)-1,3,5-triazine [1]: 26 g of ferrous sulfate and 90 g of iron powder were added to a suspension of 19.3 g (0.045 mol) of [5] in a mixture solvents of ethanol (300 mL), DMSO (100 mL), and water (100 mL) with stirring and refluxing at 85–90°C. After 5 h the solution was separated, the filtrate was poured into a large quantity of water at 0–5°C. The white product was obtained by separation. The yield was 15.3 g (92%), recrystallized from methanol, mp 220°C.

ANAL. Calcd: C<sub>21</sub>H<sub>19</sub>N<sub>7</sub>: C, 68.27%; H, 5.18%; N, 26.54%. Found: C, 68.21%; H, 5.10%; N, 26.35%. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>)  $\delta$  (ppm): 9.18 (s,1H, —NH— of 2-anilino); 9.46 (s,1H, —NH— of 4-anilino); 4.88 (s,2H, —NH<sub>2</sub> of 4-amino); 5.78 (s,2H, —NH<sub>2</sub> of 6-amino); 6.60–8.30 (m,13H, aromatic).

Other diamines [2]–[4] were prepared by the reduction of [6]–[8] in a similar method above.

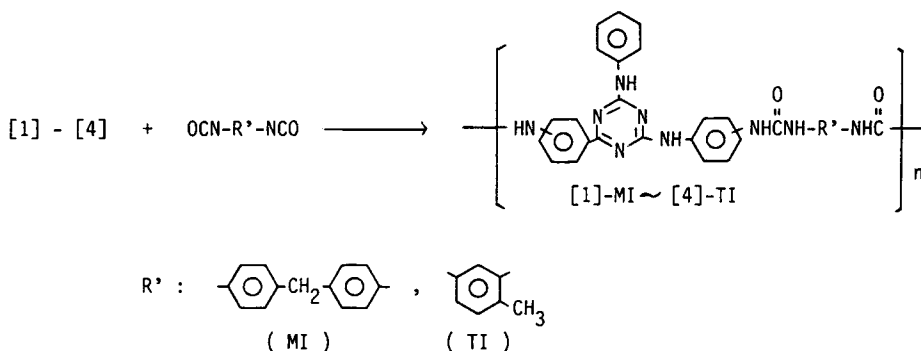
2-Anilino-4-(*p*-aminoanilino)-6-(*m*-aminophenyl)-1,3,5-triazine [2] was prepared by the reduction of [6]. Yield 93%, mp 185°C. (Found: C, 68.29%; H, 5.16%; N, 26.38%). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>)  $\delta$  (ppm): 9.35 (s,1H, —NH— of

TABLE III  
Preparation of Polyimides<sup>a</sup>

Polymer no.	Starting polymer	$\eta$ sp/C <sup>b</sup> (dL/g)
[1]-PI	[1]-PA	0.28
[2]-PI	[2]-PA	0.25
[3]-PI	[3]-PA	0.24
[4]-PI	[4]-PA	0.25

<sup>a</sup> Cyclodehydration condition; 1–3 mmHg at 200°C for 8 h.

<sup>b</sup> Measured at a concentration of 0.2 g/dL in DMAc at 30°C.



Scheme 4

2-anilino); 9.60 (s,1H, —NH— of 4-anilino); 4.89 (s,2H, —NH<sub>2</sub> of 4-amino); 5.24 (s,2H, —NH<sub>2</sub> of 6-amino); 6.60–8.00 (m,13H, aromatic).

2-Anilino-4-(*m*-aminoanilino)-6-(*p*-aminophenyl)-1,3,5-triazine [3] was prepared by the reduction of [7]. Yield 87%, mp 222°C. (Found: C, 68.38%; H, 5.20%; N, 26.30%). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>) δ (ppm): 9.38 (s,1H, —NH— of 2-anilino); 9.56 (s,1H, —NH— of 4-anilino); 5.02 (s,2H, —NH<sub>2</sub> of 4-amino); 5.83 (s,2H, —NH<sub>2</sub> of 6-amino); 6.40–8.38 (m,13H, aromatic).

2-Anilino-4-(*m*-aminoanilino)-6-(*m*-aminophenyl)-1,3,5-triazine [4] was prepared by the reduction of [8]. Yield 94%, mp 180°C. (Found: C, 68.45%; H, 5.21%; N, 26.53%). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>) δ (ppm): 9.57 (s,1H, —NH— of 2-anilino); 9.74 (s,1H, —NH— of 4-anilino); 5.03 (s,2H, —NH<sub>2</sub> of 4-amino); 5.25 (s,2H, —NH<sub>2</sub> of 6-amino); 6.40–8.10 (m,13H, aromatic).

## Polymerization

### Preparation of polyamides [1]-TC-[4]-IC

For example, [1]-TC: 0.275 g (1.35 mmol) of TC was added to the solution of 0.5 g (1.35 mmol) of [1] in 7 mL of NMP and 3 mL of hexamethylphosphoric

TABLE IV  
Preparation of Polyureas<sup>a</sup>

Polymer no.	Yield (%)	$\eta_{sp}/C^b$ (dL/g)
[1]-MI	92	0.20
[2]-MI	95	0.20
[3]-MI	94	0.18
[4]-MI	98	0.21
[1]-TI	89	0.20
[2]-TI	96	0.19
[3]-TI	86	0.17
[4]-TI	87	0.16

<sup>a</sup> Polymerization was carried out with 1.35 mmol of [1]–[4] and 1.35 mmol of diisocyanates in 10 mL of DMAc at room temperature for 6 h and 60°C for 2 h.

<sup>b</sup> Measured at a concentration of 0.2 g/dL in DMAc at 30°C.

TABLE V  
 Solubility of Polymers<sup>a</sup>

Polymer	Solvent <sup>b</sup>							
	DMSO DMAc	NMP DMF	HMPA	Pyridine	THF	Benzene chloroform	Formic acid	H <sub>2</sub> SO <sub>4</sub>
[1]-TC	+	+	±	+	-	-	+	+
[2]-TC	+	+	±	+	-	-	+	+
[3]-TC	+	+	±	+	-	-	+	+
[4]-TC	+	+	+	+	-	-	+	+
[1]-IC	+	+	±	+	-	-	+	+
[2]-IC	+	+	±	+	-	-	+	+
[3]-IC	+	+	+	+	-	-	+	+
[4]-IC	+	+	+	+	-	-	+	+
[1]-PA	+	+	±	+	-	-	+	+
[2]-PA	+	+	+	+	±	-	+	+
[3]-PA	+	+	+	+	±	-	+	+
[4]-PA	+	+	+	+	±	-	+	+
[1]-PI	+	+	-	+	-	-	+	+
[2]-PI	+	+	-	+	-	-	+	+
[3]-PI	+	+	-	+	-	-	+	+
[1]-MI	+	+	±	+	±	-	+	+
[2]-MI	+	+	±	+	±	-	+	+
[3]-MI	+	+	±	+	±	-	+	+
[4]-MI	+	+	+	+	±	-	+	+
[1]-TI	+	+	±	+	±	-	+	+
[2]-TI	+	+	±	+	±	-	+	+
[3]-TI	+	+	±	+	±	-	+	+
[4]-TI	+	+	+	+	±	-	+	+

<sup>a</sup> Solubility: +, soluble; ±, partially soluble; -, insoluble.

<sup>b</sup> DMSO: dimethyl sulfoxide; DMAc: *N,N*-dimethylacetamide; NMP: *N*-methyl-2-pyrrolidone; DMF: *N,N*-dimethylformamide; THF: tetrahydrofuran.

triamide (HMPA) with stirring under nitrogen atmosphere at room temperature. After 24 h, the solution was poured into 300 mL of methanol. Polymer was obtained almost quantitatively (94%), and purified by reprecipitation from NMP into methanol and drying at 50°C *in vacuo*. Other polyamides were prepared in a similar manner.

#### Preparation of polyimides [1]-PI-[4]-PI

Polyimides were prepared by a solution polymerization and cyclodehydration in two stages. Equal moles of [1]-[4] and PA were reacted in similar above-mentioned conditions to give intermediate polyamic acids, then polyimides were prepared by the cyclodehydration of polyamic acids at 200°C for 8 h *in vacuo*.

#### Preparation of polyureas [1]-MI-[4]-TI

For example, [1]-MI: Equal moles (1.35 mmol) of [1] and MI was polymerized in 10 mL of DMAc at room temperature for 6 h and at 60°C for 2 h. The solution was poured into 300 mL of methanol. The resulting polyurea [1]-MI

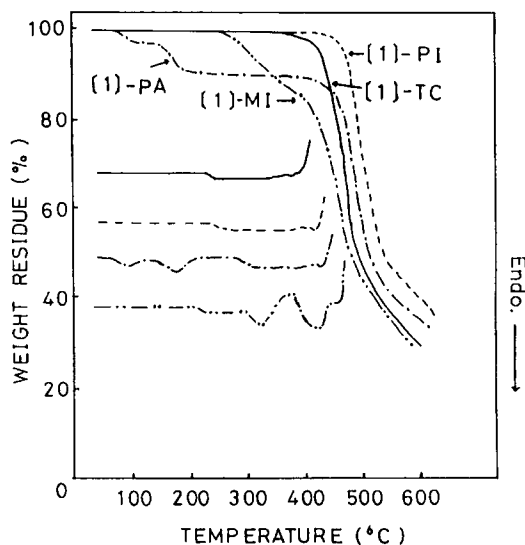


Fig. 1. TG and DTA curves of polyamide [1]-TC, polyamic acid [1]-PA, polyimide [1]-PI, and polyurea [1]-MI at a heating rate of 10°C/min in air.

was obtained after separating, purifying and drying. Other polyureas were prepared in a similar manner.

### Measurements

IR spectra were recorded on a Hitachi IR-285 spectrometer utilizing KBr pellets. <sup>1</sup>H-NMR spectra were performed using a Hitachi R600 FTNMR (60 MHz) spectrometer in DMSO-d<sub>6</sub> solution using tetramethylsilane as an internal standard. Elemental analysis were performed on a Yanaco CHN corder MT-3 analyzer. Thermal properties were measured by the differential thermal analysis

TABLE VI  
Thermal Properties of Polymers

Polyamides			Polyamic acids and polyimides			Polyureas		
No.	T <sub>g</sub> (°C)	PDT <sup>a</sup> (°C)	No.	T <sub>g</sub> (°C)	PDT <sup>a</sup> (°C)	No.	T <sub>g</sub> (°C)	PDT <sup>a</sup> (°C)
[1]-TC	240	433	[1]-PA	274	491	[1]-MI	220	307
[2]-TC	250	428	[2]-PA	275	483	[2]-MI	235	312
[3]-TC	240	422	[3]-PA	270	492	[3]-MI	226	310
[4]-TC	232	427	[4]-PA	272	490	[4]-MI	230	309
[1]-IC	258	427	[1]-PI	260	471	[1]-TI	235	306
[2]-IC	242	430	[2]-PI	258	473	[2]-TI	234	303
[3]-IC	240	435	[3]-PI	256	482	[3]-TI	223	304
[4]-IC	234	432	[4]-PI	255	477	[4]-TI	227	304

<sup>a</sup> Polymer decomposition temperature at which 5% weight loss was recorded by TG at a heating rate of 10°C/min in air.

and the thermogravimetry on a Rigaku TG-DTA 8112 BH thermal analyzer system at a heating rate of 10°C/min in air. Reduced viscosities of polymers were determined for solution of 0.2 g/dL in DMAc at 30°C using an Ostwald viscometer.

## RESULTS AND DISCUSSION

### Synthesis of Diamines

2-Anilino-4-(*p*- or *m*-aminoanilino)-6-(*p*- or *m*-aminophenyl)-1,3,5-triazines [1]–[4] were prepared according to Scheme 1.

The formation of these diamines was confirmed by <sup>1</sup>H-NMR, IR spectra and elemental analysis. The data for the elemental analysis and <sup>1</sup>H-NMR spectra are provided in Experimental. The IR spectra of [1]–[4] showed the typical absorption of 1,3,5-triazine ring at 1410 and 820 cm<sup>-1</sup>, and NH<sub>2</sub> groups at 3200–3500 cm<sup>-1</sup>. The structures of [1]–[4] were characterized from these data.

### Preparation of Polymers

Polyamides, polyimides, and polyureas were prepared by the reaction of [1]–[4] with aromatic dicarboxylic acid dichlorides (TC and IC), pyromellitic dianhydride (PA), and diisocyanates (MI and TI), respectively.

Polyamides [1]-TC-[4]-IC were prepared by the solution polycondensation of [1]–[4] with TC and IC in NMP/HMPA (7/3 volume) at room temperature (Scheme 2). Polyamides were given almost quantitatively, and had reduced viscosities in the range of 0.31–0.40 dL/g (Table I). It could be seen that the reactivities of [1]–[4] are almost not influenced by the substitution position of diamino groups.

The IR spectra of all polyamides showed the typical absorption bands of amides at 3450–3150, 1660, and 1300 cm<sup>-1</sup>, and the bands of triazine rings at 1410 and 820 cm<sup>-1</sup>.<sup>8,9</sup> Elemental analysis values of the polymers were in good agreement with the calculated values. The elemental and IR analyses conclusively demonstrate that polyamides were prepared.

Polyimides were prepared by the two-step cyclopolycondensation method (Scheme 3). In the first step, the polyamic acids were synthesized by the reaction of [1]–[4] with PA in good yields as slight yellow powders. The elemental analysis values of polyamic acids took into consideration absorbed water which was also confirmed in TG curves. The water loss ratio of absorbed water and cyclodehydration were evaluated from the TG curves of polyamic acids. The amount of absorbed water agreed with that estimated values of elemental analysis, and the results of water loss by cyclodehydration were also in good agreement with their calculated values (Table II).

Polyimides were obtained as a brown powders by the cyclodehydration of the polyamic acids at 200°C for 8 h *in vacuo*. The results of preparation of polyimides are listed in Table III. The IR spectra of intermediate polyamic acids showed absorption bands at 3650–3050, 1720, and 1660 cm<sup>-1</sup>. These bands disappeared after cyclodehydration, and new absorptions at 3500–3300, 1785, 1730, and 1320 cm<sup>-1</sup> associated with the imide structure were observed.<sup>17,18</sup> The absorption bands of triazine rings were also found at 1410 and 820 cm<sup>-1</sup>.



Polyureas were synthesized by the polyaddition of [1]–[4] with MI and TI in DMAc (Scheme 4). The results of preparation of polyureas are summarized in Table IV. Polyureas had lower reduced viscosities than polyamides and the polyimides in DMAc at 30°C. The absorption bands of polyureas were similar to the spectrum regions of polyamides due to ureylene groups<sup>18</sup> and triazine rings.

### Characterization of Polymers

The solubility behavior of the polymers is listed in Table V. All the polymers were soluble in organic polar solvents such as DMF, DMAc, DMSO, NMP, and pyridine as well as soluble in formic acid and conc. sulfuric acid. The solubilities of these polymers were better than those of the analogous polymers<sup>8,9</sup> that were prepared by the use of 2-amino-4-aminoanilino-6-aminophenyl-1,3,5-triazines instead of these diamines [1]–[4]. For example, the previous polyimides were only soluble in the conc. sulfuric acid. This may be explained by the presence of anilino pendant groups on the triazine rings.

The thermal properties of polymers were studied by TG, DTA, and DSC. The typical TG and DTA curves are given in Figure 1, and the thermal properties are listed in Table VI. The TG curve of the polyamic acids exhibit two-stage initial weight loss. The first weight loss below 110°C was caused by the loss of adsorbed water, and the second weight loss at 140–220°C was attributable to the cyclodehydration. DTA curves of polyamic acids also supported the above observation with two broad endotherms. This adsorbed water almost could not be found in the polyamides, polyimides, and polyureas. It is considered to be due to the existence of hydrophilic carboxylic acids of the polyamic acids.

Initial decomposition occurred near 430°C for polyamides, 470°C for polyimides, and 300°C for polyureas. The glass transition temperatures  $T_g$  of polymers were about 220–260°C by the measurement of DSC. Thermal properties of these polymers were compared with those of previous analogous polymers.<sup>8,9</sup> It could be found that this modification of the polymers by the introduction of anilino pendant groups into triazine rings caused a general depression of the  $T_g$  about 30–50°C, and their thermal stabilities had a slight decrease about 20–30°C.

In conclusion, these aromatic polyamides and polyimides containing 1,3,5-triazine rings have been demonstrated to possess high glass transition temperatures above 200°C and decomposition temperatures above 400°C with good solubility. Therefore they might be used as new processable thermally stable polymers.

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