

# Synthesis and Characterization of Phenylated Aromatic Poly(amide–amide)s

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**ABSTRACT:** A modified new aromatic diamine 2,5-bis[(4-aminophenyl)4-benzamide]-3,4-diphenyl thiophene (**VI**) with preformed amide linkages and pendant phenyl substituents was synthesized, characterized by IR, NMR, mass spectroscopy, and a physical constant. Novel poly(amide–amide)s were synthesized from **VI** and aromatic diacid chlorides in *N,N*-dimethylacetamide by a solution polycondensation technique. The polymers were obtained in 98–100% yields and showed reduced viscosities in the range of 0.80–2.68 dL/g. They were readily soluble in aprotic polar solvents. These poly(amide–amide)s showed glass transition temperatures of 277–280°C as measured by DSC and showed no weight loss below 412°C in a nitrogen atmosphere. The polymers showed moisture regain in the range of 9.52–12.67%. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1523–1530, 1998

**Key words:** 2,5-bis[(4-aminophenyl)4-benzamide]-3,4-diphenylthiophene; terephthaloyl chloride; isophthaloyl chloride; phenylated poly(amide–amide)s; thermal properties; moisture regain

## INTRODUCTION

Aromatic polyamides (aramides), because of their all-aromatic composition, high degree of orientation, crystallinity, and strong intermolecular hydrogen bonding,<sup>1–3</sup> are well known for their excellent thermal and physical properties. Hence, they generally find use in various high-temperature applications, especially as strong fibers and tough films. McKinney found these polyamides useful in reverse osmosis (RO) applications as desalination membranes,<sup>4</sup> wherein the prime requirements of

polymers suitable as a barrier material<sup>5</sup> for use in RO separation are high molecular weight, mechanical strength, and optimum polarity. The high percentage of polar groups in the polymer backbone also imparts the desired range of the moisture-regain property to the polymer, making them promising candidates for RO separation. Such aromatic polyamide membranes are superior for use at high-pressure and high-temperature conditions<sup>6,7</sup> in RO applications as a desalination membrane. However, fully aromatic polyamides are difficult to fabricate because of their limited solubility in common organic solvents. The introduction of pendant phenyl groups along with the polymer backbone is one of the approaches to increase the solubility of the polymers and we have successfully utilized the same to obtain soluble polyimides and polyamides<sup>8,9</sup> from **IV**.

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In continuation of our earlier studies on soluble high-performance polymers, we thought it would be interesting to synthesize a novel modified phenylated aromatic diamine (**VI**) containing preformed amide linkages and to investigate the properties of poly(amide–amide)s from **VI** since these polymers will be sequence-ordered and will have varying percentages of amide groups in the repeat unit, compared to Kevlar/Nomex or polyamides from **IV**. It was expected that an increase in amide content in poly(amide–amide)s would enhance the moisture-regain properties, whereas pendant phenyl groups would assist in the increase in the solubility of the resulting poly(amide–amide)s without any appreciable loss in the thermal stability.

Thus, in the present study, we report the synthesis of a modified phenylated aromatic diamine, 2,5-bis[(4-aminophenyl)4-benzamide]-3,4-diphenyl thiophene (**VI**), containing preformed amide linkages, its spectral characterization by IR, NMR, and mass, and the preparation of a series of a sequence-ordered poly(amide–amide)s from **VI**. IR spectral data, viscosity, solubility, moisture-regain, and thermal characteristics of these poly(amide–amide)s are also discussed.

## EXPERIMENTAL

### Measurements

Viscosity measurements were made with a 0.5% polymer concentration in *N,N*-dimethylacetamide (DMAc) at 30°C using suspended-type Ubbelohde viscometer. The solubility of the poly(amide–amide)s and copoly(amide–amide)s was determined at a 3% concentration in various solvents. Transmission IR spectra were recorded on a Perkin–Elmer 883 IR spectrophotometer as a KBr pellet or polymer film. <sup>1</sup>H-NMR spectra were recorded in DMSO-*d*<sub>6</sub> on a Bruker 90 MHz spectrometer using tetramethylsilane (TMS) as an internal standard reference, whereas <sup>13</sup>C-NMR spectra were recorded on a Bruker 200 MHz spectrometer. Mass spectra were recorded on an IIMS-30 double-beam mass spectrometer. Moisture-regain values were determined gravimetrically, equilibrating oven-dry samples at the relative humidity (RH) of 92% at 30°C. Differential scanning calorimetry (DSC) and thermogravimetric (TG) analyses were performed on a Perkin–

Elmer DSC-7 and a Perkin–Elmer TGA-7, respectively, at a heating rate of 10°C/min under a flow of nitrogen gas.

### Materials

Terephthaloyl chloride (TPC), isophthaloyl chloride (IPC), and 4-nitrobenzoyl chloride (NBC) were synthesised from the corresponding acids using a reported procedure and were purified by vacuum distillation followed by recrystallization from dry hexane before use. Toluene, pyridine, and DMAC were purified and dried by following the standard procedure.

### Synthesis of Monomers

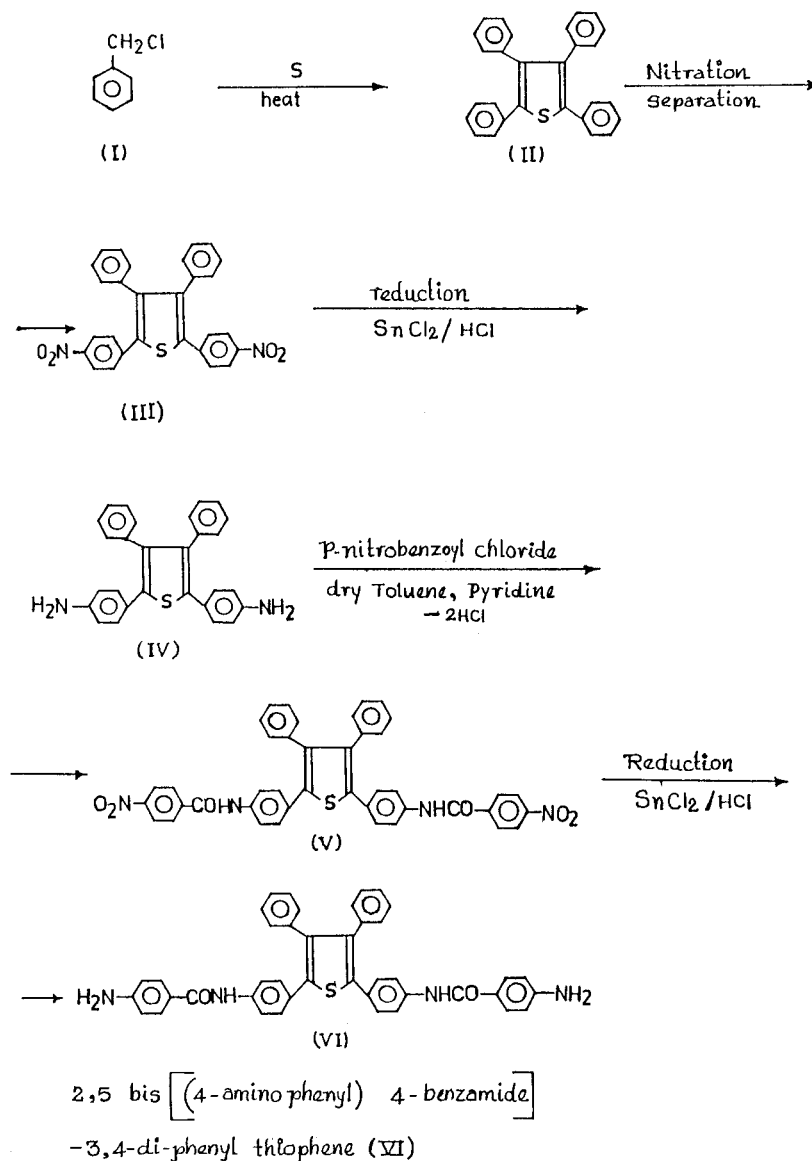
2,5-Bis[(4-aminophenyl)4-benzamide]-3,4-diphenyl thiophene was synthesized from **IV** as follows: 2,5-Bis[4-aminophenyl]-3,4-diphenyl thiophene (**IV**) was prepared as in the literature,<sup>8</sup> starting from benzyl chloride and sulfur in three steps.

### Synthesis of 2,5-bis[(4-nitrophenyl)4-benzamide]-3,4-diphenyl Thiophene (**V**)

In a 500-mL round-bottom flask equipped with a magnetic bar and a calcium chloride guard tube were placed 12.54 g (0.03 mol) of **IV**, 225 mL dry toluene, and 30 mL pyridine. The mixture was stirred to yield a pale cream suspension and 11.13 g (0.06 mol) of NBC was added in small portions. The mixture was stirred for 24 h to ensure completion of the reaction. The dark yellow solid suspension was filtered, washed with benzene, allowed to dry in air, and washed with water, and, finally, with methanol. The product was recrystallized from *N,N*-dimethylformamide and dried at 80–100°C under a vacuum. Yield: 18.15 g (84.5%); mp 276–278°C.

ANAL. Calcd for C<sub>42</sub>H<sub>28</sub>N<sub>4</sub>O<sub>6</sub>S: C, 70.39%; H, 3.91%; N, 7.82%; S, 4.47%. Found: C, 70.30%; H, 3.89%; N, 7.72%; S, 4.30%.

IR (KBr pellet): 3360 (NH stretch), 1658 (CONH), 1520 and 1348 cm<sup>-1</sup> (NO<sub>2</sub>). Mass: (*m/e*) 716 (M)<sup>+</sup>, 566 (M-150, loss of –COPhNO<sub>2</sub>), 416 (M-300, loss of 2 units of COPhNO<sub>2</sub>).



**Scheme 1** Synthesis of amide-containing diamine.

**Synthesis of 2,5-bis[(4-aminophenyl)4-benzamide]-3,4-diphenyl Thiophene (VI)**

In a three-neck round-bottom flask equipped with a magnetic stirrer, a thermowell, and a reflux condenser were placed 7.16 g (0.01 mol) of **V** and 130 mL methanol. To the stirred mixture, a solution of 25 g stannous chloride (dihydrate) in 125 mL concentrated hydrochloric acid was added at 25°C and then heated to 100°C using an oil bath. After 2 h, an additional solution of 25 g of stannous

chloride (dihydrate) in 125 mL concentrated hydrochloric acid was added and heating with stirring was continued for 4 h, when the yellow color changed to pale white. The reaction mixture was allowed to cool to 60°C and a precipitate of **VI**-hydrochloride was filtered while hot at suction and washed with hot dilute hydrochloric acid (500 mL). The solid **VI**-hydrochloride was stirred with a dilute sodium hydroxide solution to liberate **VI**, which was filtered, washed with water, and then recrystallized from N,N-dimethylformamide. Yield: 4.4 g (67%); mp 325°C.

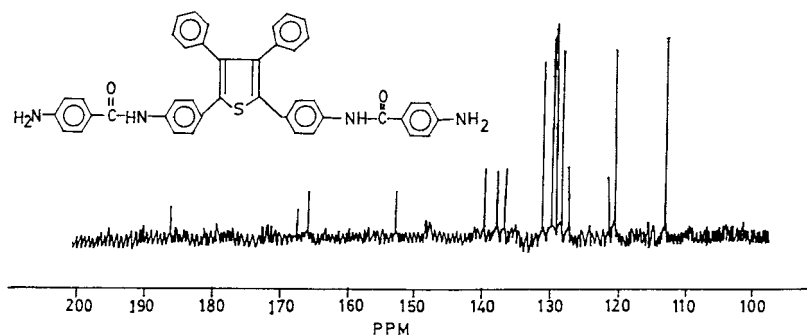


Figure 1  $^{13}\text{C}$ -NMR spectrum of VI.

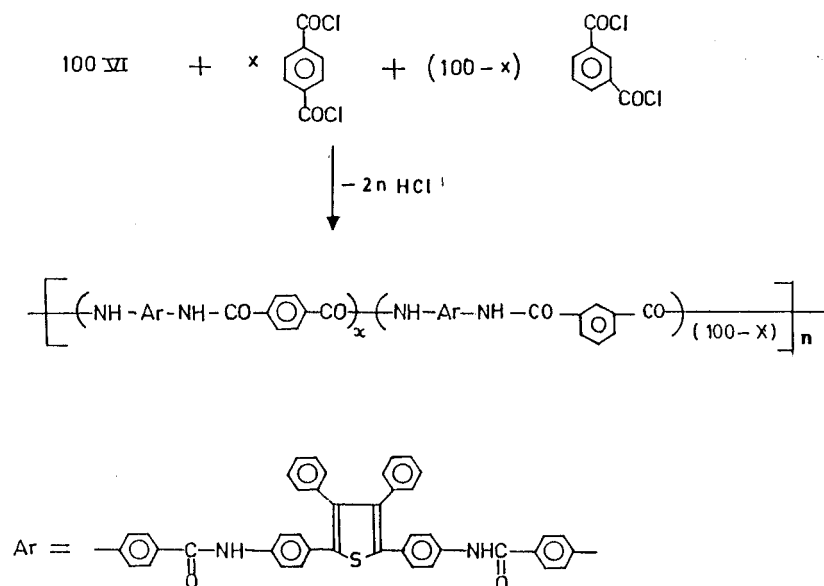
ANAL: Calcd for  $\text{C}_{42}\text{H}_{32}\text{N}_4\text{O}_2\text{S}$ : C, 76.83%; H, 4.88%; N, 8.40%; S, 4.88%. Found: C, 76.90%; H, 4.85%; N, 8.62%; S, 4.80%.

IR (KBr pellet): 3431, 3390 ( $\text{NH}_2$ ), 3217 (NH) 1691 ( $\text{CONH}$ )  $\text{cm}^{-1}$ . Mass: ( $m/e$ ) 418 (loss of 2 units of  $-\text{COPhNH}$ ).  $^1\text{H}$ -NMR: ( $\delta$  in ppm), 9.8 (broad s 2H, CONH), 7.65 (dd 8H), 7.1 (m, 10 H), 7.0 (d, 4H), 6.55 (d, 4H), 5.75 (broad s, 4H,  $\text{NH}_2$ ).  $^{13}\text{C}$ -NMR: ( $\delta$  in ppm), 185.84, 167.70, 163.80, 152.90, 139.63, 137.74, 136.69, 130.99, 129.84, 129.31, 128.42, 127.32, 121.41, 120.36, 113.65.

#### Polymerization: Poly(amide-amide) [PA-1] from VI and IPC

In a 100 mL three-neck round-bottom flask equipped with a magnetic stirrer, a nitrogen gas

inlet, and a calcium chloride guard tube were placed 0.656 g (1 mmol) VI and 3 mL DMAc, stirred and cooled to 0 to  $-15^\circ\text{C}$ . To the reaction mixture, 0.203 g (1 mmol) solid IPC was added all at once. The polymerization proceeded as the solid dissolved. Stirring was continued for 1.5 h at  $0^\circ\text{C}$  and then at  $30^\circ\text{C}$  for 12 h. To this mixture, 0.075 g (1.04 mmol) lithium carbonate was added. The mixture was heated to  $80^\circ\text{C}$  and degassed by applying a vacuum. The viscous solution was poured into water to precipitate yellow fibrous flakes. The polymer was filtered and washed with water and methanol. The polymer was purified by dissolving in DMAc, filtering to remove insoluble material, if any, and reprecipitating in water. It was filtered, washed with water and methanol, and dried under a vacuum at



Scheme 2 Polymerization.

**Table I Synthesis of Poly(amide-amide)s**

Sample No.	Polymer Code	Acid Chloride (mol %)		Viscosity <sup>a</sup> (dL/g) $\eta_{\text{red}}$
		IPC	TPC	
1	PA1	100	—	0.80
2	PA2	75	25	0.87
3	PA3	50	50	1.64
4	PA4	25	75	1.58
5	PA5	—	100	2.68

Polymerization was carried out with 1 mmol each of **VI** and diacid chloride(s) and all the polymers were obtained in yields over 98%.

<sup>a</sup> Measured with a 0.5% (w/v) solution of the polymer in DMAc at 30°C.

100°C for 6 h. Yield: 0.712 g (99.4%);  $\eta_{\text{red}}$  0.805 dL/g. Other poly(amide-amide)s, PA-2-PA-5, were synthesized similarly.

## RESULTS AND DISCUSSION

The modified diamine **VI** was synthesized from **IV** in two steps, wherein, initially, **IV** was reacted with 4-nitrobenzoyl chloride to give **V**, which, subsequently, on reduction with stannous chloride and hydrochloric acid gave a new diamine (**VI**) containing aromatic diamide linkages (Scheme 1). The formation and structures of **V** and **VI** were confirmed by IR, NMR (<sup>1</sup>H and <sup>13</sup>C), and mass spectroscopy. The infrared (IR) spectrum of **V** showed characteristic absorption bands at 3360

**Table III Moisture-regain Properties of Poly(amide-amide)s**

Polymer	Moisture Regain (%)
PA1	11.62
PA2	9.52
PA3	12.63
PA4	12.67
PA5	11.66

Determined gravimetrically by equilibrating the oven-dry polymers at an RH of 92% at 30°C.

(NH), 1628 (—CO—NH—), and 1520 and 1348 cm<sup>-1</sup> (NO<sub>2</sub>). The absorption bands due to —NH<sub>2</sub> at 3431 and 3390 and to —COCl at 1758 cm<sup>-1</sup> were absent. The mass spectrum of **V** showed a molecular ion peak at *m/e* 716 corresponding to the molecular formula weight, whereas the peaks at *m/e* 566 and 416 correspond to molecular fragments M-150 and M-300 corresponding to the loss of —CO—Ph—NO<sub>2</sub> and two —CO—Ph—NO<sub>2</sub> units, respectively.

The infrared spectrum of **VI** showed characteristic absorptions at 3390, 3431 (—NH<sub>2</sub>), 3217 (NH), and 1691 (—CONH—) cm<sup>-1</sup>. The absorption due to NO<sub>2</sub> at 1520 cm<sup>-1</sup> was absent. The mass spectrum of **VI** showed a peak at *m/e* 418 corresponding to the loss of two units of —COPhNH from the molecular ion peak. The proton NMR spectrum is consistent with the structure of **VI**. The <sup>1</sup>H decoupled <sup>13</sup>C-NMR spectrum of **VI** showed 15 peaks assignable to 15 different carbons, of which the most downfield weak

**Table II Solubility of Poly(amide-amide)s**

Solvents	Polymer				
	PA1	PA2	PA3	PA4	PA5
DMAc	++	++	++	++	+
DMF	++	++	+	±	±
NMP	++	++	++	++	+
DMSO	±	±	±	±	±
Concentrated H <sub>2</sub> SO <sub>4</sub>	++	++	++	++	++
CHCl <sub>3</sub>	--	--	--	--	--
Formic acid	--	--	--	--	--

++, Soluble at room temperature; +, soluble on heating; ±, partly soluble; --, insoluble.

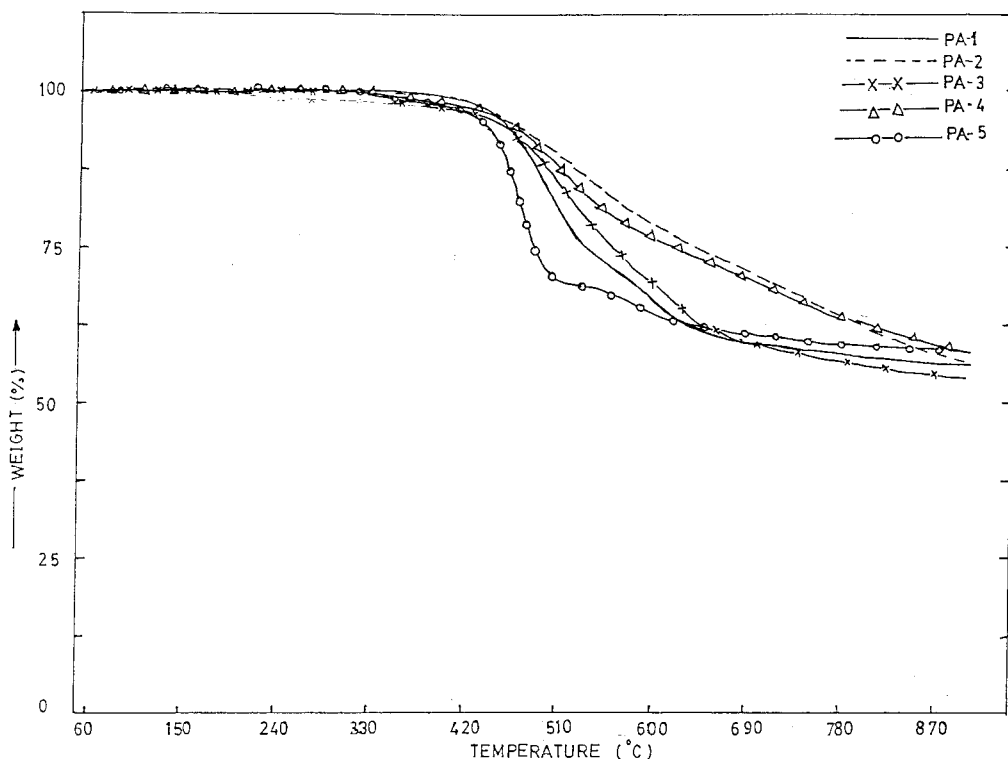


Figure 2 TG curves of poly(amide-amide)s PA-1-PA-5.

signal at  $\delta$  185.84 ppm was due to the carbonyl carbon of the amide function (Fig. 1). Elemental analysis for C, H, N, and S in **V** and **VI** very closely fits the values theoretically calculated for their molecular formulas.

Aromatic poly(amide-amide)s were synthesized by condensation of **VI** with IPC or TPC by low-temperature solution polymerization in DMAc. In a similar manner, co-poly(amide-amide)s were also prepared from **VI** and a mixture of IPC and TPC in different mole proportions (Scheme 2). The viscosities and yields of these poly(amide-amide)s and copoly(amide-amide)s are given in Table I. All these poly(amide-amide)s were obtained in almost quantitative yields, as pale yellow fibrous material. Tough, flexible, and transparent pale yellow films of all the polymers could be cast from a 10% solution of polymers in DMAc and from the polymerization mixture itself.

The poly(amide-amide)s exhibited reduced viscosities in the range of 0.8–2.6 dL/g. On comparing the reduced viscosities of the poly(amide-amide)s, PA-1-PA-5, it was observed that PA-1 derived from IPC had a reduced viscosity of 0.8 dL/g and the reduced viscosities increased

through PA-2 to PA-5 as the proportion of TPC increased. This was attributed to the corresponding increased reactivity of TPC with *para*-catenation in PA-2 to PA-5 and, interestingly, very high molecular weight poly(amide-amide)s were obtained. The importance of these poly(amide-amide)s lies in the fact that these polymers are sequence-ordered, which can be reflected in better physical properties, compared to obtaining the same molecular structure but random polyamides from diamine (**IV** + 1,4-diaminobenzene) and aromatic diacidchlorides (IPC/TPC). The formation of the poly(amide-amide)s was evidenced by the IR spectra. The IR spectra of all the poly(amide-amide) films exhibited characteristic bands at 1631 and 1507  $\text{cm}^{-1}$  due to amide I and amide II, respectively. The disappearance of the peak of primary amine at 3431 and  $\text{—COCl}$  at 1770  $\text{cm}^{-1}$  also confirmed the high molecular weight poly(amide-amide) formation.

The solubility of the poly(amide-amide)s and copoly(amide-amide)s was checked in various organic solvents and the results are summarized in Table II. It was observed that poly(amide-amide)s derived from IPC dissolved more readily

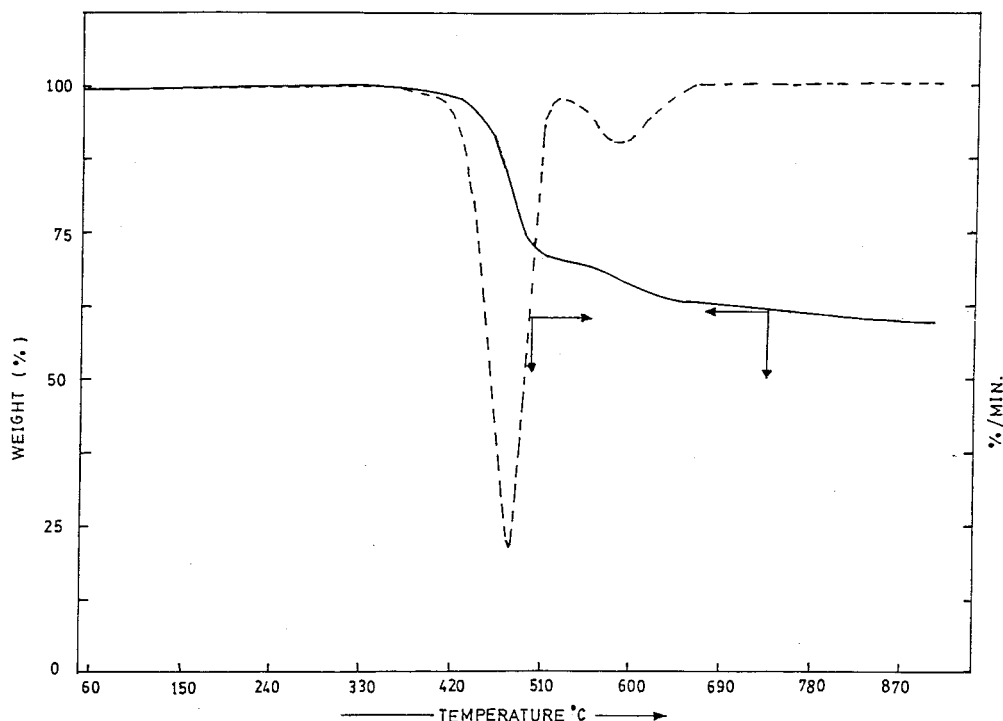


Figure 3 TG and DTG curves of poly(amide-amide) PA-5.

than did those derived from TPC (PA-5). The better solubility of the PA-1 and PA-2 may be attributed to the lack of symmetry of the molecule because of the *meta* catenation of the phenylene ring and the distortion of the phenyl groups in the tetraphenylthiophene unit. Polymers are soluble in amide-type solvents such as DMAc and *N*-methylpyrrolidone, and results are similar to an earlier report<sup>9</sup> on the solubility of phenylated polyamides from IV.

The polymers were characterized for the moisture-regain property and the values ranged from 9.52 to 12.67% (Table III). The higher moisture-regain values of the polymers are due to hydrogen bonding with an increased number of polar groups present in the polymers and secondary hydrogen bonding between the water-water molecule at the sites.<sup>10</sup>

The thermal properties of these polymers were evaluated by thermogravimetry and differential scanning calorimetry. The TGA and DTG curves of poly(amide-amide)s are shown in Figures 2 and 3, respectively. Table IV incorporates the thermal characteristics such as initial decomposition temperature ( $T_i$ ), maximum decomposition temperature ( $T_{max}$ ), and residual weight at 900°C. More than a 54% weight residue at 900°C

for all the polymers and no weight loss below 412°C indicated the high thermal stability of these polymers.

## CONCLUSIONS

A series of new poly(amide-amide)s and copoly(amide-amide)s was prepared from a new di-

Table IV Thermal Properties of Poly(amide-amide)s

Polymer	$T_i^a$ (°C)	$T_{max}^b$ (°C)	Residual Mass (%) at 900°C	$T_g^c$ (°C)
PA1	420	495	59.4	280
PA2	412	505	54.8	278
PA3	435	514	55.1	277
PA4	443	511	56.7	278
PA5	420	474	54.5	279

Thermogravimetric analysis conducted at a heating rate of 10°C/min in a nitrogen atmosphere.

<sup>a</sup> Temperature at which initial loss of mass was observed.

<sup>b</sup> Temperature of maximum rate of decomposition from DTG.

<sup>c</sup> Glass transition temperature determined by DSC.

amine **VI**, containing preformed aromatic diamide linkage, and IPC and/or TPC. The polymers showed very high molecular weights (viscosity 0.80–2.68 dL/g) and good solubility in aprotic organic solvents. The polymers possessed an excellent thermal stability with no weight loss below 412°C. Moisture-regain properties indicate that these poly(amide–amide)s can be used in RO applications.

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