

# Synthesis of Soluble and Thermally Stable Polyimides from 3,5-Diamino-*N*-(4-(8-quinolinoxy) phenyl) Aniline and Various Dianhydrides

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**ABSTRACT:** Three novel polyimides (PIs) having pendent 4-(quinolin-8-yloxy) aniline group were prepared by polycondensation of a new diamine with commercially available tetracarboxylic dianhydrides, such as pyromellitic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, and bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride. These PIs were characterized by FTIR, <sup>1</sup>H NMR, and elemental analysis; they had high yields with inherent viscosities in the range of 0.4–0.5 dl g<sup>-1</sup>, and exhibited excellent solubility in many organic solvents such as *N,N*-dimethyl acetamide, *N,N'*-dimethyl formamide, *N*-methyl pyrrolidone (NMP), dimethyl sulf-

oxide, and pyridine. These PIs exhibited glass transition temperatures ( $T_g$ ) between 250 and 325° C. Their initial decomposition temperatures ( $T_i$ ) ranged between 270 and 450°C, and 10% weight loss temperature ( $T_{10}$ ) up to 500°C with 68% char yield at 600°C under nitrogen atmosphere. Transparent and hard polymer films were obtained via casting from their NMP solutions. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 983–988, 2011

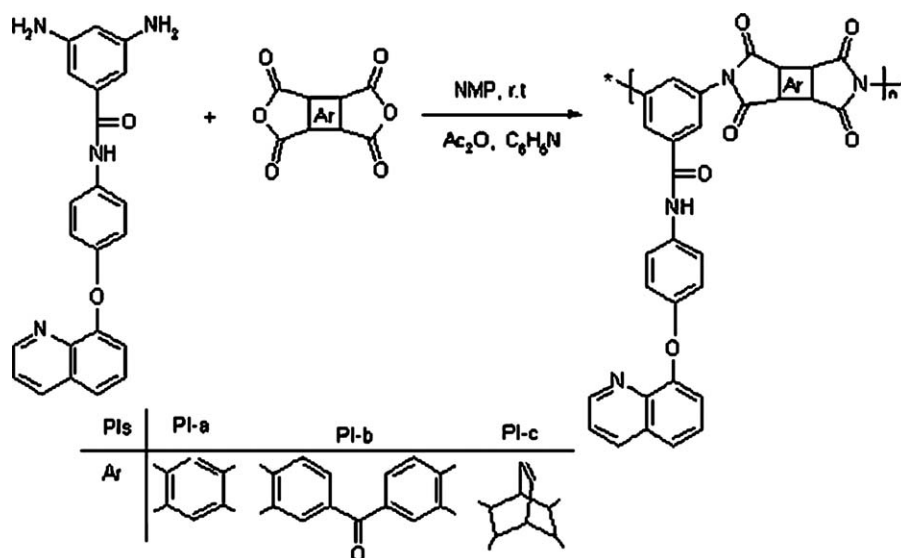
**Key words:** polyimides; polycondensation; synthesis; solubility; thermal properties

## INTRODUCTION

The rapid development of polyimides has resulted in great improvements in their properties and new applications. Properties which are typically identified with polyimides are heat resistance, solvent resistance, good mechanical strength, good toughness, excellent dimensional stability, low coefficient of friction, outstanding radiation resistance, high dielectric strength, low outgassing, and resistance to creep and wear.<sup>1–4</sup> Therefore, they are used as adhesives, films, composite matrices, coatings, membranes, and so on in severe environments. However, all of the polyimides synthesized for the purpose of high temperature properties have more or less difficulties in processing owing to their generally low solubility and high melting or softening temperatures. To balance the thermal stability and the processability, numerous methods to obtain polyimides with chemically modified chain structures have been introduced. These methods include incorporation of hinge atoms or kink units or flexible spacer units either into the dianhydride fragment or diamine fragment or both.<sup>5–7</sup> Much effort has been achieved in

designing and synthesizing new dianhydrides<sup>8–11</sup> and diamines,<sup>12–15</sup> and therefore producing a great variety of soluble and processable polyimides for various purposes and applications. Incorporation of flexible units such as —NHCO—, —O—, and —SO<sub>2</sub>—,<sup>16</sup> replacing symmetrical aromatic rings by unsymmetrical ones which lead to reduction in crystallinity,<sup>17</sup> introduction of bulky lateral substituents which decrease close-packing in the polymer backbone and lead to enhanced solubility of the polymer,<sup>18–22</sup> and introduction of noncoplanar units<sup>23</sup> are the most important approaches to overcome these processing problems. Among these approaches, introducing bulky pendent substituents and heteroaromatic rings into polyimide chains has been considered to be efficient, which can provide not only enhanced solubility but also good thermal and thermo-oxidative stability. In this work, we report a series of new soluble and thermally stable polyimides (PIs) based on diamine monomer containing noncoplanar and bulky pendent with 4-(8-quinolinoxy) aniline unit. Introduction of bulky (quinolinoxy) aniline group in meta-linked polyimides is expected to provide molecular irregularity and good solubility. On the other hand, the presence of a bulky pendent group with a quinolinoxy unit to the backbone of polyimide decreases interchain interaction and the ability for polymer chains to pack while provides a barrier to segmental mobility,

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Scheme 1 Synthesis of polyimides.

thus resulting in an enhanced solubility and increased  $T_g$  for the polyimide. Following our previous work,<sup>24</sup> the diamine monomer, 3,5-diamino-*N*-(4-(8-quinolinoxy)phenyl)aniline was synthesized and used in polycondensation reaction with three tetracarboxylic dianhydrides to prepare PIs. The PIs were characterized by FTIR and <sup>1</sup>H NMR spectroscopy, and their inherent viscosity, solubility, and thermal properties were studied.

## EXPERIMENTAL

### Materials

*N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), acetic anhydride, and pyridine were purchased from Merck and purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieve. Pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), and bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCDA) were dried in a vacuum oven at 110°C for 5 h. All other solvents, such as DMAc, *N,N'*-dimethylformamide (DMF), pyridine, and dimethyl sulfoxide (DMSO), and materials such as, 8-quinolinol, *p*-nitrofluorobenzene, hydrazine monohydrate, 3,5-dinitrobenzoylchloride, Pd/C, and triethylamine were purchased from Merck and used as received.

### Measurements

Infrared measurements were performed on a Bruker-IFS 48 FTIR spectrometer (Ettlingen, Germany). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in dimethyl sulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>) solution using a Bruker Advance 500 MHz instrument (Germany).

Elemental analyses were performed by a CHN-Rapid Heraeus elemental analyzer (Wellesley, MA). Differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780 (London, UK) at 10°C/min and under N<sub>2</sub> atmosphere. The dynamic mechanical measurements were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) (Model MK-II, Surrey, UK) over a temperature range of 25–350°C at 1 Hz and a heating rate of 5°C/min under N<sub>2</sub> atmosphere. Inherent viscosity was measured by using an Ubbelohde viscometer in a concentration of 0.5 dL/g in NMP at 25°C.

### Polyimide synthesis

General procedure for the preparation of polyimides is illustrated in Scheme 1. A typical example of polymerization is as follows. A 100-mL two-necked, round-bottomed flask equipped with a magnetic stirrer bar, nitrogen gas inlet tube, and calcium chloride drying tube was charged with 0.5 g (1.35 mmol) of the diamine (IV) and 10 mL of dry NMP. The mixture was stirred at room temperature for 0.5 h. Then 1.35 mmol of a dianhydride was added and the mixture was stirred at room temperature for 24 h, forming a viscous solution of poly(amic acid) (PAA) precursor in NMP. The PAA was converted into polyimide by chemical imidization process. The chemical imidization was carried out by adding 3 mL of a mixture of acetic anhydride/pyridine (6/4, v/v) into the PAA solution with stirring at room temperature for 1 h. Then the mixture was stirred at 130°C for 10 h to yield a homogeneous solution. The polymer solution was poured slowly into methanol

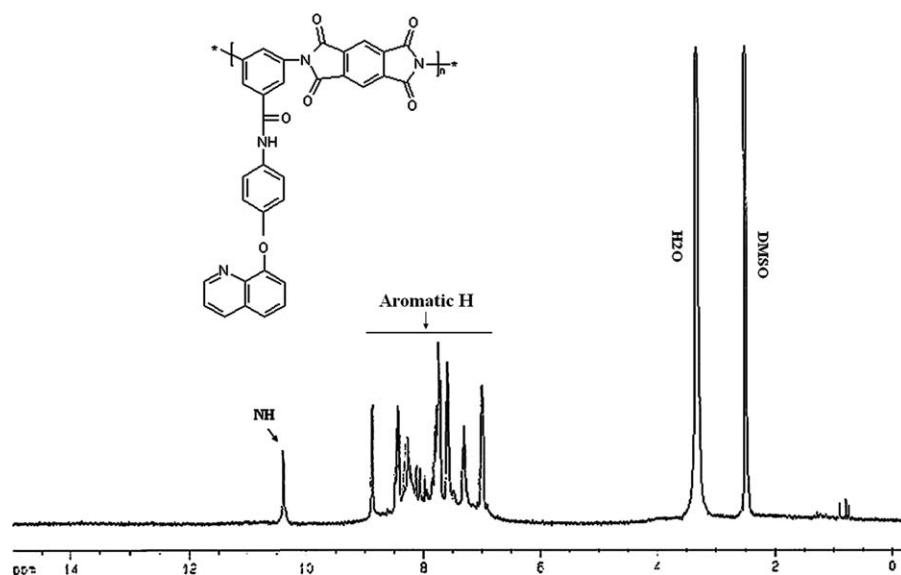


Figure 1  $^1\text{H}$  NMR spectrum of PI-a.

to form a precipitate. The precipitate was collected by filtration, washed thoroughly with hot methanol and dried at  $80^\circ\text{C}$  in vacuum overnight.

#### PI-a

The yield 97%, FTIR (KBr,  $\text{cm}^{-1}$ ): 3150 (aromatic C—H stretching), 1775 (C=O asymmetric stretching), 1714 (C=O symmetric stretching), 1658 (C=O stretching of amide group), 1527 (C=N stretching), 1466 (C=C stretching), 1375 (C—N stretching).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  6.96–8.87 (15 H, aromatic protons), 10.45 (1 H, amide proton). The yield of reaction was 92%. Anal. Calcd. for  $(\text{C}_{32}\text{H}_{16}\text{N}_4\text{O}_6)_n$ : C, 10.18; H, 2.91; N, 69.60. Found: C, 10.14; H, 2.89; N, 69.56.

#### PI-b

The yield 96%, FTIR (KBr,  $\text{cm}^{-1}$ ): The IR spectra of PI-b and PI-a were identical.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  6.95–8.84 (19 H, aromatic protons), 10.41 (1H, amide proton). The yield of reaction was 90%. Anal. Calcd. for  $(\text{C}_{39}\text{H}_{20}\text{N}_4\text{O}_7)_n$ : C, 8.55; H, 3.06; N, 71.38. Found: C, 8.53; H, 3.04; N, 71.34.

#### PI-c

The yield 90%, FTIR (KBr,  $\text{cm}^{-1}$ ): The IR spectrum of PI-c was similar to the spectra of PI-a and PI-b, except for absorption bands at 3373 and 2990.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  2.06 (2 H), 3.56(4 H), 6.35–8.86 (15 H, aromatic protons), 10.4 (1 H, amide proton). The yield of reaction was 87%. Anal. Calcd. for  $(\text{C}_{34}\text{H}_{22}\text{N}_4\text{O}_6)_n$ : C, 9.39; H, 3.70; N, 68.23. Found: C, 9.36; H, 3.67; N, 68.22.

## RESULTS AND DISCUSSION

### Polyimides synthesis and characterization

The diamine monomer, 3,5-diamino-*N*-(4-(8-quinolinoxy) phenyl) benzamide was synthesized as reported previously.<sup>24</sup> Three new PIs containing pendent 4-(8-quinolinoxy) aniline group were prepared in good yields (90–97%) by polycondensation of equal molar amounts of the diamine with commercially available aromatic and cyclo-aliphatic dianhydrides, such as BTDA, PMDA, and BCDA, as shown in Scheme 1. The polycondensation was carried out in NMP at room temperature for 24 h to form poly(amic acid)s, followed by chemical imidization with acetic anhydride and pyridine. Inherent viscosity of the polymers, as a suitable criterion for evaluation of molecular weight, was measured at a concentration of 0.5 g/dL in NMP at  $25^\circ\text{C}$ . The inherent viscosities of the polyimides were in the range of 0.4–0.5 dL/g, indicating moderate molecular weights. All the polymers were characterized by using FTIR,  $^1\text{H}$  NMR, and elemental analysis techniques. The FT-IR spectra of the resulting PIs exhibited the characteristic absorption bands of the five-membered imide ring at 1775 and 1714  $\text{cm}^{-1}$  (typical of imide carbonyl asymmetric and symmetric stretching), 1375  $\text{cm}^{-1}$  (C—N stretching), and at 1087 and 780  $\text{cm}^{-1}$  (imide ring deformation), together with a strong absorption band at 1264  $\text{cm}^{-1}$  due to the C—O stretching.<sup>1</sup>  $^1\text{H}$  NMR spectra for polyimides PI-a and PI-c are shown in Figures 1 and 2. The spectra show characteristic resonance signals of aromatic protons in the region of 6.96–8.87 ppm and a signal at  $\delta = 10.46$  ppm due to the N—H protons of amide group in the polymer side chain.

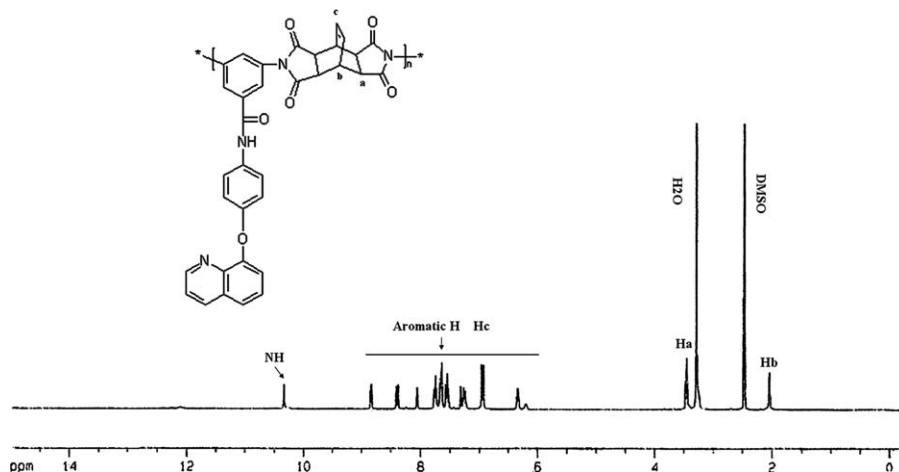


Figure 2  $^1\text{H}$  NMR spectrum of PI-c.

### Polyimides solubility and thermal properties

One of the major objectives of this study was to produce modified PIs with improved solubility. The solubility behavior of the new PIs was determined for the powdery samples at concentration of 5% (W/V) in a number of solvents and the results were tabulated in Table I. As it is shown in this table, all PIs exhibited excellent solubility in polar aprotic solvents such as NMP, DMAc, DMF, DMSO, and even in less polar solvents like pyridine at room temperature and partial solubility in *m*-cresol on heating. The good solubility of these polyimides may be elucidated by their flexible bulky pendent 4-(8-quinolinyl)oxy) benzene group in the diamine residue. A dense chain packing of the polymer chains was probably disturbed by the bulky pendent group; consequently, the solvents molecules were able to penetrate easily to soluble the polymer chains. The PI-c exhibited rather faster solubility behavior in organic solvents in comparison with the polyimides PI-a and PI-b due to presence of bicyclic unit into the structure of PI-c instead of rigid phenyl group. However, the solubility of the synthesized polyimides was in general identical due to the presence of bulky pendent group in the diamine residue which is sufficient to override the effect of the dianhydrides residue. We believe, however, that the

presence of polar amide group in the pendent unit and the polarizability resulting from the nitrogen atom in quinolinol ring can also contribute effectively in the solubility of these PIs.

Thermal properties of the PIs were investigated by thermal analysis techniques including DSC, TGA, and DMTA. None of the polymers showed clear melting endotherms in the DSC thermograms. These observations revealed the amorphous nature of the PIs which can be attributed to their asymmetric structural units and bulky quinolinyl oxy pendent group, which increased the inter-chain distance, resulting in loose polymer chain packaging and aggregates. The ( $T_g$ s) of the polymers which were evaluated on the second heating DSC scans (the midpoint of the change in slope of baseline) ranged between 250–325°C. Figure 3 displays the dynamic storage modulus ( $E'$ ) and  $\tan \delta$  as a function of temperature for these polyimides. The high temperature relaxation is an  $\alpha$ -relaxation process. The  $\alpha$  relaxation corresponds to the glass transition while the  $\beta$  relaxation is a subglass transition process. The  $\beta$  relaxation processes were observed in the range from room temperature to 200°C, possibly due to the local molecular motions related to the diamine constituent of the polymer chain. Regarding the peak temperature in the  $\tan \delta$  curves as the glass transition temperature ( $T_g$ ) of these polymers, DMTA analysis

TABLE I  
Inherent Viscosity and Solubility of Polyimides

PIs	$\eta$ (dL/g)	DMAc	DMF	NMP	DMSO	PY	THF	<i>m</i> -cresol
PI-a	0.5	++	++	++	++	++	–	+-
PI-b	0.45	++	++	++	++	++	–	+-
PI-c	0.4	++	++	++	++	++	–	+-

DMAc: *N,N*-dimethyl acetamide; DMF: *N,N'*-dimethyl formamide; NMP: *N*-methyl pyrrolidone; DMSO: dimethyl sulfide; DO: dioxane; Py: pyridin; THF: tetrahydrofuran.

++: Soluble at room temperature; +: Soluble on heating at 60°C; +- partially soluble on heating at 60°C; – Insoluble on heating at 60 °C.



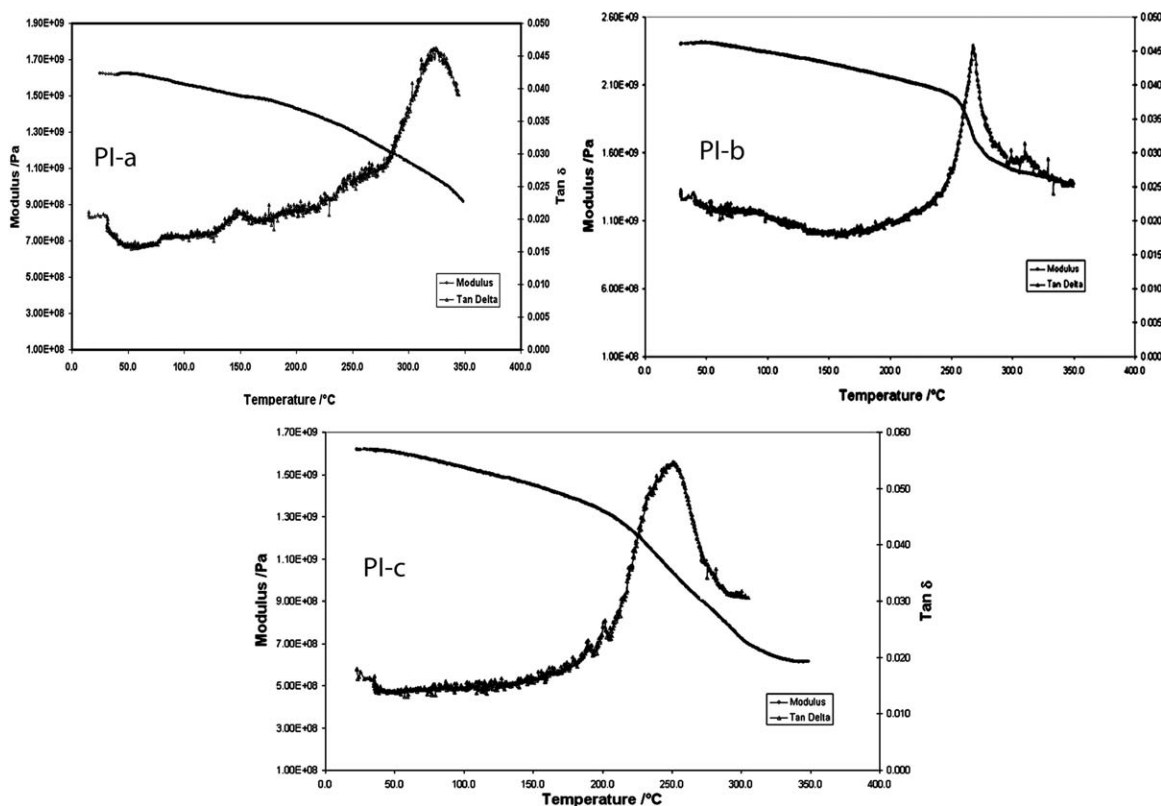


Figure 3 DMTA thermograms of the polyimides: (a) PI-a, (b) PI-b, and (c) PI-c.

confirmed the results of DSC. As it is expected, the ( $T_g$ ) values of these polyimides depended on the structure of the dianhydride component, and decreased with increasing flexibility of the polyimides backbones based on the applied structure of dianhydride. The ( $T_g$ ) of PI-a (325°C) is higher than the ( $T_g$ ) of PI-b (265°C). The lower ( $T_g$ ) of PI-b can be correlated with that of chain flexibility because of the presence of carbonyl linkage between the phthalimide units. It is evident that the bridging carbonyl group between two phenyl rings presents in BTDA, facilitated bond rotation and reduced ( $T_g$ ). The PI-c is based on bicyclic aliphatic dianhydride (BCDA) and showed the lowest  $T_g$  value (250°C) because of the absence of rigid phenyl groups which inhibit the molecular motion. The decreasing trend of ( $T_g$ ) was comparable to the decreasing order of stiffness and polarity of the polymer backbone. Generally, polymers with bulky pendent groups lead to lower ( $T_g$ ) than polymers without bulky side groups owing to the greater interchain distance, which lowers the force of the amide–amide hydrogen bonds that are to some extent responsible for the generally high  $T_g$  of the aromatic PIs. However, the high  $T_g$  of the prepared PIs is mainly due to presence of bulky and polar pendent unit which as a barrier for segmental mobility prevent bond rotation and increase the stiffness of the polymer chains by side chain-side chain

and side chain-main chain interactions through H-bonding. The  $T_g$  values of PIs are listed in Table II.

Thermal stability of polymers was evaluated by TGA under  $N_2$  atmosphere at a heating rate of 10°C/min. The TGA diagrams of the PIs are shown in Figure 4. The PIs showed less than 5% weight loss around 100°C which is due to the loss of the absorbed moisture. For evaluating thermal stability of the polyimides, the data of ( $T_i$ ) and ( $T_{10}$ ) extracted from the original thermograms are summarized in Table II. Regarding the temperature at which a sharp decrease start to occur in the weight of a sample as the initial decomposition temperature ( $T_i$ ), these polymers exhibited ( $T_i$ ) in the range of 270–450°C. The PI-a containing pyromellitic dianhydride ring in the main chain has the highest ( $T_i$ ) and showed better thermal stability than the PI-b with the carbonyl

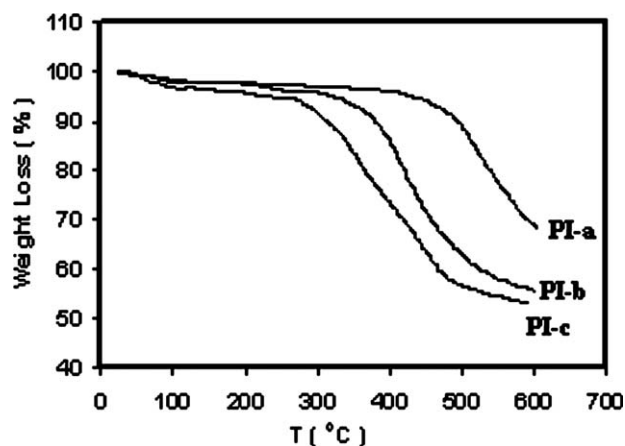
TABLE II  
Thermal Characteristic Data of Polyimides

Pis	$T_g$ (°C)	$T_i$ (°C)	$T_{10}$ (°C)	Char yield at 600°C (%)
PI-a	325	~ 450	~ 500	68
PI-b	265	~ 320	~ 380	55
PI-c	250	~ 270	~ 310	50

$T_g$ , glass transition temperature.

$T_i$ , initial decomposition temperature.

$T_{10}$ , temperature for 10% weight loss.



**Figure 4** TGA thermograms of the polyimides in  $N_2$  atmosphere.

group between two aromatic rings. The PI-c showed the lowest thermal stability which can be related to introduction of bicyclic aliphatic unit in PI-c backbone. The temperatures at 10% weight loss which are an important criterion for evaluation of thermal stability were in the range of 310–500 °C. The polyimide PI-c left about 50% char yield while PI-b and PI-a left about 56% and 68%, respectively, at 600°C in  $N_2$  atmosphere. These results implying that these polyimides possess reasonable thermal stability.

### CONCLUSIONS

Three new polyimides have been prepared from the reaction between a diamine bearing a bulky pendent 4-(8-quinolinylxy) aniline group and commercially available tetracarboxylic dianhydrides. The introduction of flexible bulky pendent 4-(8-quinolinylxy) aniline group into the polymer backbone led to significantly improved solubility of the polymer in various organic solvents. Most of these polymers exhibited a desired combination of properties requiring high-performance materials that include good thermal stability, and excellent solubility in organic sol-

vents for fabrication. These polymers showed nice balance of properties because of incorporation of pyridine, ether, amide bulky groups were important modifications. Transparent and hard polymer films were obtained via casting from their NMP solutions.

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