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Polyimides Containing a Quinazolinone Moiety

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ABSTRACT: A novel heterocyclic diamine monomer, 2-(4-aminophenyl)-6-amino-4(3*H*)-quinazolinone was synthesized from readily available compounds in three steps in high yield. A series of novel polyimides containing the quinazolinone moiety were synthesized either by a one-step solution polymerization reaction or by a two-step procedure that included a ring-opening polyadddition to give poly(amic acid)s, followed by cyclodehydration to polyimides. In the one-step method in *m*-cresol or *p*-chlorophenol with isoquinoline catalyst, polyimides with inherent viscosities of 0.44−0.63 dL/g were obtained. Polyimides **4f** and **4g** from dianhydrides which have a flexible linkage, hexafluoroisopropylidene dianhydride (**2f**) and BPA dianhydride (**2g**), were soluble in hot *m*-cresol and could be cast into tough films from *m*-cresol solution. In the two-step method, poly(amic acid)s with inherent viscosity between 0.63 and 1.40 dL/g were obtained in DMAc at room temperature. The poly(amic acid)s were converted to the corresponding polyimide films by thermal cyclodehydration. The T_g values of the polyimides ranged from 298 to 350 °C. Polyimide **4a** from pyromellitic dianhydride (**2a**) did not show a clear transition in the DSC. Polyimides **4b** from biphenyltetracarboxylic dianhydride (**2b**) and **4g** were semicrystalline and showed clear endothermic peaks for T_m at 465 and 356 °C, respectively. Degradation temperatures for 5% weight loss all occurred above 540 °C in nitrogen and above 537 °C in air. Young's moduli of thin films ranged from 2.34 to 4.89 GPa at room temperature and they maintained the high moduli to high temperatures. The monomer was successufuly copolymerized with 4,4′-oxydianiline and **2g**. With increasing incorporation of quinazolinone units, the copolymers had higher T_g values, were more thermally stable, and had higher moduli.

Introduction

Aromatic polyimides possess outstanding thermal, mechanical, and electrical properties as well as excellent chemical resistance. A large number of new polyimides with unique properties have been introduced for various industrial and consumer product applications since their commercialization in the beginning of the 1960s.[1−9] One of the directions in the development of new polyimides is the synthesis and study of extended rod or rigid rodlike aromatic polyimides because such polyimides have potential as materials for thermally stable, high-modulus, high-strength fibers, as materials with low thermal expansion coefficient (TEC) for packaging materials in microelectronic applications, or as materials for gas separation membranes. In general, rodlike polymers, due to strong enthalpic interactions and the minimal increase in conformational entropy associated with their dissolution or melting, are basically intractable or only processable under extreme conditions.[10] To overcome these difficulties, structural modifications of the polymer backbone, such as the addition of bulky lateral substituents,[11−15] flexible alkyl side chains,[16] noncoplanar biphenylene moieties,[17] and kinked comonomers[18,19] have been utilized to modify the polymer properties, either by lowering the interchain interactions or by reducing the stiffness of the polymer backbone. Fluorine-containing polyimides have received a great deal of attention because fluorine lowers the TEC. Rigid rod polyimides from fluorinated benzenetetracarboxylic dianhydrides,[20] from 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl,[20−22] and from 2,2′-bis(fluoroalkoxy)benzidine[23] have been prepared and all of these polymers had high moduli and low TEC.

The effects of linearity and rigidity of polyimide chains on moduli of polyimide films were investigated using uniaxially stretched polyimide films.[24] The linearity of the polymer chain is more important for high modulus than the rigidity. The relationship between molecular packing coefficient or free volume and modulus has

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also been studied.[25] Large packing coefficients tended to increase the moduli for the polyimides, but the rod-like polyimides with side groups, which have small packing coefficients, have high moduli. The X-ray scattering study suggests that a high degree of liquid crystallinity or crystalline ordering results in the high modulus.[26, 27]

Some effort has been reported on incorporation of heterocyclic units into polyimides to increase the rigidity of the polyimide backbone or to provide strong intermolecular associations which generally resulted in increased glass transition temperatures. A recent major approach has been the introduction of amine functionality or dianhydrides into the heterocyclic ring by formation of ether linkages by a nucleophilic aromatic substitution reaction. Benzothiazole,[28] quinoxaline,[29−31] and benzimidazole,[28] were incorporated into polyimides in this manner and formed high modulus films.

Previously poly(quinazolinone)s have been synthesized by heating an aromatic diamine and a bis(amic acid)[32] or by a reaction of polybenzoxazinones with primary amines followed by cyclization by heating in the presence of an inorganic salt such as lithium chloride.[33]

In this paper, we describe the synthesis of a novel heterocyclic diamine monomer, 2-(4-aminophenyl)-6-amino-4(3*H*)-quinazolinone. Polyimides from this amine would be expected to form high modulus films because of the rigid quinazolinone moiety and hydrogen bonding forming ablity of the quinazolinone. Polymerization of this diamine with a variety of aromatic diamines and characterization of the resulting polyimides are described.

Experimental Section

Materials. 2-Amino-5-nitrobenzonitrile, 4-nitrobenzoyl chloride, hydrazine monohydrate, *m*-cresol, and hydrogen peroxide were purchased from Aldrich Chemical Co. and used as received. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA, **2b**; from CHRISKEV), 4,4′-oxydiphthalic anhydride (ODPA, **2e**; from CHRISKEV), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, **2c**; from TCI), 4,4′-sulfonyldiphthalic anhydride (SDPA, **2d**; from CHRISKEV), and 4,4′-(hexafluoroisopropylidine)diphthalic anhydride (CF_3DA, **2f**, Hoechst) were dried at 150 °C under reduced pressure before use. Bisphenol-A dianhydride (BPADA, **2g**; from General Electric) was recrystallized from acetic anhydride. Pyromellitic dianhydride (PMDA, **2a**; from TCI) was sublimed before use. NMP (Lancaster) and DMAc (Aldrich) were vacuum distilled with P_2O_5 before use. Other common organic solvents were used as received unless otherwise stated.

Characterization. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL 270 spectrometer in DMSO-d_6 using tetramethylsilane as an internal reference. The chemical shift (δ) and coupling constant (J) data are quoted in ppm and hertz, respectively. The following abbreviations are used to describe peak patterns where appropriate: s = singlet, d = doublet, m = multiplet, and br = broad. Melting points (mp) were measured on a Fisher-Johns melting point apparatus or a Mettler FP800 DSC (determined by taking peak of endothermic peak) and are uncorrected. IR spectra were performed on an Analet AQS-60 FTIR spectrophotometer. Microanalyses were obtained from Galbraith Laboratories Inc., Knoxville, TN. Low-resolution mass spectroscopy data were recorded on a ZAB_2FHS spectrometer, ion source 240 °C and 70-eV electron impact, direct inlet: *m*/*e* (assignment).

The T_g's and T_m values of the polymers were obtained using a Seiko 220 DSC instrument at a heating rate of 20 °C/min, or 30 °C/min for rigid polyimides, in N_2 (160 mL/min). The T_g was taken from the midpoint of the change in slope of the baseline. The T_m was taken from the onset of the change in slope to the minimum of the endotherm peak. The weight loss data were obtained from a Seiko TG/DTA instrument at a heating rate of 20 °C/min in N_2 and air (200 mL/min). For all differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements, polymer pellets were pressed under 5 tons of pressure. Inherent viscosity data were obtained with a calibrated Ubbelohde viscometer. The measurements were done in concentrated sulfuric acid at 25 °C or in *m*-cresol at 50 °C for the polyimides, and in DMAc or NMP at 25 °C for the polyamic acids with a 1B (205) viscometer.

Film Casting. Polymer films were cast from *m*-cresol solution. A typical procedure is as follows: 130 mg of polymer was dissolved in 2−5 mL of *m*-cresol on heating. This solution was transferred into a glass ring (diameter = 3.5 cm, height = 2 cm, thickness = 0.4 cm) located on a glass plate. The solvent was slowly evaporated in a forced-air oven at 130 °C for 24 h to yield tough and flexible films (thickness = 0.070−0.120 mm) which were fingernail creasable. If the films could not be removed from the glass plate, they were placed into a beaker of hot water for 1−10 h, followed by drying at 220 °C in vacuo for 24 h. Typical film thickness was in the range 0.080−0.120 mm.

Measurement of Mechanical Properties. A typical procedure to obtain Young's modulus measurements was performed as follows: A stamp was used to cut out a film strip (length = 5 mm, width = 2 mm, thickness = 0.15−0.22 mm) which was mounted between two chucks in a Seiko TMA/SS 120 instrument. For Young's modulus at 25 °C, the parameters were set as offset load = 10−20 g, load amplitude = 5−10 g, and cycling frequency = 0.05 Hz. After these data were collected for 30 min, the same film was used without changing the parameters to measure Young's modulus (*E*') variation with temperature by heatiing to 450 °C studied at a ramp rate of 3 °C/min in static air.

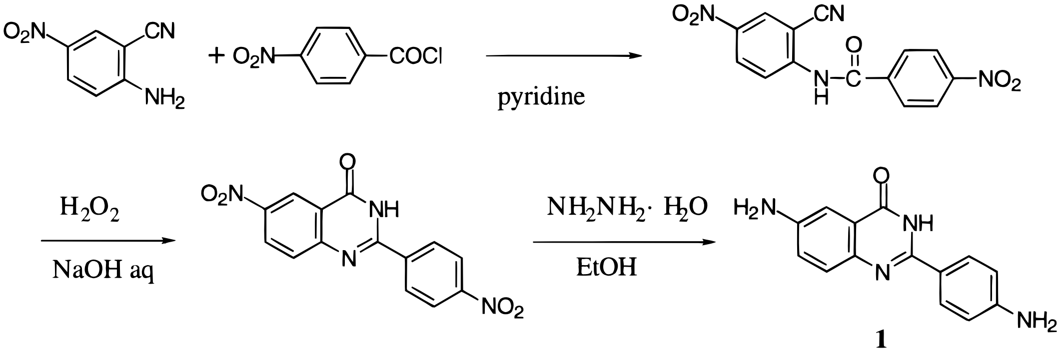
Monomer Synthesis.[34] ***N*-(2-Cyano-4-nitrophenyl)-4-nitrobenzamide.** A mixture of 24.47 g (0.15 mol) of 2-amino-5-nitrobenzonitrile, 27.83 g (0.15 mol) of 4-nitrobenzoyl chloride, and 200 mL of pyridine was heated under reflux for 6 h, cooled, and poured into 1.5 L of 2% HCl. The separated orange solid was collected by filtration, washed well with water, and dried. Recrystallization from aqueous DMF yielded a yellow powder: yield 40.15 g (86.5%), mp 200−203 °C.

^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.90 (d, J_2 = 9.15, 1H), 8.25 (d, J_2 = 8.91, 2H), 8.45 (d, J_2 = 8.91, 2H), 8.59 (d−d, J_2 = 9.43, J_3 = 2.73, 1H), 8.82 (d, J_3 = 2.73, 1H), 11.38 (s, 1H), MS (m/e, relative intensity %): 312 (M, 49.4), 150 (100), 104 (56.3) Anal. Calcd for $C_{14}H_8N_4O_5$: C, 53.85; H, 2.58; N, 17.94; O, 26.62. Found: C, 53.95 ; H, 2.54; N, 17.99.

2-(4-Nitrophenyl)-6-nitro-4(3H)-quinazolone. To a three-neck round bottom flask equipped with a mechanical stirrer and a water-cooled condenser was added 31.22 g (0.10 mol) of *N*-(2-cyano-4-nitrophenyl)-4-nitrobenzamide, 500 mL of 16% sodium hydroxide, and 1 L of 3% hydrogen peroxide. The orange suspension was heated carefully until the initial vigorous reaction subsided and then refluxed gently for 1 h. The mixture turned to a dark orange solution and then to an orange slurry. It was cooled to room temperature, then an additional 600 mL of 3% hydrogen peroxide was added and the reaction mixture was refluxed and stirred for 30 min. The cooled mixture was then filtered and the yellow solid was collected and then suspended in 5% sulfuric acid and stirred for several minutes. Filtration, drying, and recrystallization from aqueous DMF gave a yellow powder: yield 27.79 g (89%); mp 319.8 °C. ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.96 (d, J_2 = 8.96, 1H), 8.37−8.45 (m, 4H), 8.58 (d−d, J_2 = 8.98, J_3 = 2.81, 1H), 8.83 (d, J_3 = 2.81, 1H),13.1−13.3 (br), MS (*m*/*e*, relative intensity %): 312 (M, 100), 282 (39.2), Anal. Calcd for $C_{14}H_8N_4O_5$: C, 53.85; H, 2.58; N, 17.94; O, 25.62. Found: C, 53.99; H, 2.54; N, 17.93.

2-(4-Aminophenyl)-6-amino-4(3*H*)-quinazolinone (1). To a dispersion of 2-(4-nitrophenyl)-6-nitro-4(3H)-quinazolinone (24.72 g, 0.079 mol) in ethanol (600 mL) was added 5% palladium on charcoal (1.0 g); hydrazine monohydrate (15.84 g) was added to the stirred mixture dropwise at 85 °C for 15 min. After addition was completed, the mixture was stirred at 85 °C for another 8 h. The solution was then filtered to remove Pd−C. The crude product was recrystallized from

Scheme 1



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95% ethanol to give pale yellow needles: yield 18.16 g (91%); mp 303.5 °C. ^{1}H-NMR (270 MHz, DMSO-d_6) δ 5.51 (s, 2H), 5.66 (s, 2H), 6.60 (d, $J_2 = 8.67$, 2H), 7.05 (d−d, $J_2 = 8.67$, $J_3 = 2.73$, 1H), 7.17 (d, $J_3 = 2.73$, 1H), 7.36 (d, $J_2 = 8.64$, 1H), 7.85 (d, $J_2 = 8.67$, 2H), 11.71(s, 1H). ^{13}C-NMR (270 MHz, DMSO-d_6) δ 106.93, 113.66, 120.33, 121.88, 123.12, 128.40, 128.83, 140.93, 147.42, 148.41, 151.71, 162.80. MS (*m/e*, relative intensity %): 252 (M, 100). Anal. Calcd for $C_{14}H_{12}N_4O$: C, 66.66; H, 4.79; N, 22.21; O, 6.34; found: C, 66.37; H, 4.67; N, 22.07.

Polymerization: One-Step Solution Method. Polyimides were prepared following a general procedure from the dianhydrides and diamines in either *m*-cresol or *p*-chlorophenol with isoquinoline as a catalyst. The polymer concentration was 5 or 8 wt %. To a 50-mL three-neck round bottom flask equipped with a nitrogen inlet and a water-cooled condenser was added 2-(4-aminophenyl)-6-amino-4-quinazolinone (**1**) (0.3784 g, 1.5 mmol), 2 drops of isoquinoline, and 23.18 g of *m*-cresol. Bisphenol-A dianhydride (0.7806 g, 1.5 mmol) was added to the reaction mixture in small portions with vigorous stirring at room temperature. The flask was purged with nitrogen and the solution was stirred for 8 h under a N_2 atmosphere at room temperature. During this period in all cases a clear yellow homogeneous solution was formed. The solution became viscous as the poly(amic acid) formed. The reaction system was slowly heated to reflux at 220 °C (salt bath temperature) with stirring for 24 h. The water formed during imidization was removed by a slow stream of N_2 passing through the solvent. In some cases, depending on the polyimide and solvent, the polymer precipitated as a powder or formed a clear gel. The reaction mixture was cooled and precipitated into 400 mL of methanol and collected by filtration. **2f** and **2g** formed fibrous polymer; the others were yellow powders. The polymers were extracted with acetone for 24 h and dried under high vacuum at 200 °C for 24 h. The yields were about 90%. The polyimide structure and complete imidization were confirmed by FTIR spectroscopy.

Polymerization: Two-Step Method. (a) Poly(amic acid) Synthesis. A typical example of polymerization is as follows. The solids composition was maintained at 15 wt % except for PMDA (10 wt %). Into a 50-mL round bottom three-neck flask equipped with a nitrogen inlet and a stir bar, 0.3784 g (1.5 mmol) of 2-(4-aminophenyl)-6-amino-4(3*H*)-quinazolinone (**1**) was charged by washing with 8.62 g of DMAc under a strong nitrogen flow. To this solution, 0.4833 g (1.5 mmol) of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, **2b**) was added with slow stirring, and the reaction mixture was stirred at room temperature in nitrogen atmosphere affording a viscous polymer solution after 24 h. The inherent viscosities of the poly(amic acid)s were subsequently determined at a concentration of 0.5 g/dL in DMAc at 25 °C.

(b) Thermal Conversion of Poly(amic acid) to Polyimides. About 1.5 g of the poly(amic acid) solution was spread on a glass plate and dried at 80 °C for 24 h in a forced air oven. The films on glass were then converted to the polyimide by heating in air at 100 °C for 15 min, 140 °C for 20 min, 200 °C for 25 min, 250 °C for 30 min, 280 °C for 30 min 300 °C for 1 h, and 320 °C for 30 min. The film was stripped from the plate by soaking in hot water. The films were dried at 120 °C in vacuo before mechanical testing. The average film thickness was 0.20 mm.

Results and Discussion

Monomer Synthesis. A new aromatic diamine, 2-(4-aminophenyl)-6-amino-4(3*H*)-quinazolinone (**1**), was prepared in three steps from readily available starting materials (Scheme 1). 2-Amino-5-nitrobenzonitrile was reacted with 4-nitrobenzoyl chloride in pyridine at reflux overnight. The *N*-(2-cyano-4-nitrophenyl)-4-nitrobenzamide was cyclized to the dinitroquinazolinone in the presence of sodium hydroxide and hydrogen peroxide. The reduction with hydrazine monohydrate/Pd-C gave **1**. The yields in each step were very high.

Polymer Synthesis. There are two major methods used for the preparation of polyimides. One procedure involves two steps and proceeds via poly(amic acid)s intermediates. The other is a one-step solution polymerization. The one-step method has some advantages over the two-step method. Polyimides in bulk are more easily produced, and polyimides with higher crystallinity can be more readily obtained.[32] The one-step method is also useful for unreactive diamines and dianhydrides which cannot form high molecular weight polyamic acids by the two-step method.[35] The disadvantage of the one-step method is that insoluble polyimides cannot form high molecular weight polyimides because of premature precipitation. Since the quinazolinone diamine is deactivated by the electron-withdrawing heterocyclic moiety, we first tried the one-step solution method even though with some of the dianhydrides we would expect to form insoluble polyimides because of the rigid structure. The quinazolinone diamine and a series of dianhydrides were then reacted in *m*-cresol or *p*-chlorophenol in the presence of a catalytic amount of isoquinoline (Scheme 2). At room temperature, after 8 h, a homogeneous, yellow to orange clear solution was formed. The temperature was then increased slowly to 220 °C and maintained at that temperature for 24 h. The water formed during imidization was removed continuously with a stream of nitrogen. Depending on the rigidity of the dianhydrides, the reaction mixture became either a homogeneous solution, a clear gel, or a heterogeneous slurry due to the precipitation of the polymer in the later stages of the reaction. Polymers prepared from dianhydrides **2a**−**d**, precipitated out of *m*-cresol, so *p*-chlorophenol was used as a solvent. A clear gel formed and polyimides with higher viscosity were obtained for **2b**−**d**. With **2a**, even in *p*-chlorophenol, the polymer still came out of the solution as a powder. Using dianhydrides which have flexible linkages, **2f** and **2g**, the polymer stayed in *m*-cresol solution and high molecular weight polyimides

Scheme 2

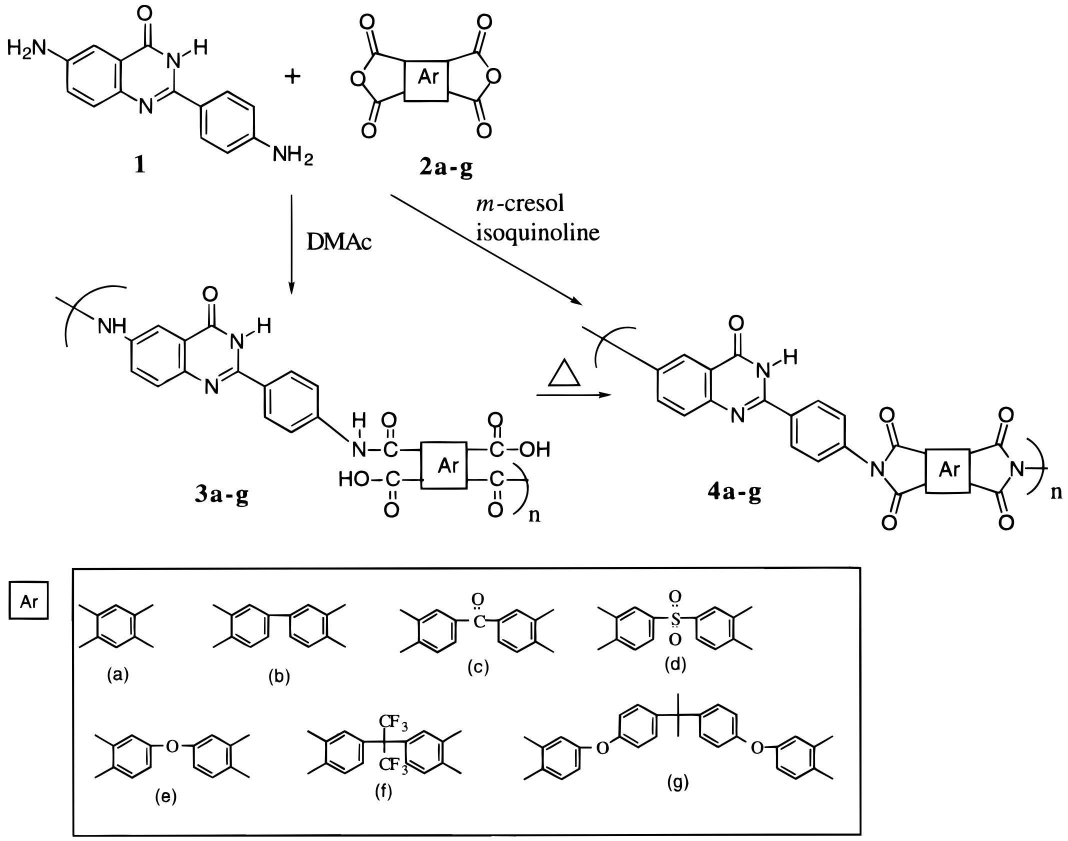


Table 1. Synthesis of Polyimides from 1 and Various Aromatic Tetracarboxylic Dianhydrides (One-Step Method)

polymer	solvent	concn (wt %)	conditions[a]	η_{inh} (dL/g)[b]	film
4a	*p*-chlorophenol	5	ppt	0.63	
4b	*p*-chlorophenol	5	gel	0.46	
4c	*p*-chlorophenol	5	gel	0.64	
4d	*m*-cresol	5	ppt	0.23	
4d	*p*-chlorophenol	5	gel	0.49	
4e	*m*-cresol	5	ppt	0.53	
4f	*m*-cresol	8	sol	0.59	flexible
4g	*m*-cresol	8	sol	0.44[c]	flexible

[a] Key: sol, clear, viscous solution; gel, no precipitation, but gelation occurred during polymerization; ppt, precipitation of polymer occurred during polymerization. [b] 0.5 g/dL in concentrated H_2SO_4 at 25 °C. [c] 0.1 g/dL in *m*-cresol at 50 °C.

Table 2. Synthesis of Polyimides from 1 and Various Aromatic Tetracarboxylic Dianhydrides (Two-Step Method)

Ar	η_{inh} (dL/g)		film
	PAA[a]	PI[b]	
a	1.41	0.91	brittle
b	0.95	0.89	slightly flexible
c	0.81	0.72	slightly flexible
d	1.11	0.88	slightly flexible
e	0.84	0.83	slightly flexible
f	1.07	0.86	flexible
g	0.63	0.57[c]	flexible

[a] PAA, polyamic acid, 0.5 g/dL in DMAc at 25 °C. [b] PI, polyimide, 0.1 g/dL in concentrated H_2SO_4 at 25 °C. [c] 0.1 g/dL in *m*-cresol at 50 °C.

were obtained. Even though precipitation or gelation took place in some cases, moderately high molecular weight polyimides with inherent viscosities of 0.44–0.63 dL/g were obtained (Table 1). Presumably the molecular weight was built up in the early stages of the polymerization as a polyamic acid before imidization. Polymers **4f** and **4g** can be cast into free-standing transparent films, which indicates the formation of high molecular weight polymers. IR and TGA analyses indicated that imidization of the polymers was complete.

Polyimides were synthesized by the conventional two-step procedure, involving a ring-opening polyaddition and subsequent thermal cyclodehydration. The dianhydrides were added to a solution of the quinazolinone amine **1** in DMAc at room temperature (Scheme 2). The solids composition was maintained at 15% except for **3a** (10 wt %). High molecular weight poly(amic acid)s with inherent viscosities of 0.63–1.40 dL/g were obtained in 24 h (Table 2). Transparent yellow, flexible films of the polyamic acids could be obtained by casting the resulting polymer DMAc solutions at 80 °C for 24 h. The thermal conversion to polyimides was carried out by heating the polyamic acid films at 100 °C for 15 min, 140 °C for 20 min, 200 °C for 25 min, 250 °C for 30 min, 280 °C for 30 min, 300 °C for 1 h, and 320 °C for 30 min. More rapid temperature elevation resulted in cracked or brittle films. The poly(amic acid)s **3b**–**3g** formed free-standing films. However, poly(amic acid) from **2a** formed a brittle film. Crystallization of **3a** was very rapid so that a film could not be obtained. Poly(amic acid)s prepared in NMP solution were cast into films and heated up in the same manner. Polymers **3a**–**e** formed brittle or cracked films despite the high viscosity of the poly(amic acid)s solutions. The polyimide films were transparent and dark reddish brown in color. The films shrank to about 90% of their original dimensions after thermal imidization. The inherent viscosities in concentrated sulfuric acid were somewhat lower than those of the poly(amic acid)s. Complete imidization was confirmed by FTIR and TGA.

Table 3. Thermal Properties of The Polyimides 4a−g

polymer[a]	T_g (°C)	T_m (°C)	TGA (°C)[b] N$_2$	TGA (°C)[b] air
4a	−[c]	−[c]	583	581
4b	−[c]	465	588	585
4c	339	−[c]	568	571
4d	350	−[c]	540	545
4e	338	−[c]	588	589
4f	342	−[c]	544	546
4g	298	356	540	537

[a] Prepared by a two-step method. [b] 5% weight loss. [c] Not detectable.

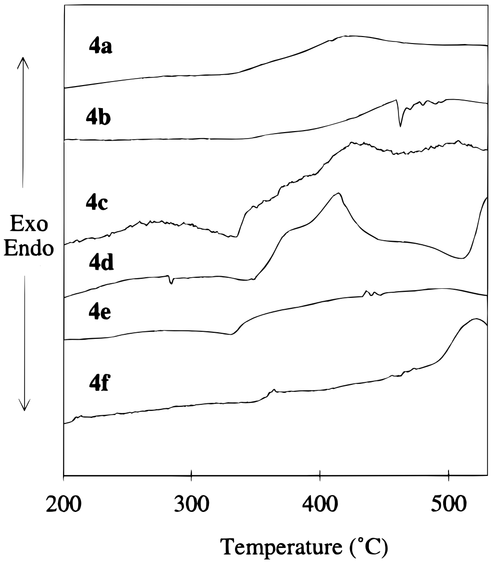


Figure 1. DSC thermograms of polyimides **4a**−**f**.

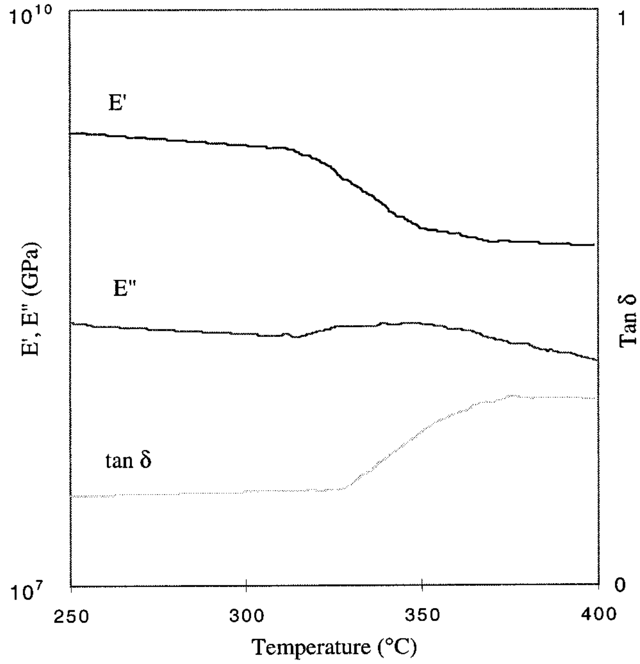


Figure 2. Thermomechanical analysis of polyimide **4b**.

Table 4. Thermomechanical Properties of the Polyimides 4a−g

polymer	preparation	modulus (GPa) at 25 °C	modulus (GPa) at 200 °C	tan δ (max) (°C)	E″(max) (°C)
4b	2 step	3.19	2.26	388	353
4c	2 step	4.89	3.13	362	332
4d	2 step	3.99	2.44	355	334
4e	2 step	3.61	2.23	343	320
4f	1 step	1.48	0.89	400	350
4f	2 step	2.65	1.64	413	374
4g	1 step	2.25	1.41	293	282
4g	2 step	2.34	1.61	308	290

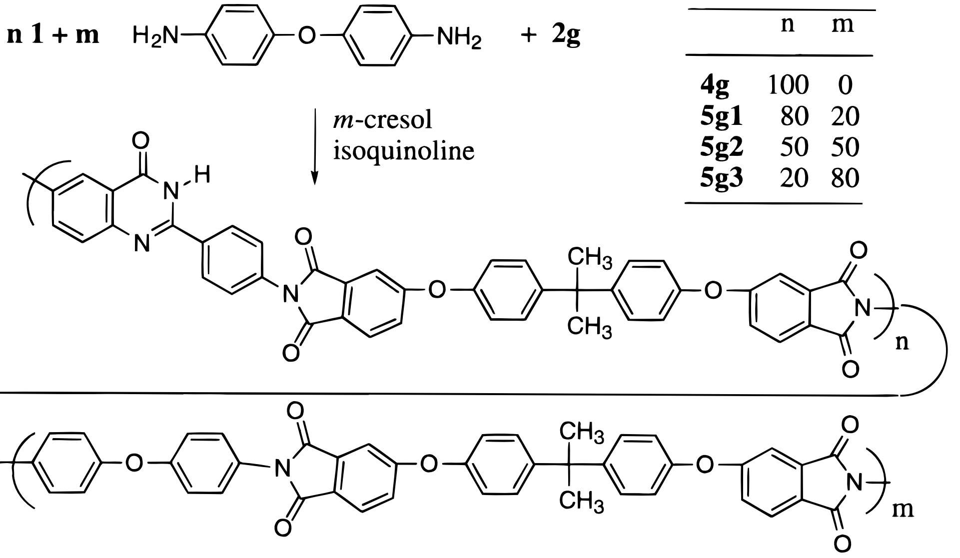
Solubilities. The polyimides prepared by the one-step method and those by the two-step method have similar solubilities. All of them are soluble in concentrated sulfuric acid at room temperature after 3 days. They are insoluble in common organic solvents, except polyimides **4f** and **4g**, which dissolve in hot *m*-cresol. When the *m*-cresol solutions were cooled to room temperature, they formed a clear gel even at 3 wt %. The solution behavior and solubility suggest strong interchain association presumably because of hydrogen bonding of the quinazolinone.

Thermal Properties. The thermal properties of the polyimides were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Table 3). The data shown are for the polyimide films prepared by the two-step method. The results of the TGA analyses showed the general excellent thermal stability of the polyimides. The 5% weight losses in nitrogen were 540−588 °C. In air these temperatures were in all cases similar, suggesting high thermooxidative stability. Generally, the thermal stability of a polymer backbone will be determined by the strength of its weakest bond. The order of thermal stability of polyimides from the different dianhydrides is **2a** > **2b** > **2e** > **2c** > **2d**.[5] The 5% weight losses of the polyimides **4a**−**g** followed this order and no weight losses were observed under 400 °C. These results suggest a high thermal stability of the quinazolinone ring.

Thermal transitions were investigated by DSC in the temperature range from 100 to 530 °C. Due to the chain stiffness, transitions were not observed for polymers **4a**−**d** at the rate of 20 °C/min. A distinct glass transition was observed for **4g** at 298 °C (Figure 3). This polyimide is semicrystalline with a melting endotherm maximum at 356 °C. At a rate of 30 °C/min, thermal transitions of the polyimides **4b**−**f** were detected. No clear transition was observed for **4a**. Polyimide **4b** is semicrystalline and showed a melting endothermic peak at 465 °C. T_g values of **4c**−**4f** ranged from 338 to 342 °C. Polymers **4a**, **4c**, **4d**, and **4f** showed a broad exotherm above 400 °C (Figure 1). This may be attributed to the crystallization that occurs in the semicrystalline polymers above their glass transition temperatures. The other possible explanation is a cross-linking reaction.

Themomechanical Properties. Young's moduli (E'), maximum values of loss moduli (E''), and maximum values of tan δ of the polyimide films are tabulated in Table 4. They were measured by TMA in the tensile stress−strain mode. Loads were chosen such that a linear stress-strain relationship was obtained. These films have very high moduli, 2.34−4.89 and maintained the high moduli at high temperatures (Table 4). The flexible polyimides **4f** and **4g** showed lower moduli than the rigid polyimides. Typical TMA curves are shown in Figure 2. The rigid polyimide **4b** showed a high modulus, and the E' values dropped gradually at high temperature and did not show a clear maximum for tan δ and E''. Polyimide **4c**, which has the carbonyl linkage as a spacer, showed the highest modulus. In this case rapid decrease in the modulus took place and it exhibited a maximum of tan δ at 343 °C, which corresponds to the T_g. T_g values by TMA for **4d**, **4e** and **4g** agreed

Scheme 3



	n	m
4g	100	0
5g1	80	20
5g2	50	50
5g3	20	80

5g1-3

Table 5. Copolymerization of 1 and 4,4′-Oxydianiline with 2g

					TGA (°C)[b]		modulus (GPa)		
polymer	n (mol %)	η_{inh}[a] (dL/g)	T_g (°C)	T_m (°C)	N_2	air	20 °C	200 °C	tan δ(max) (°C)
4g	100	0.44	298	356	540	537	2.34	1.61	283
5g1	80	0.92	282		533	533	2.22	1.89	280
5g2	50	0.83	263		537	533	1.96	0.99	256
5g3	20	0.87	240		509	502	0.89	0.76	227

[a] Inherent viscosity measured in *m*-cresol at 50 °C at a concentration of 0.1 g/dL. [b] 5% weight loss.

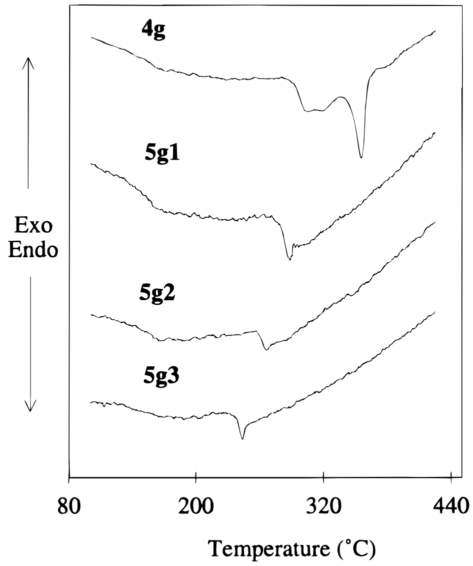


Figure 3. DSC Thermograms of polyimides **4g** and **5g 1**−**3**.

with the T_g values determined by DSC. However, T_g values by TMA for **4c** and **4f** were considerably higher than those determined by DSC. There may be a cross-linking reaction occurring even though no weight loss was observed below 400 °C by TGA. Polyimides containing the benzimidazole group have been shown to cross-link on heating.[27] A modulus increase over 350 °C was observed for **4f**. A modulus increase above T_g was also observed for the polyimide from PMDA and 4,4′-oxydianiline,[36] which suggests side reactions in these polyimides resulting in cross-linking occurring at elevated temperature. The films of the polyimides prepared by the one-step method showed lower E' values for **4f** and **4g**. This can be explained by a difference in morphology of the films resulting from the thermal history or an effect due to a small amount of residual *m*-cresol.

Copolymerization. Copolymerization of **1** with 4,4′-oxydianiline and BPADA was carried out (Scheme 3). High molecular weight polymers with inherent viscosities over 0.87 dL/g were obtained (Table 5). Transparent yellow flexible tough films could be obtained by casting from *m*-cresol. Polymers **5g1**−**3** are only soluble in *m*-cresol, and the solutions behave similar to the homopolyimides. Even when 20% of quinazolinone was incorporated in BPA dianhydride−ODA polyimide copolymers, they were insoluble in common organic solvents. This suggests a strong influence of hydrogen bonding because of the quinazolinone structure. T_gs (Figure 3) and moduli increased as quinazolinone content increased. Thermooxidative stability also increased as quinazolinone content increased as indicated by the 5% weight losses in TGA.

Conclusions

A new aromatic diamine, 2-(4-aminophenyl)-6-amino-4(3*H*)-quinazolinone, was synthesized in high yield from readily available compounds in three steps. High molecular weight polyimides were synthesized from this diamine and a variety of aromatic dianhydrides. All polyimides synthesized have very high glass transition temperatures and excellent thermal stabilities. Films made from the polyimides had high moduli and maintained the high moduli to high temperatures.

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