Macromolecules **1995,** *28,* 4207–4212

Synthesis and Properties of Poly(aryl prehnitimide)s

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Received October 19, 1994; Revised Manuscript Received February 10, 1995[⊗]

ABSTRACT: A series of novel poly(aryl prehnitimide)s based on diphenylprehnitic dianhydride (5,6-diphenylbenzene-1,2,3,4-tetracarboxylic dianhydride) are synthesized and characterized. Polyimides having intrinsic viscosities of 0.45–1.81 dL/g in *N*-methyl-2-pyrrolidinone were obtained by one-step solution polymerization in *m*-cresol. These polyimides are readily soluble in many common organic solvents such as *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidinone, dimethyl sulfoxide, and *N,N*-dimethylformamide. The poly(aryl prehnitimide) derived from *m*-phenylenediamine is also very soluble in tetrahydrofuran, pyridine, and chloroform. Glass transition temperatures were in the range of 362–443 °C, as determined by differential scanning calorimetry and thermomechanical analysis. Degradation temperatures for 5% weight loss occurred all above 483 °C in nitrogen and 449 °C in air. Young's moduli of thin films for some polyimides ranged from 2.07 to 3.94 GPa as assessed by thermomechanical analysis.

Introduction

The design and synthesis of new monomers is one of common approaches to the development of high-performance polymers with desirable properties and functions. For condensation-type polyimides, much effort has been directed toward the design and preparation of novel dianhydride and diamine monomers. A greater flexibility in the design and synthesis of aromatic diamines arises from the well-established chemistry of aniline and its derivatives.[1] Among many aromatic diamines, 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl recently developed for soluble, high-strength polyimides is an example of the outcome of benzidine chemistry.[2] In aromatic dianhydride monomers, the reactive functionality exists mainly in two types: 5-membered-ring phthalic and 6-membered-ring naphthalic anhydrides. To design a new dianhydride monomer, one of the approaches is to tailor the moiety that links either two phthalic or two naphthalic anhydrides. For example, the dianhydride used for Ultem poly(ether imide) can be prepared via the condensation of methyl 4-nitrophthalimide and Bisphenol A. Two naphthalic anhydrides can also be linked together through a variety of connectors such as arylene ethers, sulfonyl, keto, and alkylene groups.[3] Introduction of a kink or a hinge or a flexible unit into a dianhydride (or a diamine) serves dual functions: to improve the solubility and to provide a new polymer with other desirable properties. In all known aromatic dianhydrides, two anhydride groups, either a phthalic or naphthalic unit, are apart from each other by at least one atom. Pyromellitic dianhydride (PMDA), as an important monomer for commercial polyimides, has two anhydride groups located opposite to each other at 1,2- and 4,5-positions of the benzene, respectively. Unlike other known aromatic dianhydrides, PMDA is the smallest rigid monomer and leaves only two positions on the benzene ring available for functionalizations. Conceivably, substitutions of PMDA at the 3,6-positions would produce the monomers for a variety of new polyimides with unique properties. Indeed, PMDA has been modified by introducing phenyl,[4] trifluoromethyl,[5] and trifluoromethoxy[6] at the 3,6-positions.

Considering structural modifications for dianhydride monomers, we realize that adjusting the positions of the two anhydride groups, namely, moving two anhydride groups in any dianhydrides close in proximity, is another type of structural alternation which should open a new avenue to synthesis of a variety of novel dianhydride monomers by design. Biphenyl-2,2′3,3′-tetracarboxylic dianhydride, as an isomer of commonly known biphenyl dianhydride (BPDA), is an example of the kinked monomer having two adjacent anhydride groups.[1a] We have recently designed and synthesized phenylated isomeric PMDA, diphenylprehnitic dianhydride (**1**).[7] Two anhydride groups in **1** are locked on one benzene ring at the 1,2,3,4-positions, which means that the resulting polyimides should have a rigid but a bent diimide unit. Dianhydride **1** is truly a structural isomer of diphenylpyromellitic dianhydride,[4] but the former is found to be able to impart greater solubility to the polyimides than the latter. In this paper, we describe the detailed synthesis and properties of a series of polyimides based on this new dianhydride.

Experimental Section

Materials. *m*-Cresol, *o*-chlorophenol, isoquinoline, and 4,4′-methylenedianiline (**2d**) were purchased from Aldrich Chemical Co. and used as received. 4,4′-Bis(4-aminophenoxy)biphenyl (**2e**), bis[(4-aminophenoxy)phenyl] sulfone (**2f**), and 9,9′-bis(4-aminophenyl)fluorene (**2g**) were received from New Seika Corp. and used without further purification. *m*-Phenylenediamine (**2b**) and *p*-phenylenediamine (**2a**) (Aldrich) were purified by sublimation under vacuum. 4,4′-Oxydianiline (**2c**) (Aldrich) was recrystallized from ethanol. Other common organic solvents are reagent grade unless otherwise stated.

Characterization. The ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Gemini-200 or a Bruker-400 instruments using tetramethylsilane as an internal reference. Infrared measurements were performed on a Perkin-Elmer 1600 FTIR spectrometer. Low-resolution mass spectra were obtained on a Du Pont 21-492B spectrometer. The apparent molecular weights of the polymers were determined by gel permeation chromatography (GPC) using chloroform at ambient temperature. Molecular weight calculations were based on polystyrene standards. A PL gel column (1.0 × 30 cm, 5 μm) with a chloroform elution rate of 1.0 mL/min was used. Elution of the polymers from the column was detected by a Perkin-Elmer UV–vis spectrophotometric detector set at 254 nm. Intrinsic viscosities were measured in a *N*-methyl-2-pyrrolidinone or *o*-chlorophenol solution at 30 °C using an Ubbelohde dilution viscometer. Melting points were taken from a Fisher-Johns melting apparatus or a differential scanning calorimeter. The glass transition temperatures (T_gs) were determined on a Seiko 220C differential scanning

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1995.

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calorimeter with a heating rate of 10 °C/min under nitrogen (50 mL/min). Two consecutive runs were performed for each polymer (with normal cooling in between scans), and the T_g was taken from the second scan as the midpoint of the change in slope of the baseline. Thermal and thermooxidative stabilities of the polymer samples were determined using a Seiko 120 TG/DTA analyzer run from 25 to 700 °C or 1000 °C at a heating rate of 10 °C/min. Isothermal aging tests were conducted in air at a fixed temperature of 400 °C for 25 h. The tensile mechanical properties of the polymer films were measured using a Seiko 120C TMA/SS analyzer run in stress–strain mode. A stamp was used to cut out a film strip (length = 10 mm, width = 2 mm, thickness = 0.025–0.125 mm) which was mounted between two chucks in the TMA/SS instrument. These films were tested by measuring the stress and strain, while applying a linear load program. For Young's modulus at 25 °C, the parameters were set as offset load = 20 g, load amplitude = 10 g, and cycling frequency = 0.05 Hz. Young's moduli were obtained from the slope of the linear portion of the stress–strain plots (E'). After the data were collected, the same film was used without changing the parameters to Young's modulus variation with temperature by heating to 450–500 °C at a ramp rate of 3 °C/min in static air.

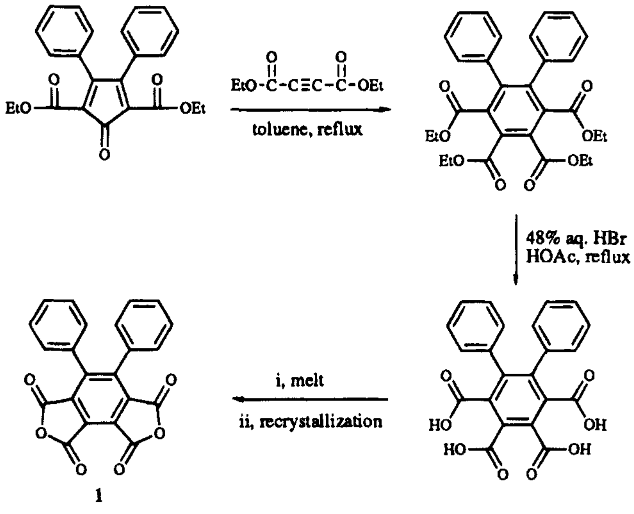
Film Casting. All polymer films were cast from a 1,1,2,2-tetrachloroethane (TCE) solution. A typical procedure for film casting is as follows: the purified and dried polymer (100–200 mg) was dissolved in 2–4 mL of TCE. The solution was then transferred by pipette filtration into a cylindrical glass mold (diameter = 40 cm, height = 25 cm, thickness = 2 cm) placed on a glass plate. The mold was covered with a glass plate. An orifice at the top edge of the mold allowed the solvent to evaporate slowly at room temperatures for a period of 3–5 days. The film was removed from the glass mold by adding water to peel off the film. The circular and clear films were then placed in a vacuum oven. The oven temperature was initially at 80 °C for 24 h, then gradually raised to 150 °C, and held at this temperature for 2 weeks.

X-ray Structure Determination of 1. Crystal structure determination was performed at the Department of Chemistry, University of Ottawa, Ottawa, Canada. The single crystal of **1** was grown during sublimation at 200 °C under vacuum and cut with dimensions of 0.2 × 0.2 × 0.2 mm. All measurements were made on a Rigaku diffractometer with Mo Kα radiation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 25 reflections in the range $40 < 2\theta < 50$ corresponded to a triclinic cell with dimensions a = 12.826 (3) Å, b = 13.188 (3) Å, c = 12.473 (4) Å, α = 110.242 (21)°, β = 113.420 (22)°, and γ = 67.645 (18)°. For Z = 4 and FW = 370.31, the calculated density is 1.411 g/cm^3. Based on the systematic absences, the space group was determined to be $P1$. The data were collected at 22 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 49.9. The residuals are as follows: for significant reflections, R_f = 0.065 and R_w = 0.031; for all reflections, R_f = 0.131 and R_w = 0.031. A total of 6388 reflections was collected. The unique set contains only 6085 reflections. The standards were measured after every 150 reflections. No crystal decay was noticed. The data were collected for Lorentz and polarization effects. No absorption correction was made. The structure was solved by direct methods. There are two molecules per asymmetric unit. All the phenyl groups were refined as rigid groups to increase the ratio reflections/parameters. All the atoms were refined anisotropically except the hydrogen. The hydrogen atoms were calculated assuming a distance C–H of 1.007 Å. Calculations were performed using the NRCVAX crystallographic software package.

Monomer Synthesis. The synthesis of ethyl 5,6-diphenylbenzene-1,2,3,4-tetracarboxylate (tetraester) was reported before.[7a] The improved syntheses of diphenylprehnitic acid and diphenylprehnitic dianhydride (**1**) are described as follows.

Diphenylprehnitic Acid. The tetraester (104 g) was dissolved in 350 mL of acetic acid in a 1-L round-bottomed flask equipped with a condenser, followed by addition of 140 mL of an aqueous HBr solution (48%). The mixture was heated at reflux for 48 h. In about 24 h, some white precipitates were formed, indicating the formation of the tetraacid. After the hydrolysis was complete, the reaction mixture was cooled to room temperature to produce more precipitates. By filtration the white solid was collected. Concentration of the filtrate afforded more product. After drying in air, diphenylprehnitic acid was obtained as white powders: 76.4 g (93.7%).

Scheme 1. Synthesis of Diphenylprehnitic Dianhydride (1)



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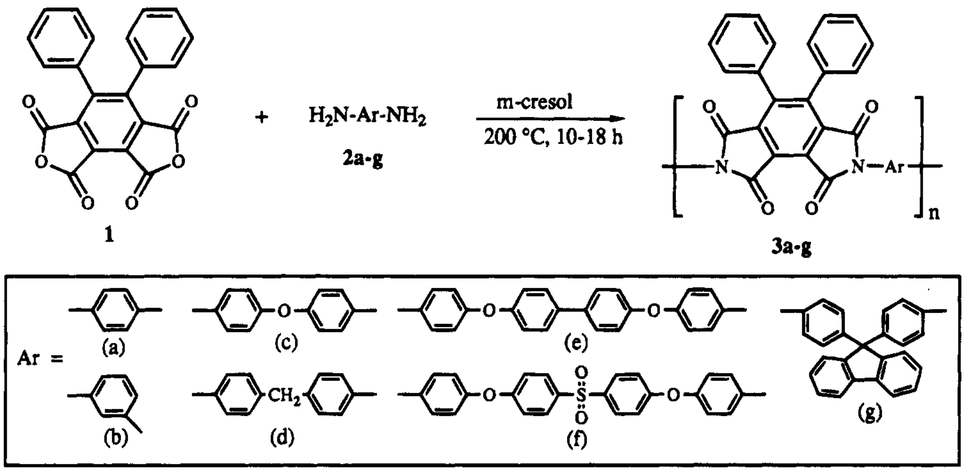
Diphenylprehnitic Dianhydride (1). A 250-mL round-bottomed flask containing the crude tetraacid (63.8 g) was placed in an aluminum heating block preheated at 320 °C. After the tetraacid completely melted, the melt was kept under vacuum (water pump) at the melting temperature for 1 h. The product in the flask was cooled to room temperature and recrystallized from chlorobenzene (100 mL). The yellowish dianhydride was dried under high vacuum at 210 °C for 2 days and stored in a desiccator over P_2O_5. The yield was 49.8 g (84.3%); mp 255–256 °C.

Polymerization. A typical procedure for the preparation of polyimide **3a** is as follows: To a 100-mL three-neck, round-bottomed flask were added dianhydride **1** (1.4813 g, 4.000 mmol), freshly sublimed *p*-phenylenediamine (**2a**) (0.4326 g, 4.000 mmol), *m*-cresol (48 mL), and isoquinoline (10 drops). The reaction mixture was heated up to 90 °C and held at this temperature for 2 h, and then the temperature was elevated to 220 °C (oil bath temperature) under nitrogen. The reaction continued for 18 h, and during this period of time about 10 mL of *m*-cresol was distilled off. The reaction solution was cooled to about 100 °C. The polymer was precipitated into methanol (400 mL) and collected by filtration. The yellowish polymer was further washed with methanol using a Soxhlet extractor overnight. After drying under high vacuum at 150–200 °C, polyimide **3a** was obtained as yellow powders: 1.53 g (86%).

End-Capped Polymer 4. In a 100-mL, three-neck, round-bottomed flask were added dianhydride **1** (1.9000 g, 5.1307 mmol), freshly sublimed *m*-phenylenediamine (**2b**) (0.5493 g, 5.0799 mmol), 3,5-di-*tert*-butylaniline (0.0209 g, 0.1016 mmol), *m*-cresol (19 mL), and isoquinoline (5 drops). The reaction mixture was heated up to 220 °C under nitrogen and held at this temperature for 24 h. During the course of the reaction, 10 mL of *m*-cresol was distilled off. The viscous solution was cooled to room temperature and diluted with chloroform (10 mL). The polymer was then precipitated into methanol (400 mL) and collected by filtration. After washing with methanol and drying in air, the polymer was redissolved in chloroform (120 mL), to which methanol (about 40 mL) was added to precipitate the polymer. The gummy precipitate was dissolved in chloroform (20 mL) and precipitated into methanol (200 mL). After filtration and drying under high vacuum at room temperature overnight, polymer **4** was obtained as yellow powders: 1.55 g (69%); $[\eta]$ = 0.36 dL/g (NMP, 30 °C); M_n = 35 000 (by NMR); M_n = 9780, M_w/M_n = 1.80 (by GPC).

Scheme 2. Synthesis of Polyimides 3



Results and Discussion

The modified synthesis of the dianhydride monomer **1** and polycondensations with a series of diamines **2a**−**g** are shown in Schemes 1 and 2.

Monomer Synthesis. The key compound for the synthesis of dianhydride **1** is bright-orange-colored 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone (cyclone)[8] as a starting material shown in Scheme 1. Being easily prepared by aldol condensation of inexpensive benzil and ethyl 1,3-acetonedicarboxylate, the cyclone can readily undergo Diels−Alder reaction with many dienophiles such as diethyl acetylenedicarboxylate and maleic anhydride. When reacting with diethyl acetylenedicarboxylate, it produces the tetraester derivative of monomer **1** in high yield. Although the hydrolysis can be done using either a base or an acid, it has been found that the acid hydrolysis with 48% HBr in acetic acid at reflux offers some advantages over the base hydrolysis (e.g., KOH in boiling ethylene glycol), such as a cleaner product, simple workup, and better control of the reaction. Consequently, the formation and purification of dianhydride **1** have also been simplified. The dehydration was accomplished by melting diphenylprehnitic acid under vacuum, and the resulting dianhydride was then simply recrystallized from chlorobenzene. The monomer obtained as such is in high purity and can be stored in a dry container over months without any deterioration.

The structure of dianhydride **1** was confirmed by spectroscopic means (IR, NMR, MS).[7] Its structural features have been further detailed by a single-crystal X-ray diffraction analysis (Figure 1). The crystal structure shows that the tricyclic part of benzenetetracarboxylic dianhydride is almost flat. Dihedral angles (62.5° and 69.6°) between pendant phenyl rings and the central benzene core are relatively larger than that (49.8°) between two phenyls, revealing that three benzene rings are highly twisted. The bulky phenyl groups push two carbonyls at the 1,4-positions away, causing a slight distortion of phthalic anhydride rings. The length of the C(7)−C(8) bond (1.495 Å) is slightly longer than that of the C(9)−C(10) bond (1.481 Å), indicating that carbonyls at the 2,3-positions of **1** should be slightly more reactive than the other two at the 1,4-positions without considering a steric hindrance caused by two phenyl rings. The bond angles of C(3)−C(10)−C(9) and C(10)−C(7)−C(8) are 133.4 and 108.0 Å, respectively, both about 12−13° off from 120°, which suggests that the bent angle between two imide groups is about 122°.

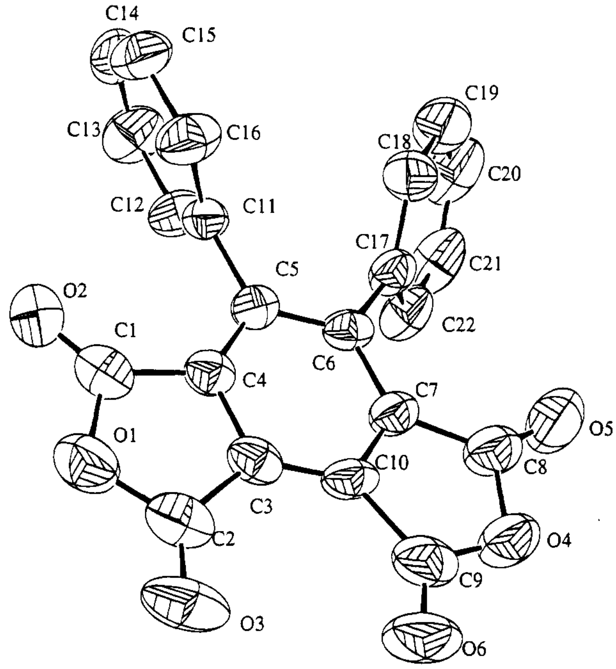


Figure 1. X-ray crystal structure of dianhydride **1** (hydrogens are omitted for clarity).

Polymer Synthesis and Solubility. Polyimides derived from rigid dianhydrides without a flexible bridging unit such as PMDA are practically insoluble and have to be applied as poly(amic acid) solutions in amide-type solvents which are subsequently cured at elevated temperatures to effect imidization. This process only allows the polyimide for uses as thin films or coatings and also may induce significant stress in films. On the other hand, one-step solution polymerization is more desirable, since polyimides in bulk can be produced. Therefore, good solubility in common polymerization solvents like NMP, DMAc, and *m*-cresol is a prerequisite. Since our preliminary results showed that a soluble polyimide could be produced even with the rigid *p*-phenylenediamine,[7a] it is felt that this dianhydride can impart solubility to polyimides derived from many known diamines. Thus, one-step polymerizations with various aromatic diamines **2a**−**g** were best carried out in *m*-cresol in the presence of a catalytic amount of isoquinoline at 200 °C (Scheme 2). The water formed from imidization was removed, together with a small amount of *m*-cresol, with a stream of nitrogen. Depending on the diamine used, the solution concentration

Table 1. Solubilities of Polymers 3a–g[a]

polymer 3	$CHCl_3$	TCE	DMF	DMSO	DMAc	NMP	m-cresol	THF	pyridine
a	−	+	+	+	+	+	+	−	+
b	+	+	+	+	+	+	+	+	+
c	−	+	+	+	+	+	+	−	+
d	±	+	+	+	+	+	+	−	+
e	−	−	−	−	−	−	±	−	−
f	±	+	+	+	+	+	+	−	+
g	−	+	+	+	+	+	+	−	+

[a] Measured at room temperature. Key: +, fully soluble; ±, partially soluble; −, insoluble.

Table 2. Characterization of Polymers 3a–g

3	[η],[a] dL/g	T_g,[c] °C DSC	T_g,[c] °C TMA	TGA,[e] °C N_2	TGA,[e] °C air	E',[f] GPa	film[g]
a	0.95	N/O[d]	443	560	487	3.14	clear, tough, flexible
b	0.50	440	424	553	523	2.07	clear, tough, flexible
c	1.01	N/O	402	514	591	3.94	clear, tough, flexible
d	1.81	421	395	507	449	2.85	clear, tough, flexible
e	0.95[b]	362		483	480		brittle
f	0.77	372	340	529	489	3.14	clear, tough, flexible
g	0.45	N/O		554	516		clear, flexible

[a] Intrinsic viscosity measured in NMP at 30 °C. [b] In o-chlorophenol at 30 °C. [c] Obtained from DSC at a heating rate of 10 °C/min and TMA at a heating rate of 3 °C/min. [d] N/O: Not observed. [e] 5% weight loss at a heating rate of 10 °C/min. [f] Young's modulus measured from TMA. [g] Cast from a TCE or m-cresol solution; films cast from 3e and 3g were not tough enough for TMA measurement.

varies from 5% to 18%. With rigid or/and linear diamines like *p*-phenylenediamine and 4,4′-oxydianiline, the polymerization concentration must be kept low in order to prevent the gel formation. For flexible or bent diamines, especially for *m*-phenylenediamine, the solution concentration should be maintained as high as possible to suppress the formation of cyclic oligomers. Although dianhydride **1** is less reactive than PMDA by comparing the chemical shifts of their carbonyl carbons,[9] high molecular weight polyimides could be readily obtained with aromatic diamines in about 18 h, except for less reactive diamines such as 4,4′-diaminophenyl sulfone.

In comparison, polyimides **3** have much improved solubilities than poly(aryl pyromellitimide)s. Except for **3e**, they are readily soluble in many common organic solvents at ambient temperatures such as TCE, *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), and *N,N*-dimethylformamide (DMF), *m*-cresol, and even pyridine (Table 1). Polyimide **3b** is exceptionally soluble in chloroform and tetrahydrofuran (THF), presumably owing to the zigzag shape of its backbone. It should be noted that great solubility in certain organic solvents (e.g., THF, DMF, and DMSO) that are miscible with water enables these polyimides to be fabricated easily as asymmetric membranes. Furthermore, the rodlike polyimide **3a** derived from *p*-phenylenediamine is remarkably soluble at ambient temperatures and can be readily produced in high molecular weight via a one-step polymerization process without precipitation and gelation. In contrast, polyimides derived from PMDA or substituted PMDAs and *p*-phenylenediamine could not be prepared by one-step solution polymerization and displayed limited solubility in common organic solvents. Evidently, the significant improvement in solubility for poly(aryl prehnitimide)s **3** is attributed to the unique bent diimide and twisted pendant phenyl groups. Although being soluble in *m*-cresol during polymerization, polymer **3e** could not be redissolved completely in the same solvent.

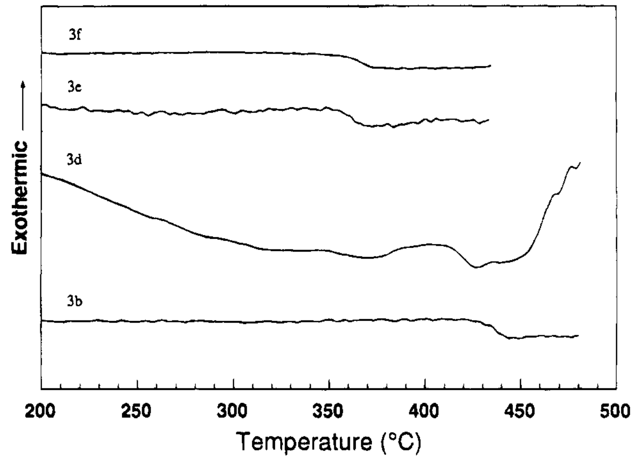
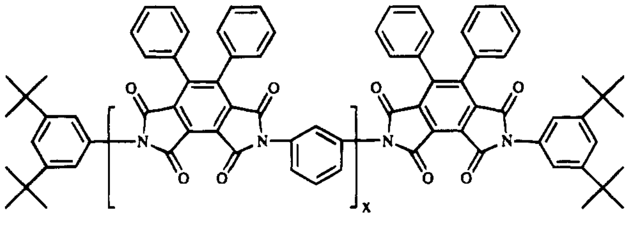


Figure 2. DSC thermograms of polyimides **3b,d,e,f**.

Intrinsic viscosities of all polyimides **3** ranged from 0.45 to 1.81 dL/g (Table 2), which are relatively lower than those of rigid-rod polyimides that usually have intrinsic viscosities above 2.0 dL/g. But the formation of transparent, creasable films from polymers **3a–f** indicates that these polyimides have reasonably high molecular weights and some degree of toughness. Polyimides **3** appear to have relatively low solution viscosities and low molecular weights by GPC relative to polystyrenes, due to the bent diimide structure. For example, polymers **3b** ([η] = 0.50 dL/g) and **3f** ([η] = 0.77 dL/g) had number-average molecular weights of 21 700 and 51 000, respectively. In order to correlate the apparent molecular weight to solution viscosity for this type of polyimide, the relations between absolute molecular weight and apparent molecular weight by GPC and solution viscosity need to be established. Thus, the end-capping polymerization was performed for polyimide **3b**. A small amount of 3,5-di-*tert*-butylaniline was used in the polycondensation of dianhydride **1** and diamine **2b**. The resulting polymer **4** was fractionated to exclude any linear or cyclic oligomers. It is surprisingly labile to acid and heat during isolation and purification. This end-capped polyimide had an intrinsic viscosity of 0.36 dL/g (NMP, 30 °C) and an absolute number-average molecular weight of 35 000 determined by NMR analysis. In comparison, the apparent number-average molecular weight measured by GPC relative to polystyrenes was only about 9780, much lower than the actual one. Therefore, these poly(aryl prehnitimide)s synthesized should have higher molecular weights than those determined by GPC.



end-capped polyimide **4**.

Thermal Properties. The synthesized polyimides were investigated with respect to their thermal properties by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The glass transition temperatures (T_gs) of polymers **3** obtained from DSC and thermomechanical analysis (TMA) are summarized

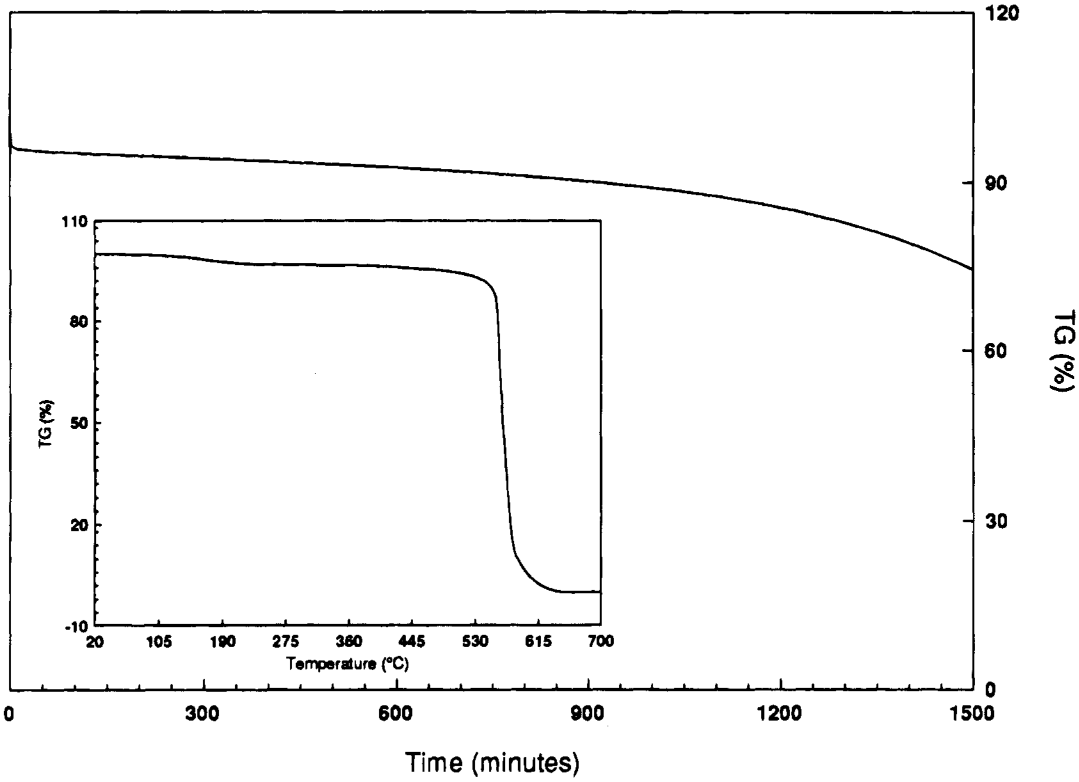


Figure 3. Isothermal aging and TGA thermograms of polyimide **3b** (in air).

in Table 2. In general, with increasing chain stiffness the detection of glass transitions by DSC becomes more difficult. Polyimides **3b,d,e,f** showed distinct high T_gs ranging from 362 to 440 °C (Figure 2). The T_gs of polyimides **3a,c,g** were not detectable by DSC. Similarly, the T_gs of poly(aryl pyromellitimide)s were also reported to be ill-defined and difficult to detect.[4a] The rigid structure of the prehnitimide and two pendant phenyl groups are responsible for high T_g values. The T_gs of polyimides **3** were also determined from the E'' values obtained from TMA in stress–strain mode. Except for polyimides **3e** and **3g** that could not form tough films for TMA measurement, these polyimides had T_gs (E'') ranging from 340 to 443 °C. As expected, the highest T_g was obtained for the most rigid polyimide **3a**. The most flexible polyimide **3f** has the lowest T_g at 340 °C. Increasing the chain stiffness or decreasing the number of bridging bonds in the diamines used shifts the T_g to higher values, as seen for polymers **3e** (362 °C) and **3c** (402 °C). Ultimately, polyimides **3a** and **3b**, derived from rodlike phenylenediamines, have T_gs over 440 °C.

Like many aromatic polyimides and poly(aryl pyromellitimide)s, all poly(aryl prehnitimide)s displayed excellent thermal stabilities. The onset temperatures for 5% weight loss in nitrogen were in the range of 483–560 °C, as assessed by TGA (Table 2). In air these temperatures were lower, in the range of 449–523 °C. Excellent thermostability of the rigid-rod-like polyimide **3a** was particular noteworthy, for its 5% weight loss at 560 °C in nitrogen. It should be mentioned that, since these polyimides are not end-capped and have different molecular weights, their molecular weights and the nature of the end group should have a direct impact on thermal and thermooxidative stabilities. As shown in Figure 3, the degradation for the uncapped polyimide **3b** began at about 485 °C in air and catastrophic decomposition appeared at about 555 °C. When being heated in air at 400 °C, this polymer lost 10% of its weight in about 14 h with a degradation rate of 0.0705 mg/h and then decomposed more rapidly at the rate of 0.196 mg/h.

The solvent-cast films for polymers **3a–f** were clear, flexible, and tough, except for polymers **3e,g**. Young's moduli of these nonoriented, amorphous films were measured using TMA in tensile stress–strain mode. Loads were chosen such that a linear stress–strain relationship was obtained. Young's moduli (E') measured for polymers **3a–f** ranged from 2.07 to 3.94 GPa (Table 2). High E' values (>3.0 GPa) were observed for polymers **3a, 3c,** and **3f**. Polymer **3b** has a relatively low Young's modulus (2.07 GPa), probably due to its zigzag-like structure. In comparison, these poly(aryl prehnitimide)s appear to have better tensile moduli than poly(4,4′-oxydiphenylene pyromellitimide); the tensile modulus of the latter nonoriented thin film has been reported to be 2.1 GPa.[4a,10] It should, however, also be noted that different casting and TMA experiment conditions can sway the TMA data.

Conclusions

A series of high molecular weight, soluble polyimides have been synthesized from novel diphenylprehnitic dianhydride. Polyimides with a bend caused by the prehnitimide structure have greatly improved solubility in common organic solvents. All polyimides synthesized have very high glass transition temperatures, excellent thermal stabilities, and good mechanical properties. These thermal and thermomechanical properties, along with exceptionally good solubility in water-miscible solvents such as THF, DMF, and DMSO, make some of these polyimides potentially excellent candidates for uses as asymmetric membranes in high-temperature separation. Future work is in progress on the syntheses of copolymers utilizing dianhydride **1** and commercially available dianhydrides.

Acknowledgment. The authors greatly appreciate the support of this research by the Natural Sciences and Engineering Research Council of Canada and Carleton University.

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MA946076V