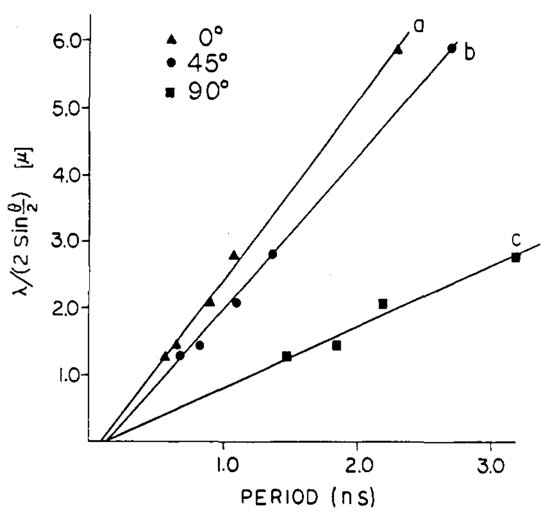

Figure 4. Plot of ($\lambda/2 \sin \theta/2$) in units of micrometers versus the observed acoustic modulation period for various angles.

the mechanical properties of oriented polymer films.

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Registry No. PBO, 60871-72-9.

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Notes

Copolyimidines. 2. Copoly(imidine–imides) from 3,5-Dibenzylidenepyromellitide, 4,4'-Diaminodiphenyl Ether, and Various Dianhydrides

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Introduction

Processable, high-termperature polymers are still very desirable materials, especially in the aerospace and electronic industries. Applications of these polymers both as neat resins and as matrix resins for composite materials are numerous. A review of properties and syntheses of high-temperature polymers has been reported.[1]

Polyimides are a well-known class of thermally stable polymers which show excellent mechanical and electrical properties over a wide temperature range, as well as good chemical resistance.[2] However, applications of polyimides are occasionally limited due to their poor solubility and molding properties.

Polyimidines constitute a relatively new class of polymers which were designed to have improved processability while retaining desirable physical and chemical properties.[3-16] These polymers are structurally similar to polyimides but possess bulky, pendant groups on the backbone which greatly enhance solubility. One inherent drawback to polyimidines has been low molecular weight and therefore an inability to form good films or fibers. In a previous paper,[17] we reported a new class of thermally stable polymers, namely copoly(imidine–imides), which was designed to have superior properties over either homopolymer. These copolymers were prepared by the sequential condensation of 3,5-dibenzylidenepyromellitide, *m*-xylylene-diamine, and various dianhydrides. The resulting copolymers were soluble in polar aprotic solvents and possessed sufficient molecular weight which allowed solution casting of tough films with moderate mechanical properties. Their thermal stabilities ranged from 410 to 475 °C by TGA.

This paper reports the synthesis and properties of copoly(imidine–imides) which do not contain any aliphatic linkages in the polymer backbone. In contrast to polymers with benzylene groups in the backbone, a wholly aromatic system affords a more rigid structure and should show improved thermal stability and mechanical properties.

Results and Discussion

Synthesis of Copoly(imidine–imides). A series of three copoly(imidine–imides) was prepared from the co-

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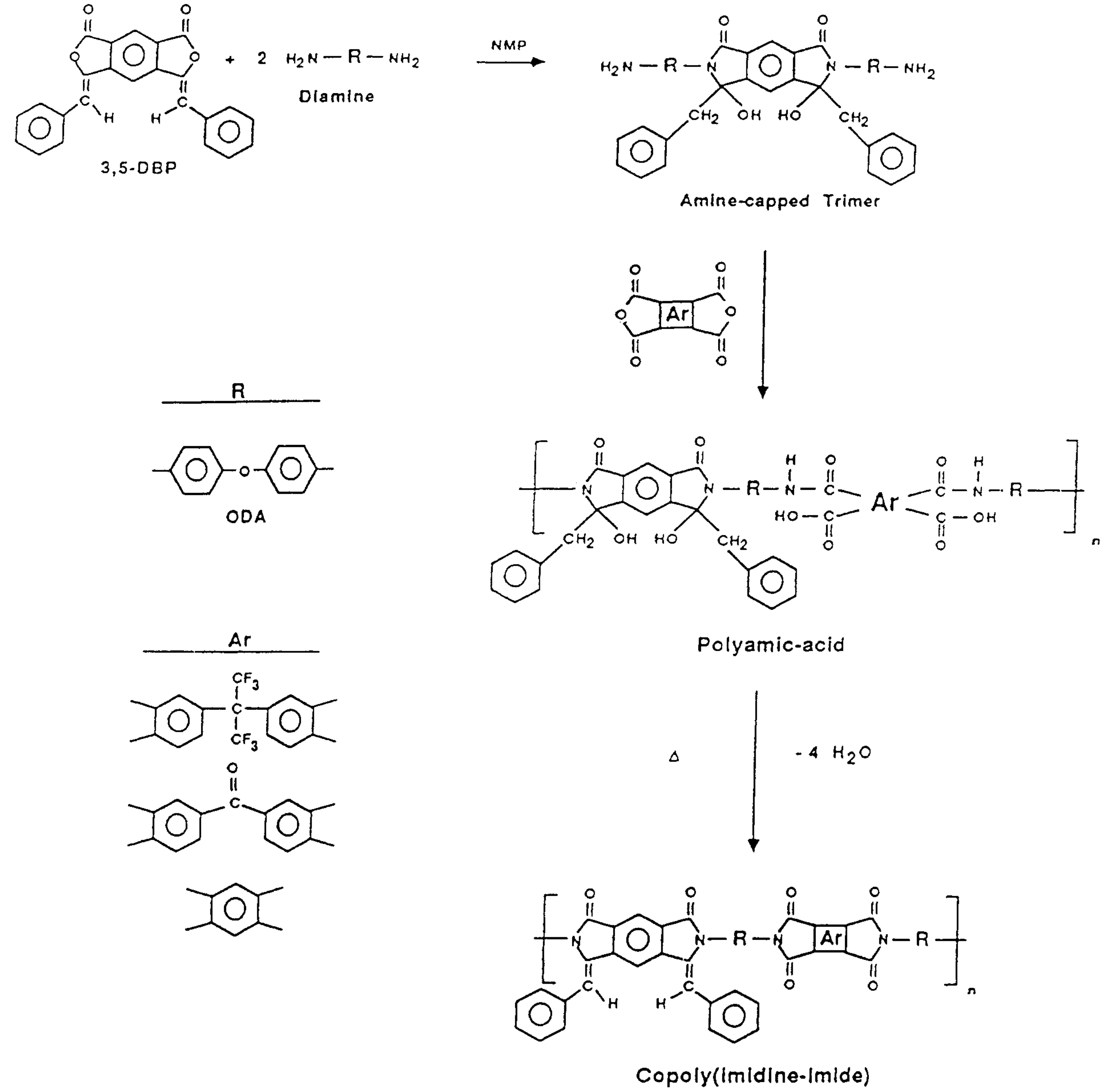

Figure 1. General reaction scheme for synthesis of copoly(imidine–imides).

polymerization of 3,5-dibenzylidenepyromellitide (3,5-DBP), 4,4′-diaminodiphenyl ether (ODA), and the following dianhydrides: pyromellitic dianhydride (PMDA) (for copolymer 1), 4,4′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis[1,3-isobenzofurandione] (6FDA) (for copolymer 2), and benzophenonetetracarboxylic dianhydride (BTDA) (for copolymer 3). First, the amine-terminated, imidine trimer was formed by the slow addition of 3,5-DBP to twice the molar amount of ODA, which was dissolved in a polar, aprotic solvent such as *N*-methylpyrrolidone (NMP) or *N*,*N*-dimethylacetamide (DMAc). The mixture was heated at ca. 130 °C for 20–72 h under an inert atmosphere in an attempt to achieve a complete reaction. Thin-layer chromatography was used to monitor the progress of this reaction (Figure 1). The second step was a polycondensation reaction between the trimer and dianhydride to afford hydrated polyamic acids, precursors to copoly(imidine–imides). After allowing the dark brown trimer solution to cool to room temperature, approximately 90% of the dianhydride was added as a solid in small portions. During this time, a significant increase in viscosity was observed. The remaining monomer was added ca. 2% at a time and each portion allowed to react for about 1 h. After 100% of the monomer was added, a 2–4% excess of dianhydride was added to end-cap the polymer.

Table I
Properties of Cured Copoly(imidine–imides)

copolymer	Tg,[a] °C	TGA,[b] °C	viscosity, dL/g
1		560	0.44[c]
2		560	0.88[d]
3	210	510	0.41[e]

[a] Determined by DSC at a heating rate of 10 °C/min. [b] Temperature of a 10% weight loss by TGA in nitrogen atmosphere. Heating rate of 20 °C/min. [c] 0.15 g/dL in *m*-cresol at 24.0 °C. [d] 0.07 g/dL in NMP at 24.6 °C. [e] 0.25 g/dL in *m*-cresol at 24.3 °C.

Conversion of the hydrated polyamic acids to the corresponding copoly(imidine–imides) was effected by thermal dehydration of a powder sample or by curing films cast from polymer solutions [Table I lists properties of cured copoly(imidine–imides)]. Heating or curing temperatures were maintained below 250 °C to prevent a cross-linking reaction of the exocyclic carbon–carbon double bond. The cured copolymers were less soluble and rather yellow compared to the corresponding precursors.

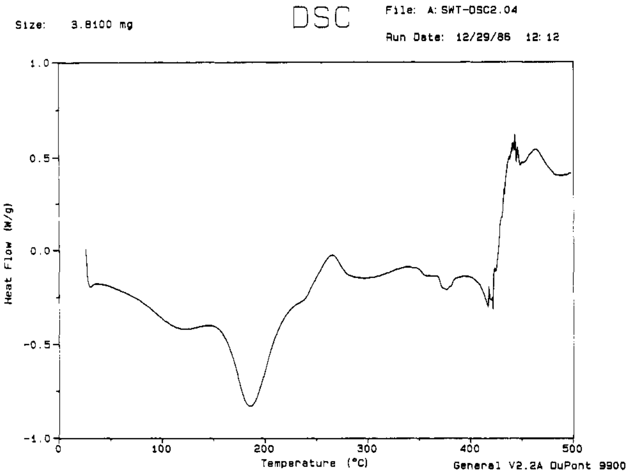

Figure 2. DSC curve of hydrated polyamic acid precursor to 1 from PMDA. Determined at a heating rate of 10 °C/min in nitrogen atmosphere.

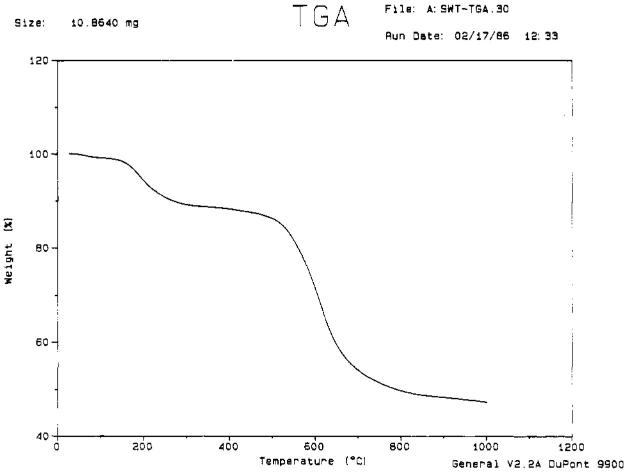

Figure 3. TGA curve of hydrated polyamic acid precursor to 1 from PMDA. Determined at a heating rate of 20 °C/min in nitrogen atmosphere.

Characterization of Polyamic Acids and Corresponding Copoly(imidine–imides). The polyamic acid precursor to copolymer 1 was pale yellow and soluble in polar, aprotic solvents, from which tough, transparent gray films could be cast. An infrared spectrum of the polymer showed strong absorptions in the carbonyl region near 1700 cm^{-1}, characteristic of an open-chain amide and lactam stretching vibrations. Broad and intense absorptions occur around 3300 cm^{-1} due to O–H and N–H stretching.

A differential scanning calorimetry (DSC) curve showed a broad endotherm centered near 125 °C which corresponds to loss of volatiles (solvent and adsorbed moisture) (Figure 2). An intense endotherm due to dehydration of the hydroxylactam function and cyclodehydration to the imide was observed near 190 °C. This scan also showed a marked exotherm near 265 °C, which is attributed to cross-linking of the exocyclic double bond at the benzylidene function.[15]

Thermogravimetric analysis (TGA) showed a 10% weight loss from 100 to 200 °C due to the evaporation of residual solvent and the loss of water of dehydration (Figure 3). The thermal stability of this copolymer, defined as the temperature of a 10% weight loss (after dehydration), is 560 °C.

The cured copoly(imidine–imide) 1 was a dark yellow powder and soluble in *m*-cresol and *o*-chlorophenol, from which tough, transparent films could be cast. An infrared spectrum of the copolymer showed strong absorptions near 1615 cm^{-1}, characteristic of a benzylidene carbon–carbon double bond stretch, and near 1780 cm^{-1}, due to the imide and imidine carbonyl. Elemental analysis gave results that were in good agreement with those expected for the proposed structure.

Table II
Mechanical Properties of Copoly(imidine–imides) and Other Polyimides[a]

polymer	tensile strength, psi	tensile modulus, psi	elongation, %
2	9600	640000	1.5
3	14000	450000	3.0
2b[b]	9400	134300	7
PMDA-ODA[20]	25000	440000	
BTDA-ODA[19]	16500	284000	10
Hoechst 6F[20]	16000	265000	

[a] Properties at room temperature. [b] Copoly(imidine–imide) from 3,5-DBP, MXDA, and 6FDA.[17]

Further characterization of copolymers **2** and **3** by infrared spectroscopy and thermal analysis gave similar results to those obtained for the PMDA-based copoly(imidine–imide). These results are summarized in Table I. The use of a fluorinated dianhydride (6FDA) greatly enhanced solubility of copolymer **2** without sacrificing thermal stability, as indicated in previous polyimide studies which incorporated the hexafluoroisopropylidene group into the polymer backbone.[19] The use of BTDA as a comonomer was expected to increase the tractability of copolymer **3** due to the incorporation of the flexible carbonyl linkage into the copolymer backbone. However, copolymer **3** was not as thermally stable as copolymer **1** or **2**.

Recently, it was reported that a lower reaction temperature is desirable for the formation of high molecular weight polyimides.[20] This is due to the fact that the reaction between the amine and the anhydride to form a polyamic acid is both exothermic and reversible. Viscosity studies indicate that a considerable amount of degradation occurs due to this reverse reaction when these polymers are dissolved in hot polar solvents. In a similar vein, the molecular weight of these hydrated polyamic acids probably decreased during solvent–nonsolvent purification in which hot solvent was used.

Mechanical Testing. Instron tensile testing of copolymers **2** and **3** was carried out to determine thin-film mechanical properties. Test samples were 0.2–0.5 mil thick and pulled at a rate of 0.2 in./min at room temperature. Table II shows the results along with data from various polyimide studies. The results indicate moderate tensile strength, tensile modulus, and percent elongation to break relative to polyimides.

Experimental Section

3,5-DBP was prepared and purified according to a published procedure.[11] ODA and PMDA were purified by sublimation and BTDA was recrystallized from acetic anhydride. Electronic grade 6FDA was supplied by Hoechst Celanese and used without further purification. Polymerization solvents such as NMP and DMAc were spectrophotometric grade from Aldrich and used as received.

Elemental analyses were performed by Desert Analytics, Tucson, AZ, and Nippon Steel Corporation, Tokyo, Japan. IR spectra were obtained on a Perkin-Elmer Model 360 spectrometer using both KBr pellet and neat film techniques. Thermal analyses (TGA and DSC) were performed on a Du Pont 9900 Thermal Analyzer at Texas Research Institute, Austin, TX, and a Metler TA3000 Thermal Analyzer at Nippon Steel Corporation, Tokyo, Japan.

Dilute solution viscosities of polymer solutions (NMP, DMAc, or *m*-cresol) were determined at 25 °C by using a Kimax 100 and 200 Ostwald-type viscometer.

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Thin-film mechanical properties were determined by the use of an Instron Model TTD Universal Testing Instrument at Texas Research Institute, Austin, TX.

Preparation of Polyamic Acid 1 from 3,5-DBP, ODA, and PMDA. To a stirred solution of 1.01 g (5.04 mmol) of ODA in 10 mL of DMAc was added 0.962 g (2.63 mmol) of 3,5-DBP at room temperature under an atmosphere of argon. The mixture was stirred at 130 °C for 20 h to give a brown solution of amine-capped trimer. After the reaction mixture cooled to room temperature, 0.583 g (2.67 mmol) of PMDA was added over a period of 6 h. The volume of solvent was adjusted in order to maintain a concentration of ca. 10% solids by weight. After 12 h of stirring, the brown, viscous solution was poured into ca. 400 mL of rapidly stirring water, and the gray precipitate was collected by suction filtration and then washed with water and dried in a vacuum desiccator. Inherent viscosity was 0.73 dL/g (0.245 g/dL in DMAc at 22.0 °C) and the pure yield was 93%. IR (film) 1712, 1605 (C=O), 3279 cm^{-1} (N—H, O—H). Anal. Calcd.: C, 70.70; H, 4.10; N, 5.70. Found: C, 68.32; H, 4.25; N, 5.87.

Preparation of Polyamic Acid 2 from 3,5-DBP, ODA, and 6FDA. A similar procedure to the one described above was followed except 1.05 g (5.24 mmol) of ODA, 0.962 g (2.63 mmol) of 3,5-DBP, and 1.25 g (2.81 mmol) of 6FDA were added to the reaction flask. The pure yield was 3.16 g (97%) of a gray precipitate. Inherent viscosity was 0.96 dL/g (0.264 g/dL in DMAc at 25.3 °C). IR (film) 1700, 1600 (C=O), 3275 cm^{-1} (O—H, N—H); Anal. Calcd.; C, 66.45; H, 3.66; N, 4.63; F, 9.41. Found: C, 64.87; H, 3.41; N, 4.72; F, 8.59.

Preparation of Polyamic Acid 3 from 3,5-DBP, ODA, and BTDA. A similar procedure to the one described above was followed except 1.62 g (8.10 mmol) of ODA, 1.47 g (4.01 mmol) of 3,5-DBP, and 1.33 g (4.13 mmol) of BTDA were added to the reaction flask. An ice bath was used prior to addition of the dianhydride in order to maintain a low temperature during the initial stages of the polymerization. The reaction proceeded readily under the previously stated conditions to give a high yield (97%) of a tan powder. Inherent viscosity was 0.71 dL/g (0.250 g/dL in NMP at 25.3 °C). IR (film) 1708, 1601 (C=O), 3268 cm^{-1} (N—H, O—H).

Thermal Cyclodehydration of Polyamic Acids to Corresponding Copoly(imidine–imides). Copolymer **1** was obtained by heating polyamic acid 1 in the Abderhalden drying apparatus using 1,2,4-trichlorobenzene (bp 214 °C) under vacuum for 68 h to complete dehydration and cyclization. The dehydrated samples were used for elemental and thermal analyses. The yellow product was soluble in *m*-cresol and *o*-chlorophenol. Anal. Calcd.: C, 76.31; H, 3.53; N, 6.14. Found: C, 74.32; H, 3.37; N, 6.29. Copolymer **2** was obtained in the same manner from polyamic acid 2 and was also soluble in *m*-cresol and *o*-chlorophenol. Anal. Calcd.: C, 70.65; H, 3.18; N, 4.92; F, 10.0. Found: C, 69.55; H, 3.07; N, 4.79; F, 9.97. Copolymer **3** was obtained by heating polyamic acid 3 at 200 °C under vacuum for 36 h to complete curing. Anal. Calcd.: C, 76.76; H, 3.57; H, 5.51. Found: C, 75.19; H, 3.62; N, 5.45.

Film Casting. An appropriate amount of the polyamic acid sample was dissolved in DMAc or NMP so that the solution was about 10–15% solids by weight. This polymer solution (dope) was used for film casting and subsequent imidization. The dope was pipeted onto a clean, dry glass plate and spread evenly using a disposable pipet or a doctor knife. The plate was then placed in an oven at 80 °C under a positive flow of argon for several hours. After the initial drying, the temperature was increased to 200 °C and the sample was heated under vacuum for 16 h. Upon cooling, the copolymer film was removed from the glass plate by soaking in distilled water.

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Registry No. 1, 117162-50-2; 2, 117162-51-3; 3, 117162-52-4.

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Long-Range Inhomogeneities in Sulfonated Polystyrene Ionomers

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Small-angle X-ray scattering (SAX) has been used extensively for morphological studies of ionomers.[1] Their scattering profiles generally exhibits a broad, so-called "ionic peak" and an "upturn" at very small scattering an-

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