Copolyimidines. 1. Copolyimides from 3,5-Dibenzylidenepyromellitide, α,α'-*m*-Xylylenediamine, and Anhydrides

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ABSTRACT: This paper reports a new class of thermally stable condensation polymers, namely copoly(imidine–imides). Three amorphous, film-forming polymers were derived from the polycondensation of 3,5-dibenzylidenepyromellitide, *m*-xylylenediamine, and the following dianhydrides: pyromellitic dianhydride, 5,5′-(1,1,1,3,3,3-hexafluoro-2-propylidene)bis(5,5′-isobenzofuran-1,3-dione) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride. Solution polymerizations were carried out in *N*-methyl-2-pyrrolidone (NMP) at room temperature via a two-step process to give the corresponding polyamic acids in high yields. Subsequent thermal imidization occurred readily and gave flexible, transparent, yellow films. The resulting polymers showed good solubility in chloroform and polar, aprotic solvents. Thermal analysis indicated thermal stability above 400 °C in an inert atmosphere by TGA. Thin-film mechanical testing of the fluorinated polymer showed moderate tensile strength, tensile modulus, and percent elongation to break relative to polyimides. Gas permeation studies indicated a relatively high selectivity factor and a low transport rate for this polymer. A model compound study is also reported.

Introduction

Advances in the aerospace and electronic industries have led to the need and, therefore, development of a new specialty area within polymer science, that of high-temperature (or thermally stable) polymers. Applications of these high-performance polymers include resins for composite matrices, structural adhesives, selectively permeable membranes, and coatings. A review of properties and syntheses of high-temperature polymers has been reported.[1] Recent research has emphasized the processability and tractability of these high-melting commercial materials.

Polyimides are a well-known class of polymers which exhibit a high degree of thermal stability, excellent radiation and chemical resistance, and good mechanical and electrical properties over a wide temperature range.[2] One inherent drawback to this system is the lack of solubility, and therefore processability, of the cured polymer. One approach to this problem has been to modify these wholly aromatic polyimides by incorporating various functional groups such as carbonyl, ether, sulfide, sulfone, isopropylidene, and perfluoroisopropylidene into the polymer backbone in order to impart some flexibility in these rigid chains.[3,4] Another approach has been to place reactive end groups on low molecular weight oligomers which are capable of undergoing thermally induced chain extension and/or cross-linking.[5] Other ways to improve solubility include a variation of the cure method and a reduction of electronic chain–chain interactions (charge transfer).

Polyimidines are a relatively new class of thermally stable polymers which have been reported by Cassidy and co-workers[6–13] and by Imai et al.[14–19] These polymers are similar in structure to polyimides but possess pendant phenyl or benzylidene groups on the polymeric backbone which greatly enhance solubility. The resulting polymers are soluble in chloroform and polar, aprotic solvents such as *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), and *N*,*N*-dimethylformamide (DMF), as well as other solvents. In addition, thermal stabilities above 500 °C have been observed in both air and nitrogen atmospheres. It was found that the pendant benzylidene groups created a more facile polymerization than did the phenyl groups and tough, transparent films could be cast from NMP solutions of the polymers with inherent viscosities of about 0.5 dL/g or above.

Recently, it has been shown that these benzylidene-pendant polyimidines underwent thermal cross-linking via the exocyclic double bond.[18,19] This addition reaction occurred above the glass transition temperature (>300 °C) and gave cured polymers with increased thermal stability. The resulting polymers showed an increase in glass transition temperatures and were almost completely insoluble in hot organic solvents. This is an attractive method of cross-linking since no volatile materials are released and the thermosetting polymers afford cured polymers which are more thermally stable.

The purpose of this paper is to introduce a new class of thermally stable polymers, namely copoly(imidine–imides). Copolymerization is an effective method used to adjust polymer properties such as modulus, flexibility, processability, cost, etc. Also, synergistic interaction of different polymer systems can impart superior properties to the copolymer over that of either homopolymer. The excellent chemical, mechanical, and electrical properties of polyimides make them attractive as comonomers for high-temperature materials. In this case, introduction of the imide with the imidine function into a backbone was used to synthesize a thermally stable system with moderate processing conditions. This paper also reports a model compound study to elucidate structures for intermediates for poly(imidine–imides).[13]

Results and Discussion

Model Studies for Poly(pyromellitimidines). Model studies for reactions leading to benzylidene-substituted poly(dithiopyromellitimidines) were carried out by the reaction of 3-benzylidene-1-thiophthalide with benzylamine. The reaction proceeded smoothly in chloroform at ambient temperatures to give an isolable intermediate. This pale-yellow precipitate at first was thought to be the intermediate, 2-phenacetyl-*N*-benzylthiobenzamide (II-S), which, along with its oxo analogue (II-O), has been reported to occur in the open-chain form.[20–22] Inspection of the ^{1}H NMR spectrum (Figure 1), however, led to the conclusion that, at least in this case, the compound isolated was the cyclic hydroxylactam, *N*-benzyl-3-hydroxy-1-thio-3-isoindole (I-S), and not the open-chain thioamide (II-S). This lactam readily dehydrated to *N*-benzyl-3-benzylidene-1-thiophthalimidine (III-S), either thermally or under the influence of strong acid catalyst (Figure 2).

A comparison of the NMR spectrum of the isolated intermediate with an estimated spectrum of the open-chain thioamide, derived from deoxybenzoin and *N*-benzylbenzamide, is shown in Table I. Key absorptions for

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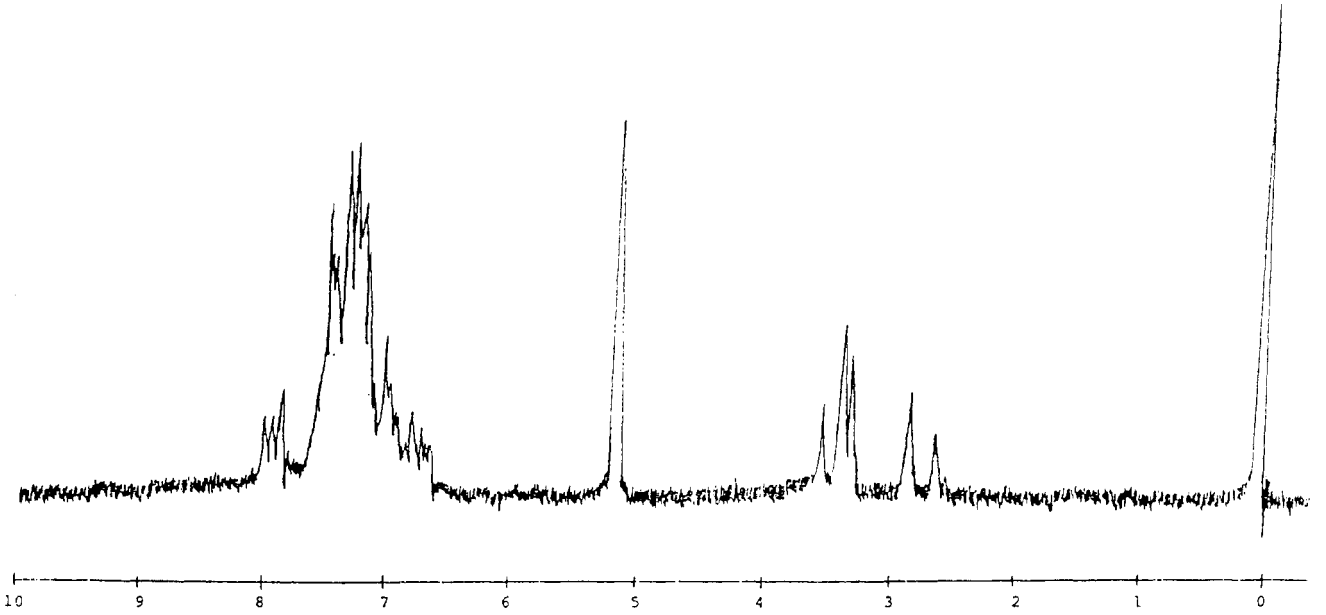


Figure 1. ^{1}H NMR spectrum of *N*-benzyl-3-hydroxy-1-thio-3-benzylisoindole (I-S).

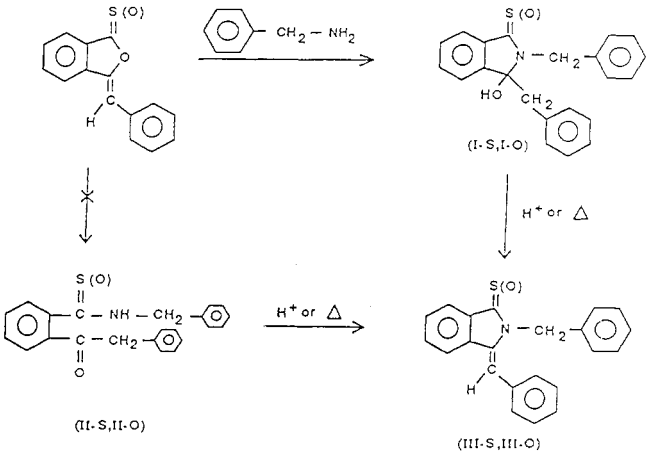
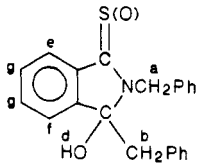


Figure 2. Synthetic pathway to N-substituted phthalimidines.

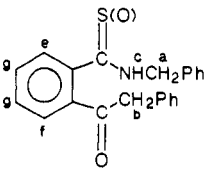
determining the structure are those due to the benzylic protons labeled "a" and "b", the amide proton labeled "c", and the hydroxyl proton labeled "d". In this case, the *N*-methylene protons of the benzyl group, a, are observed as a sharp singlet at 5.04 ppm. However, one would expect these protons in the open-chain compound to absorb at somewhat higher field and to be split into a doublet by the amide proton, c, as seen with *N*-benzylbenzamide.[23,24] In addition, the amide proton in the latter gives a broad multiplet at 8.8 ppm. In the case of the isolated intermediate, no absorption due to an amide proton could be detected. Perhaps even more crucial are the absorptions due to the methylene protons, b. In the hydroxylactam, these protons neighbor a chiral center and are thus diastereotopic. They are observed as a set of doublets at 2.69 and 3.33 ppm with a coupling constant of J = 14 Hz. The open-chain amide would be expected to show a sharp singlet at a considerably lower field.

The infrared spectrum of the isolated intermediate also gives valuable evidence to confirm the identity of the hydroxylactam. A very strong and broad absorption centered at 3300 cm^{-1} is attributed to the hydroxyl proton, and not an amide proton. The NMR signal for this proton was observed as a sharp singlet at 3.24 ppm and shifted with a change in concentration due to the amount of hydrogen bonding with the solvent. Furthermore, two absorptions

Table I
NMR Comparison of Intermediates[a] (H, ppm)



I-S: 1-thio-3-hydroxy-3-benzyl-3*H*-isoindole
I-O: 3-hydroxy-3-benzyl-3*H*-isoindol-1-one



II-S: 2-phenylacetyl-*N*-benzylthiobenzamine
II-O: 2-phenylacetyl-*N*-benzylbenzamide

	I-S	I-O	II-S[b]	II-O[b]
a	5.04 (s, 2 H)	4.50 (d, 2 H)	4.5 (d, 2 H)	4.5 (d, 2 H)
b, b′	"AB"	"AB"		
	2.69 (d, 1 H)	2.77 (d, 1 H)	4.2 (s, 2 H)	4.2 (s, 2 H)
	3.33 (d, 1 H)	3.33 (d, 1 H)		
	J = 14 Hz	J = 14 Hz		
c			8.8–9 (br m, 1 H)	8.8–9 (br m, 1 H)
d	3.24 (s, 1 H)	3.90 (s, 1 H)		
e	7.85 (m, 1 H)		7.9–8 (m, 1 H)	7.80 (m, 1 H)
f			8.0–8.1 (m, 1 H)	7.90 (m, 1 H)
g	6.6–7.6 (13 H) (f–h)	6.7–7.7 (14 H) (e–h)		
h			7.2–7.6 (12 H) (g, h)	7.2–7.6 (12 H) (g, h)

[a] Spectra were obtained using deuteriochloroform as the solvent and tetramethylsilane as the internal standard. [b] NMR spectra of the open-chain compounds are estimated using known spectra of deoxybenzoin, *N*-benzylbenzamide, and known sulfur compounds.

were observed for C=S at 1440 and 1410 cm^{-1}, with no trace of a carbonyl stretch. These data are sufficient to conclude that the isolated intermediate was the hydroxylactam (I-S) and not the open-chain amide (II-S).

The unexpected isolation of the hydroxylactam (I-S) described above raised some uncertainty about the inter-

mediate obtained from the reaction of 3-benzylidenephthalide and benzylamine. Identification of the open-chain 2-phenacetyl-*N*-benzylbenzamide (II-O) seems to rest on the assignment of infrared absorptions.[20,25] The absorptions near 1680 and 3240 cm^{-1} are attributed to amide C=O and N—H stretching, realizing that the latter is also a region for O—H stretching. However, no NMR data have been reported to date.

Reactions between 3-benzylidenephthalide and benzylamine were carried out in a variety of solvents including benzene, chloroform, and NMP. In each case, a white precipitate could be isolated and recrystallized from ethanol. The NMR data for the intermediate isolated from benzene (I-O) are given in Table I. It is obvious that the data compare quite well with the results from the sulfur analogue (I-S) and do not resemble those expected for the open-chain amide.

The infrared spectrum for this compound showed strong absorptions near 1680 cm^{-1}, due to the carbonyl, and near 3300 cm^{-1}, due to a hydroxyl proton and not a secondary amide. While infrared data are inconclusive for determining the structure, NMR data are consistent with a hydroxylactam and give no evidence of the open-chain amide reported by earlier workers.

In order to determine relative rates of these reactions and to check the possibility of an open-chain species forming in solution, the reactions were carried out in deuteriochloroform and monitored directly by NMR. In the case of the thio analogue, the spectrum of the hydroxylactam (I-S) was fully developed in less than 5 min, and no absorptions could be attributed to an open-chain compound or leftover starting materials. In the case of the oxo analogue, only a trace of reaction was observed after 1 h, and the reaction was complete between 12 and 24 h. Dehydration of the hydroxylactams to the corresponding phthalimidines was effected by the addition of 1 drop of concentrated hydrochloric acid and occurred readily in both cases.

A study of differential scanning calorimetry (DSC) of the hydroxylactams showed that these compounds undergo thermally induced dehydration at or above the melting points to give the corresponding phthalimidines. Therefore, thermal dehydration was carried out by heating the solid samples at 180 °C for time periods varying from 15 min to 1 h. NMR analysis of the products showed that the thio analogue dehydrates readily in 15 min. The dehydration of the oxo analogue was much slower and only about 60% complete after 2 h.

From these studies, it was concluded that 1-thio-3-benzylidenephthalide reacts rapidly and in good yields with benzylamine to give the corresponding thiophthalimidine compounds and reactions which serve as models for a new type of polyimidine backbone. The reaction proceeds through an hydroxylactam which dehydrates thermally or under the influence of strong acid catalyst. Other amines such as *N*-hexylamine and aniline were observed to react similarly, and this also provides a basis for future research into similar polymer backbones. A brief reinvestigation of the oxo analogue showed this reaction also proceeds through a hydroxylactam intermediate, although the rate is much slower.

Synthesis of Polyamic Acid 1 Based on PMDA and Subsequent Conversion to Copoly(imidine–imide). Initial polymerizations were performed with pyromellitic dianhydride (PMDA) as a comonomer and NMP as the reaction solvent since both of these materials have been used extensively in polyimide studies. First, the amine-terminated, imidine trimer was formed by the slow addition of 3,5-dibenzylidenepyromellitide (3,5-DBP) to twice the molar amount of *m*-xylylenediamine (MXDA) which was dissolved in NMP. Since an ideal stoichiometric balance of monomers is crucial in obtaining high molecular weight condensation polymers, the success of this first reaction must be very high. After the 3,5-DBP and MXDA were allowed to react overnight, an aliquot was removed and subjected to gas chromatography. No detectable peak was observed for MXDA, which indicates the trimer reaction must go to near completion under these conditions. Next, approximaely 90% of the PMDA was added to the tan trimer solution in small portions, allowing each to dissolve before subsequent additions. During this time, a substantial increase in viscosity was noted. The remaining monomer was added approximately 2% at a time and each portion allowed to eact for about 30 min. Theoretically, at some point an ideal stoichiometric balance between the trimer and the PMDA would be achieved. After the reaction was complete, a 4% excess of PMDA was added to end-cap the polymer. The pure yield was 70% hydrated polyamic acid 1 (Figure 3). (See Table II for a summary of all polymers.)

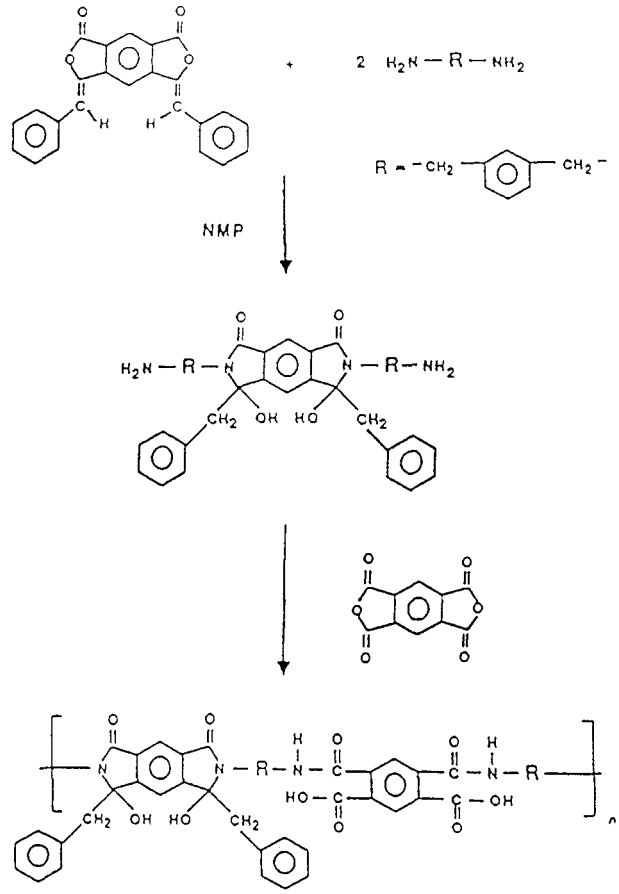
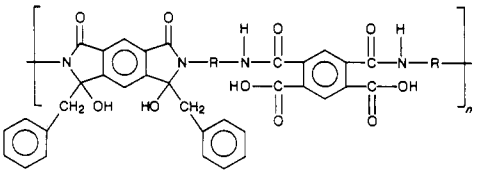
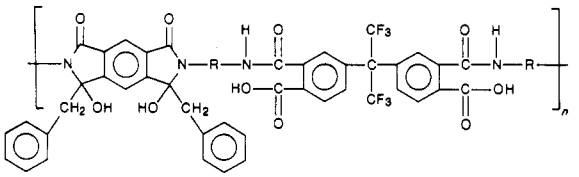
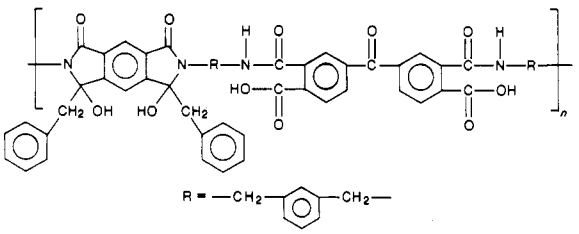


Figure 3. Synthesis of polyamic acid 1 from PMDA.

An infrared spectrum of polyamic acid 1 showed strong absorptions in the carbonyl region near 1640 cm^{-1}, characteristic of an open-chain amide, and from 1750 to 1700 cm^{-1}, due to lactam stretching vibrations. Broad and intense absorptions occur around 3300 cm^{-1} due to O–H and N–H stretching. The results of the elemental analysis of the polymer were in good agreement with those expected for the proposed structure.

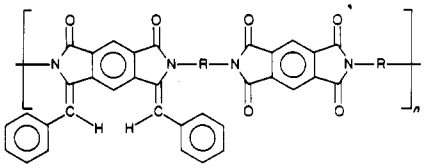
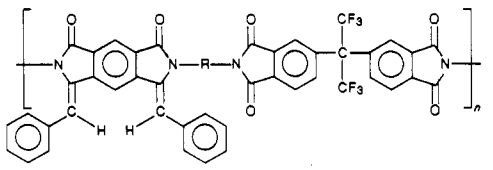
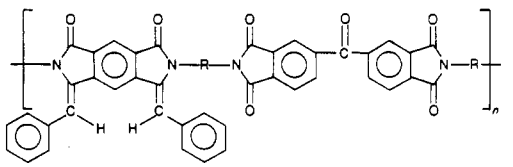
Thermal analysis (DSC) of the hydrated polymer showed a broad endotherm centered near 125 °C due to the loss of volatiles (residual solvent and adsorbed moisture). A sharp, intense endotherm was observed near 190 °C which corresponds to dehydration of the hydroxylactam

Table II
Reaction Conditions and Properties of Polyamic Acids[a]

backbone structure	polymer	viscosity, dL/g	yield, %
	1	0.32	70
	2	0.78	78
	3	0.57	80

[a] Trimerization reaction was carried out at ambient temperature for 24 h followed by polymerization of trimer with dianhydride for an additional 24 h.

Table III
Properties of Cured Copoly(imidine-imides)

backbone structure	polymer	η_{inh}, dL/g	T_g, °C	TGA,[a] °C	elemental analysis calcd, found %C	%H	%N	%F
	1	0.29	234	475	76.51, 76.47	4.12, 3.98	7.14, 7.07	
	2	1.56	213	410	70.09, 69.16	3.60, 3.51	5.54, 5.43	11.28, 10.57
	3		212	455	77.01, 76.62	4.09, 3.92	6.30, 6.10	

[a] Temperature of 10% weight loss in inert atmosphere.

and cyclodehydration of the amic acid function. The scan also showed a marked exotherm centered near 265 °C which is attributed to cross-linking of the exocyclic carbon–carbon double bond. Thermogravimetric analysis (TGA) showed a ca. 10% decrease in weight due to the loss of water from dehydration and residual solvent (Figure 4).

Dehydration of polyamic acid 1 to the corresponding copoly(imidine–imide) was effected by heating a powdered sample and by curing films cast from polymer solutions (Table III lists properties of all cured copolymers). In both cases, the temperature was maintained below 250 °C to avoid thermally induced cross-linking; the polymers were observed to change color from pale to bright yellow.

The semitough films obtained from these studies indicated a moderate molecular weight. Indeed, inherent viscosity for the polymer actually decreased slightly with curing from 0.32 to 0.29 dL/g. This result was also observed during earlier polyimidine studies involving MXDA.[14,19]

A TGA of this polymer showed thermal stability in an inert atmosphere to 475 °C, the temperature of a 10% weight loss. After annealation to 400 °C, the polymer showed a marked glass transition temperature at 234 °C by DSC. Both the intermediate polyamic acid and the cured copoly(imidine–imide) showed good solubility in polar, aprotic solvents. However, the value of this material may be limited due to its poor film-forming properties. Several more polymerizations were attempted under a variety of conditions in both NMP and DMAc, but each case resulted in low molecular weight polymer.

Synthesis of Polyamic Acid 2 Based on 5,5′-(1,1,1,3,3,3-Hexafluoro-2-propylidene)bis(5,5′-iso-

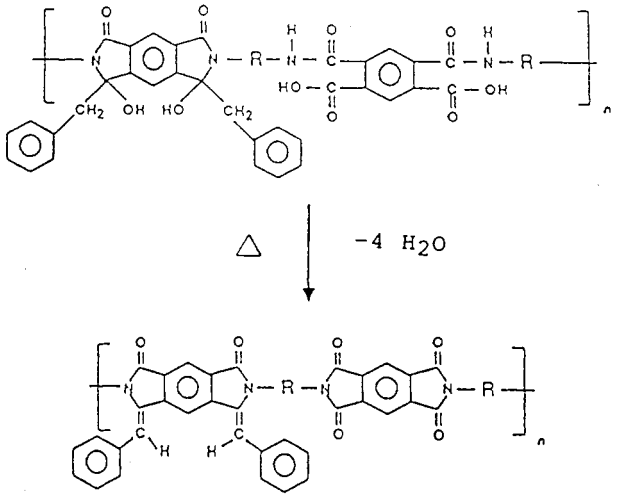


Figure 4. Conversion of polyamic acid 1 to copoly(imidine–imide).

benzofuran-1,3-dione) (6FDA) and Subsequent Conversion to Copoly(imidine–imide). Several commercial and experimental dianhydrides and diamines have been synthesized, which contain a hexafluoroisopropylidene bridging group.[26] Polyimides containing a hexafluoro dianhydride and/or a hexafluoro diamine have greatly improved solubility properties (up to 20% in amide solvents) and high optical transparency due to the bulkiness of these groups.[27]

Incorporation of a hexafluoro dianhydride, 5,5′-(1,1,1,3,3,3-hexafluoro-2-propylidene)bis(5,5′-isobenzofuran-1,3-dione) (6FDA) was used in an attempt to increase molecular weight and solubility. The polymerization of the amine-terminated trimer with 6FDA proceeded readily in NMP at room temperature to give the hydrated polyamic acid **2** in high yields. Inherent viscosity of the polyamic acid solution was 0.78 dL/g, indicating a high molecular weight material. When the polymerization was carried out in DMAc, a considerably lower molecular weight resulted, which was indicated by inherent viscosity.

Further characterization of the high molecular weight material by infrared spectroscopy showed strong absorptions due to O–H and N–H stretching as welll as in the carbonyl region. Elemental analysis of the uncured polymer gave marginally acceptable results. Percent carbon and fluorine were both approximately 1% low. Coupled with the fact that the other elements were slightly high (H, 0.12%, N, 0.30%), these results suggest that some residual solvent was still present in the polymer matrix. This phenomenon is to be expected considering the amount of extremely polar groups present in the polymer. Subsequent studies were carried out in which the hydrated polymer was leached with boiling methanol for several hours and then the methanol subjected to gas chromatography. Indeed, the chromatogram showed a peak with a retention time corresponding to NMP.

Thermogravimetric analysis (Figure 5) also gives valuable evidence to bolster this case. The anticipated results were a 6.7% weight loss due to dehydration. However, a scan rate of 20 °C/min showed an 8.5% weight loss beginning at 81 °C and ending at 286 °C.

A DSC thermogram of the hydrated polymer (Figure 6) showed a broad endotherm centered near 125 °C due to the loss of volatiles and an intense endotherm centered at 190 °C due to dehydration to the imidine–imide. As before, a marked exotherm beginning near 260 °C and ending near 310 °C was observed and indicated thermally induced cross-linking.

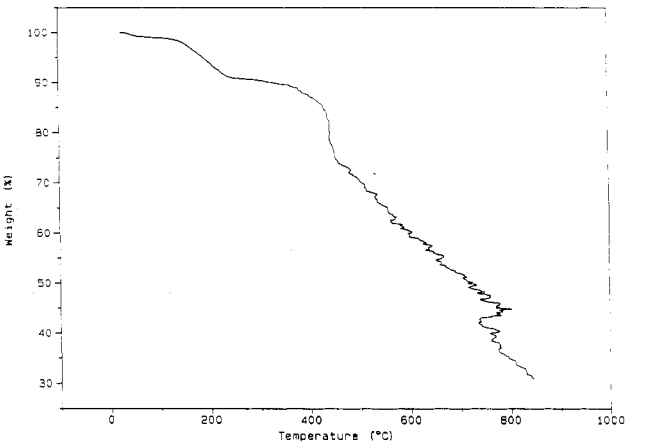


Figure 5. TGA thermogram of hydrated polyamic acid **2** from 6FDA. Determined at a heating rate of 10 °C/min in nitrogen atmosphere.

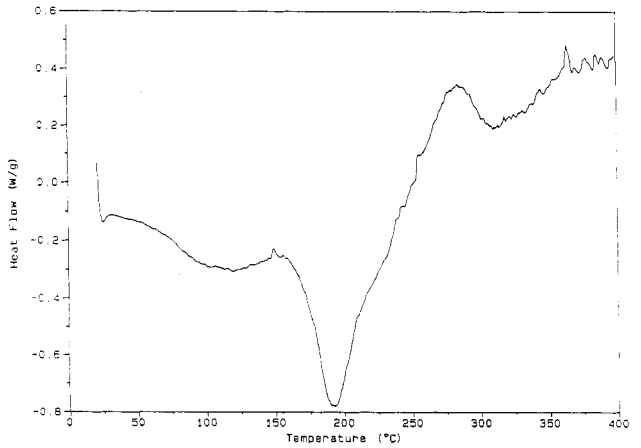


Figure 6. DSC thermogram of hydrated polyamic acid **2** from 6FDA. Determined at a heating rate of 10 °C/min in nitrogen atmosphere.

When polymer films were cured at 300 °C for 4 h, they were observed to darken and become very brittle, indicating that a considerable amount of cross-linking occurred at these elevated temperatures. The fact that the resulting polymers were insoluble in concentrated sulfuric acid and all organic solvents also gives evidence to support cross-linking. Furthermore, no weight loss corresponding to the cure was indicated by TGA, thus eliminating the possibility that some type of off-gas was occurring.

Film casting and subsequent thermal imidization below 250 °C gave tough, transparent, yellow films which showed thermal stability in a nitrogen atmosphere above 400 °C by TGA. After annealation at 400 °C, the polymer showed a marked glass transition at 211–213 °C by DSC. Elemental analysis of the fluorinated copoly(imidine–imide) gave results that were in good agreement with those expected for the proposed structure. These polymers possess outstanding film-forming properties as well as solubility in chloroform and polar, aprotic solvents, thus demonstrating the reported solubilizing effect of fluorine. The enhanced solubility of the fluorine-containing polymer allowed for thermal imidization of the powdered polyamic acid sample and subsequent film casting from a polyimide solution. This method of processing is desirable because the reaction between the amine and anhydride to give the polyamic acid is exothermic and reversible. Viscosity studies indicate that a significant amount of degradation occurs when the polyamic acid is heated while dissolved in polar solvents due to the reverse reaction. Inherent

Table IV
Mechanical Properties of Polyimides[a]

polymer	tensile strength, psi	tensile modulus, psi	% elongation
2	9400	134000	7
PMDA-ODA[28]	25000	440000	5
Hoechst 6F[26]	17400	620000	5
BTDA-ODA[3]	16500	284000	10

[a] Properties at room temperature.

viscosities of polymer solutions ranged from 1.51 to 1.56 dL/g in NMP for samples cured in the powder form, indicating high molecular weight materials and a promising area for future research.

Synthesis of Polyamic Acid 3 Based on BTDA and Subsequent Conversion to Copoly(imidine–imide). This study was also extended to include the dianhydride of 3,3′,4,4′-benzophenonetetracarboxylic acid (BTDA). It was hoped that incorporation of this flexible carbonyl linkage into the polymer backbone would result in high molecular weight while maintaining good solubility properties.

The reaction proceeded smoothly under the previously stated conditions to give hydrated polyamic acid **3** in high yields. The inherent viscosity of the uncured polymer was 0.57 dL/g, indicating a marginal molecular weight for film formation. Further characterization by infrared spectroscopy and thermal analysis gave nealy identical results as those obtained from the PMDA and 6FDA polymers.

Film casting and subsequent dehydration gave tough, flexible, yellow films with good thermal stability. Differential scanning calorimetry indicated a T_g at 212 °C. Inherent viscosity of the cured polymer was not determined due to the fact that the solubility at room temperature was less than 1.5 g/L in NMP. The fact that the cured polymer is not readily soluble in NMP may indicate that chain packing rather than high molecular weight is the cause of the limited solubility.

Mechanical Testing. Polyimides are known to possess excellent mechanical properties. Film-forming properties of fluorinated copoly(imidine–imide) **2** suggest this material may be of commercial value. Tensile testing was carried out to determine thin-film mechanical properties. Table IV shows the results along with data from various polyimide studies. Test samples were 1 mil thick and pulled at a rate of 0.2 in./min at room temperature. Results on these nonoptimized thin films indicate moderate tensile strength and modulus and a fairly low percent elongation to break. Stress–strain curves indicated a yield point, although the polymer films showed no signs of cold drawing.

Permeation Studies. Recently, polyimides have received considerable attention in the area of gas permeation and reverse-osmosis membranes. Therefore, these films were tested for transport (permeability) and selectivity with respect to certain gases in order to investigate their possible use as permselective membranes. Studies were carried out at 35 °C and 5 atm. The observed data compare quite well with those expected for these types of polymer systems as shown in Table V. While this polymer shows a fairly large oxygen/nitrogen ratio, the overall permeation rate is relatively low, as is the case with most polyimides.

Table V
Permeability Data for Polyimides[a]

polymer	P[b] N_2	O_2	CH_4	H_2	He	CO_2
2	0.075	0.450	0.058	6.50	8.00	2.13
PMDA-ODA[29]	0.100	0.610	0.060		8.00	2.70
PMDA-MDA[29]			0.094			4.03

[a] Permeability at 35 °C. [b] Units are $(cm^3)(cm)/(cm^2)(s)(cmHg)$.

Experimental Section

Melting points were determined by using a MEL-TEMP apparatus and are uncorrected. All reagents and solvents for model studies were commercial grade and used without further purification. Polymerization solvents (Aldrich) such as *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) were spectrophotometric grade and used as is or purified further by distillation from calcium hydride. *m*-Xylylenediamine (MXDA) was vacuum distilled from zinc dust prior to polymerizations. Pyromellitic dianhydride (PMDA) was purified by sublimation and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) was recrystallized from acetic anhydride. Electronic grade 5,5′-(1,1,1,3,3,3-hexafluoro-2-propylidene)bis(5,5′-isobenzofuran-1,3-dione) (6FDA), supplied by Hoechst Celanese Corporation, was dried in a vacuum oven and used without further purification.

Elemental analyses were performed by Desert Analytics in Tuscon, AZ. Infrared spectra were obtained on a Perkin-Elmer Model 360 spectrometer using both KBr pellet and neat film techniques. ^1H NMR analyses were performed on a Varian Anaspect 60-MHz spectrometer and an IBM 80-MHz spectrometer. Thermal analysis (TGA) was carried out by using a Du Pont 9900 thermal analyzer at Texas Research Institute, and differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Model DSC 2 at the University of Texas in Austin. Permeability studies were designed and carried out in the Chemical Engineering Department at the University of Texas. Thin-film mechanical properties were determined by the use of an Instron Model TTD universal testing instrument at Texas Research Institute.

Dilute solution viscosities of polymer solutions were determined at 25 °C by the use of a Kimax 100 viscometer at a concentration of 0.25 g/dL in NMP.

3-Benzylidenephthalide.[30] 3-Benzylidenephthalide was prepared in 30% yield according to the procedure given in the literature. Recrystallization from ethanol afforded yellow crystals: mp 98–100 °C (lit.[30] mp 100–101 °C).

1-Thio-3-benzylidenephthalide. 1-Thio-3-benzylidenephthalide was prepared by the action of phosphorus pentasulfide on 3-benzylidenephthalide as described previously. Recrystallization from ethanol gave dark-red crystals in 30% yield: mp 96 °C (lit.[31] mp 95 °C).

3-Hydroxy-3-benzyl-3*H*-isoindol-1-one. To a mixture of 1 g (0.004 mol) of 3-benzylidenephthalide and 10 mL of benzene was added dropwise a solution containing 0.55 mL (0.004 mol) of benzylamine and 5 mL of benzene. After being stirred overnight at room temperature, the reaction mixture was added to ca. 100 mL of stirring ligroin. The off-white precipitate was isolated by suction filtration and recrystallized from ethanol to give 0.96 g (65% yield) of colorless crystals: mp 162–163 °C (lit.[20] mp 162–163 °C).

1-Thio-3-hydroxy-3-benzyl-3*H*-isoindole. The reaction of 0.72 g (0.003 mol) of 1-thio-3-benzylidenephthalide and 0.5 mL (0.004 mol) of benzylamine was carried out in chloroform similar to the procedure described above. Recrystallization from a mixture of ethanol and water gave 0.70 g (67% yield) of pale-yellow crystals: mp 112–114 °C (lit.[22] mp 110 °C).

3,5- and 3,7-Dibenzylidenepyromellitide.[14] 3,5-Dibenzylidenepyromellitide and 3,7-dibenzylidenepyromellitide (3,5- and 3.7-DBP) were prepared as described previously. The two isomers were separated by fractional recrystallization from *N,N*-dimethylformamide (DMF). The yield of the more soluble cis isomer (3,5-DBP) was 10.0 g (15%) of long, yellow needles.

Preparation of Polyamic Acid 1 from 3,5-DBP, MXDA, and PMDA. A 15-mL, three-necked, round-bottom flask was fitted with a mechanical stirrer, a gas inlet adaptor, and a standard tapered funnel. The reaction vessel was assembled hot and allowed to cool under a positive flow of argon. A mixture containing 1.0290 g (0.0075 mol) of *m*-xylylenediamine and 5 mL of NMP was added to the flask. A mass of 1.3838 g (0.00375 mol) of 3,5-DBP was added over a period of 4 h, and the final portions were rinsed with 4 mL of NMP. The tan solution was allowed

to stir for 24 h at room temperature. Next, approximately 90% of the 0.8238 g (0.00375 mol) of PMDA was added in 4–5 portions, allowing each portion to dissolve before subsequent addition. The remaining 10% of monomer was added in 5 portions over a period of 4 h, during which time the reaction mixture became very viscous. Total volume of solvent was adjusted so that the reaction mixture was approximately 20% solids. After being stirred for 24 h at room temperature, the viscous yellow solution was diluted with a few milliliters of NMP and added dropwise to ca. 400 mL of rapidly stirred ethyl acetate. The white precipitate was filtered, dried, and purified to yield 2.2327 g (69%) of a white powder. Inherent viscosity was 0.33 dL/g.

Preparation of Polyamic Acid 2 from 3,5-DBP, MXDA, and 6FDA. The same procedure described above was followed except 0.9484 g (0.007 mol) of MXDA, 1.2754 g (0.0035 mol) of 3,5-DBP, and 1.5465 g (0.0035 mol) of 6FDA were added to the reaction flask. The precipitated polymer was filtered, purified, and dried in a vacuum oven overnight at 80 °C to give a fluffy, light-yellow powder. The pure yield was 85%, and inherent viscosity was 0.78 dL/g.

Preparation of Polyamic Acid 3 from 3,5-DBP, MXDA, and BTDA. A similar procedure to the one described above was followed except 1.1546 g (0.0085 mol) of MXDA, 1.5527 g (0.00425 mol) of 3,5-DBP, and 1.3656 g (0.00425 mol) 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 initial stages of the polymerization. The pure yield was 80% of a fluffy, yellow solid. Inherent viscosity of a polymer solution was 0.57 dL/g.

Thermal Cyclodehydration of Polyamic Acids to the Corresponding Copoly(imidine–imides). Approximately 0.1 g of the powdered sample was placed in a clean sample vial and heated in a vacuum oven at ca. 200 °C for 16 h. The dehydrated samples were then used for determining viscosity, elemental analysis, and solubility properties of the cured polymers.

Film Casting. An appropriate amount of the polyamic acid sample was dissolved in DMAc or NMP so that the solution was about 15% solids by weight. This polymer solution (dope) was used for film casting and subsequent imidization. The dope was pipeted onto a clean, dry microscope slide and spread evenly by using the disposable pipet. The slide was then placed in an oven at 80 °C under a positive flow of argon for 2 h. After this initial drying, the temperature was increased to 200 °C and the sample was heated under vacuum for 16 h. The polymer film was cooled and removed from the glass slide by soaking in distilled water. In the case of the fluorinated polymer, it was possible to cast films of the cured material directly from solution. The sample was placed under vacuum for 2 h and then heated under vacuum at 60 °C for 2 h, 90 °C for 1 h, and finally 210 °C for 2 h to allow for removal of solvent.

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Registry No. I-S, 116004-74-1; I-O, 19732-69-5; (3,5-DBP)(MXDA)(PMDA) (copolymer), 115942-74-0; (3,5-DBP)(MXDA)(PMDA) (SRU, polyamic acid), 115960-19-5; (3,5-DBP)(MXDA)(PMDA) (SRU, polyimide), 115942-71-7; (3,5-DBP)(MXDA)(6FDA) (copolymer), 115942-75-1; (3,5-DBP)(MXDA)(6FDA) (SRU, polyamic acid), 115960-21-9; (3,5-DBP)(MXDA)(6FDA) (SRU, polyimide), 115942-72-8; (3,5-DBP)(MXDA)(BTDA) (copolymer), 115942-76-2; (3,5-DBP)(MXDA)(BTDA) (SRU, polyamic acid), 115960-20-8; (3,5-DBP)(MXDA)(BTDA) (SRU, polyimide), 115942-73-9; N_2, 7727-37-9; O_2, 7782-44-7; CH_4, 74-82-8; H_2, 1333-74-0; He, 7440-59-7; CO_2, 124-38-9; $C_6H_5CH_2NH_2$, 100-46-9; 3-benzylidenephthalide, 575-61-1.

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