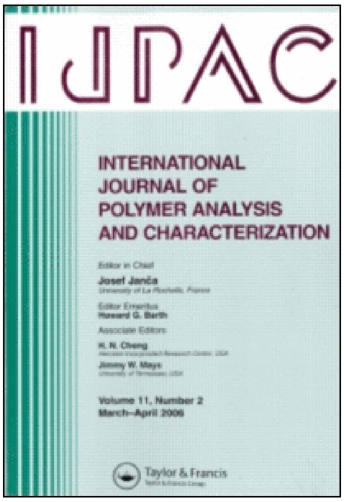

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Thermal and Nuclear Magnetic Resonance Characterization of Linear and Radial High Performance Polyimides*

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Radially oriented polyimides were prepared based on the geometrically favorable fluorene central unit by condensation with the C-terminus of the linear polyimides. Characterization of the polymers was achieved by Fourier transform infrared resonance (FTIR) spectroscopy, proton (^{1}H NMR) and ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy, X-ray diffraction, solubility and inherent viscosity. Thermal properties were investigated by thermogravimetric analysis (TGA), differential calorimetry scanning (DSC) and optical polarizing microscopy. The radially oriented polyimides were compared to their linear analogs. Thermogravimetic analyses indicate that linear and radially oriented polyimides were stable up to ca. 400°C in air and under argon atmospheres.

Keywords: Polyimide; Thermogravimetric analysis; Differential scanning calorimetry; Fluorene; Nuclear magnetic resonance spectroscopy

INTRODUCTION

The high mechanical properties (tensile and impact strength) of polyimides, in addition to their excellent resistance to solvents and high thermal and thermo-oxidative stability, make them useful candidates for high performance applications. Polyimides are utilized in high

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temperature and high load-bearing applications (struts, chassis and brackets in automotive and aircraft structures).[1] In the aircraft industry, matrix composites of polyimides with an inert material (glass or carbon fibers) are being developed for use in fans, compressors, castings, ducts, engine control systems, and turbine disk, blades and vanes.[2] The excellent heat resistance and the ability to withstand aggressive automotive lubricants, fuels and coolants will lead to further utilization of polyimides in the transportation industry.[1] Processing of polyimides is generally quite difficult, such that it limits their utility. These limitations are due to the strong enthalpic interactions and chain rigidity, which result in their inherent insolubility and infusibility.[3]

Recently, we have synthesized radially oriented polyimides with fluorene central units as an approach to improving processability and compressive strength without much effect on the thermal properties. Herein, we report on the structural (^{1}H and ^{13}C NMR (nuclear magnetic resonance)) and thermal (differential scanning calorimetry, thermogravimetric analysis and optical polarizing microscopy) characterization of these polymers.

EXPERIMENTAL

Instrumentation and Measurements

High resolution proton and ^{13}C NMR spectra were obtained in deuterated dimethylsulfoxide (DMSO-d_6) on a Bruker ARX-400 and a Bruker AM-400 spectrometer with a Silicon Graphics INDY computer in the Fourier transform mode. NMR experiments were executed with a spectral window of 1350, and pulse delay time of 1.0 s for ^{1}H NMR and 3.0 s for ^{13}C NMR. The proton spin relaxation times (τ_1) were measured by using an inversion-recovery pulse sequence, with a total of 15 evolution delays. To minimize changes in homogeneity during the course of the experiments, the evolution values were repetitively cycled.

Thermogravimetric analysis (TGA) was performed under argon and in air using open platinum pans as reference and sample containers. TGA data were determined with the Seiko Scientific Instruments (SSI)

TG/DTA22O thermogavimetric analyzer at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) experiments were performed in the Seiko Scientific Instruments (SSI) DSC220 differential scanning calorimeter in air, and under argon at a heating rate of 10°C/min. Sealed aluminum reference and sample pans were used to obtain the differential scanning calorimetry curves. Wide angle X-ray diffraction (WAXD) measurements were made using a Rigaku RU200 X-ray diffractometer equipped with a Satton camera. Nickel filtered CuKα radiation was used at 50 kV/170 nA. Intensities were extracted from the X-ray films using a Joyce-Loeble Scandig 3 densitometer.

Materials and Solutions

Commercially available materials used were sublimed 1,4-phenylenediamine, bis-4,4′-aminophenylhexafluoropropane, 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic diacidanhydride), bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride, 2,7-dinitro-9-fluorenone, aniline hydrochloride, distilled aniline, 10% palladium on carbon and hydrazine monohydrate.

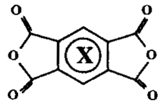
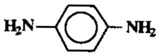
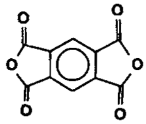
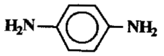
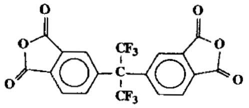
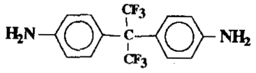
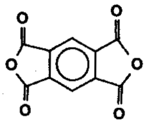
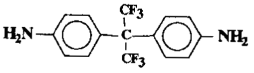
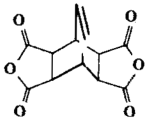
The Star-like Fluorene Unit

The synthesis of the star-like fluorene unit, 2,7-diamino-9,9-bis(4-aminophenyl)fluorene, has been reported elsewhere.[4]

Polymer Syntheses

The syntheses of the linear and radially oriented polyimides utilized a modification of the condensation polymerization method described by Becker and Schmidt.[5] The syntheses of the polymers are presented elsewhere.[4] Structural representations of the primary diamine and dianhydride monomers used in the syntheses of the linear and radially oriented polyimides are presented in Table I. A general representation of the structure of the radially oriented polyimides is presented in Figure 1.

TABLE I Primary diamines and dihydrides used in the syntheses of the polyimides

Polyimides		
Linear I Radial II		
Linear III Radial IV		
Linear V Radial VI		
Linear VII Radial VIII		

RESULTS AND DISCUSSION

The structures of the linear and the corresponding radially oriented polyimides were confirmed via experimental analysis, FTIR, proton and ^{13}C NMR spectroscopy. The characteristic imide absorptions at 1782, 1729 and 1374 cm^{-1} were observed in the infrared spectra of the linear and radially oriented polyimides.

^{1}H NMR

Proton NMR spectra of linear and radial polyimides display chemical shifts between δ 6.51 and 8.70 ppm corresponding to aromatic protons. In addition, the ^{1}H NMR spectra of linear and radial polyimides containing the bicyclic moiety (VII and VIII) exhibit a singlet at

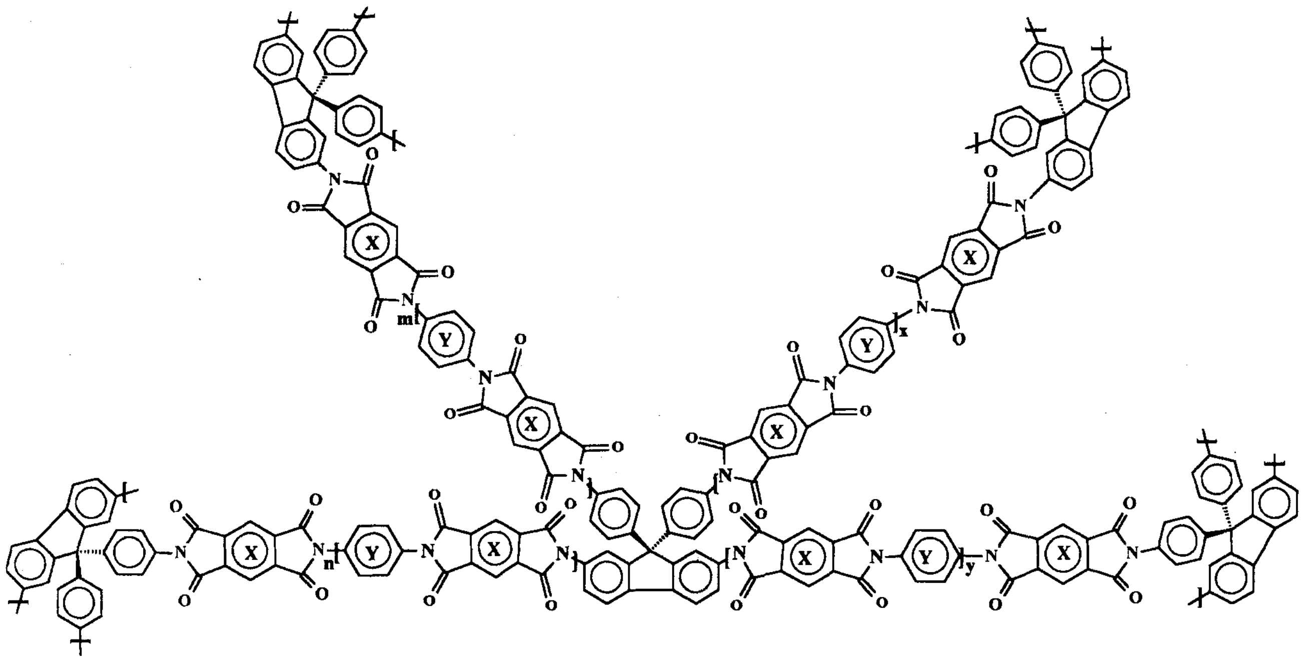


FIGURE 1 Generalized structure of the radially oriented polyimide.

δ 3.43 ppm which represents the two protons at the bridge head. The singlet at δ 3.29 ppm corresponds to the four other protons of the bicyclic unit, and the singlet that appears at δ 6.32 ppm is representative of the two protons of the bridge.

^{13}C NMR

In the ^{13}C NMR spectra of all polymers, chemical shifts were observed between δ 164.63 and 175.37 ppm corresponding to the carbon atoms of the imide. The radially oriented polyimides exhibited an additional peak in the region from δ 64 to 66 ppm corresponding to the quaternary carbon of the fluorene based central unit.

A typical ^{13}C NMR spectrum of the linear polyimides is presented in Figure 2. The ^{13}C NMR spectrum of linear polyimide VII exihibits chemical shifts at δ 33.57 and 33.19 ppm which represent the two carbons at the bridge head. The peaks at δ 42.19 and 43.05 ppm correspond to the four other carbons of the bicyclic functionality, and chemical shifts that appear at δ 131.22 and 130.55 ppm are representative of the two carbon atoms of the bridge. Paired signals are observed for the carbons of the bicyclic moiety indicating the presence of the *exo* and *endo* bicyclic isomers within the polymer chains. The spectrum exhibits three chemical shifts centered at δ 63.93, 63.69 and 63.44 ppm corresponding to the sp^3 hybridized carbon of the hexafluoro isopropyl group; the fluorinated carbons are observed as four chemical shifts at δ 117.91, 121.87, 124.72 and 128.69 ppm. The resonances at δ 132.78 and 131.46 ppm correspond to the substituted aromatic carbon atoms, and the chemical shifts at δ 129.63 and 126.72 ppm correspond to the unsubstituted aromatic carbon atoms. The chemical shift at δ 175.37 ppm indicates the presence of the carbonyl carbon atom of the imide linkage.

A typical ^{13}C NMR spectrum of the radially oriented polyimides (Figure 3) shows peaks at δ 35.61 and 34.14 ppm representing the two carbons at the bridge head. Peaks at δ 42.64 and 44.06 ppm correspond to the four other carbons of the bicyclic unit, and chemical shifts at δ 130.36 and 130.43 ppm are representative of the two carbon atoms of the bridge. A pair of peaks is observed for all the carbons of the bicyclic moiety indicating the presence of *exo* and *endo* bicyclic configurations. The spectrum exhibits four peaks at δ 65.73, 65.48, 65.23 and 64.97 ppm,

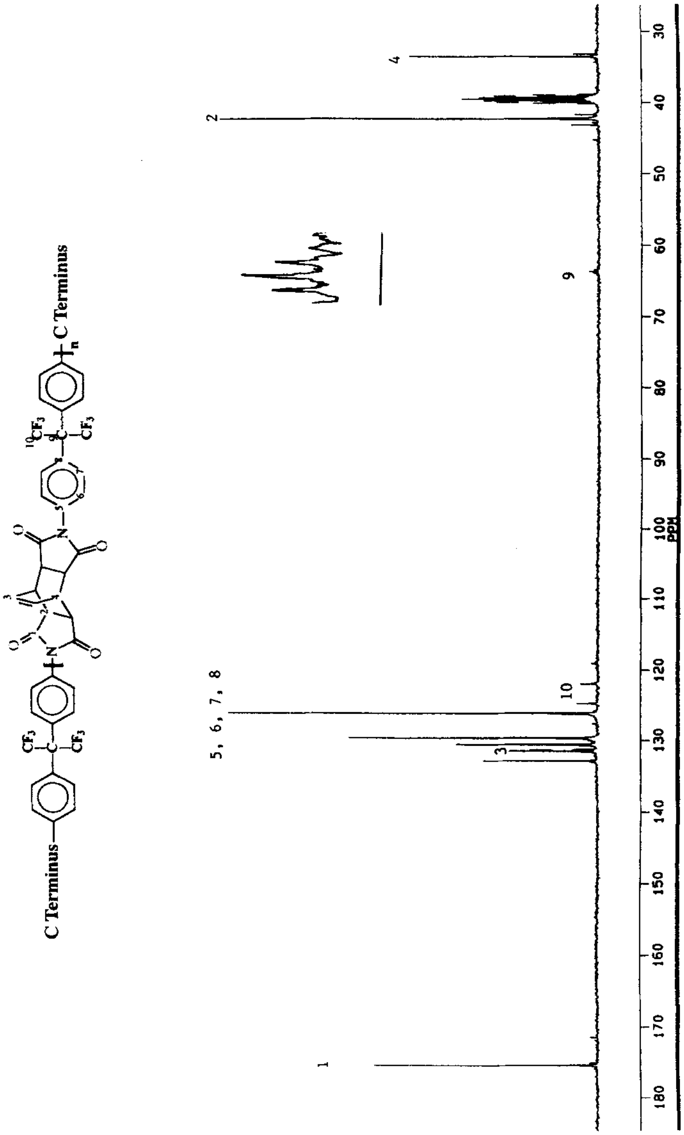


FIGURE 2 ^{1}H NMR spectrum of the linear polyimide VII in dimethyl sulfoxide-d_6 at 100°C.

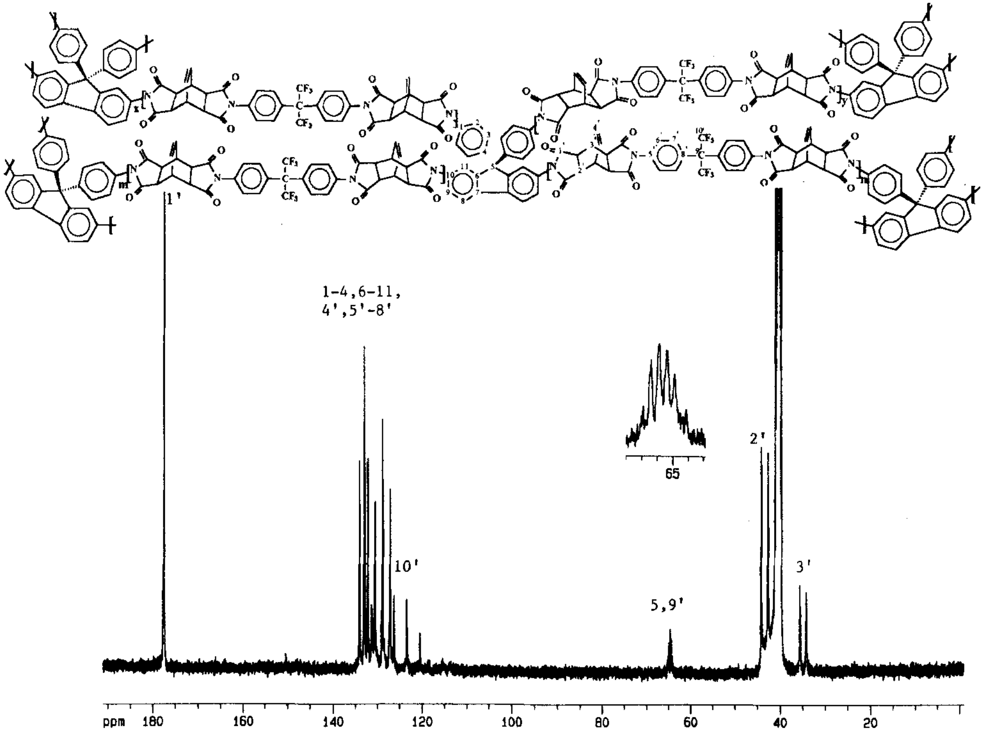


FIGURE 3 ^{13}C NMR spectrum of radially oriented polyimide VIII in dimethyl sulfoxide-d_6 at room temperature.

of which three correspond to the sp^3 hybridized carbon of the hexafluoro isopropyl group as illustrated in the ^{13}C NMR spectrum of the linear polyimide. The additional one (64.73 ppm) corresponds to the quaternary carbon of the star-like central unit. The fluorinated carbons appear at δ 120.35, 123.20, 126.41 and 129.62 ppm. The resonances between δ 126.05 and 133.96 ppm correspond to the carbons of the aromatic rings while those at δ 177.30 and 177.49 ppm correspond to the carbonyl carbon atoms of the imide and amic acid linkages.

Thermal Analyses

Thermal characterizations of the polymers were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under air and argon atmospheres. The DSC experiments were run over a temperature range from 25°C to 425°C, the temperature limit of the instrument. The DSC curves of the linear polyimides I, III, V, and radially oriented polyimides II, V, VI revealed glass transition temperatures ranging from 266°C to 378°C in air and argon atmospheres. The DSC data of the polymers are summarized in Table II, and illustrated in Figures 4 and 5.

The TGA curves of the linear and the corresponding radially oriented polyimides indicate thermal stability ranging from 400°C to 508°C in air and argon atmospheres, Figures 6 and 7. The temperatures correlating to the onset of decomposition, 5% and 10% weight losses of the linear and radially oriented polyimides under argon and

TABLE II DSC transition temperatures of the polyimides

Polyimide	*Transition temperature* °C					
	Glass (T_g)		*Crystallization* (T_c)		*Decomposition* (T_d)	
	Argon	*Air*	*Argon*	*Air*	*Argon*	*Air*
Linear I	333	333	—	—	—	—
Radial II	327	329	—	—	—	—
Linear III	308	308	—	—	—	—
Radial IV	266	266	—	—	—	—
Linear V	378	378	—	—	—	—
Radial VI	338	338	—	—	—	—
Linear VII	339	340	396	392	401	398
Radial VIII	322	322	—	—	401	401

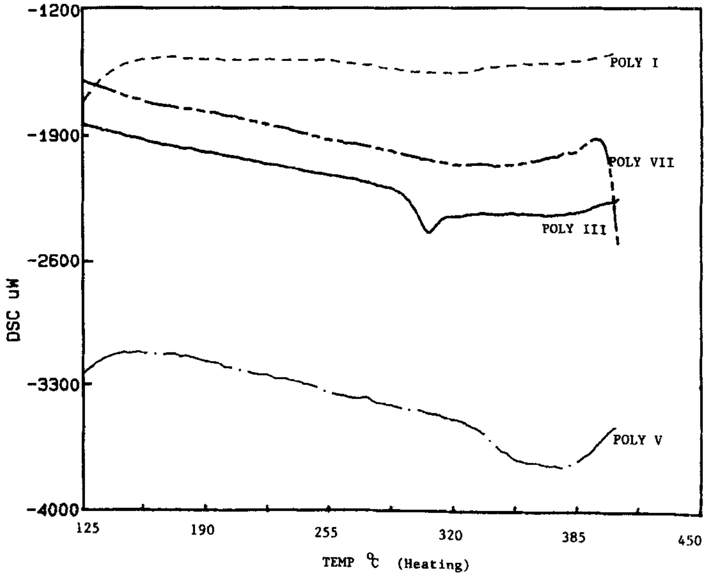


FIGURE 4 DSC curves of the linear polyimides under an argon atmosphere.

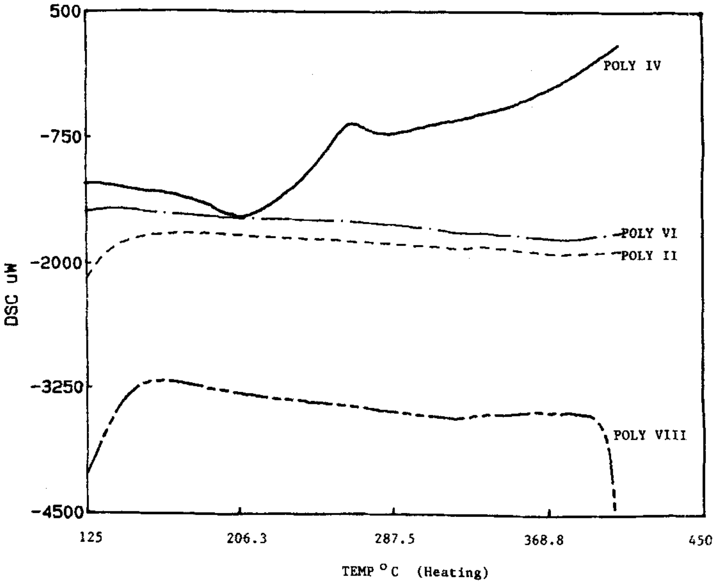


FIGURE 5 DSC curves of the radially oriented polyimides under an argon atmosphere.

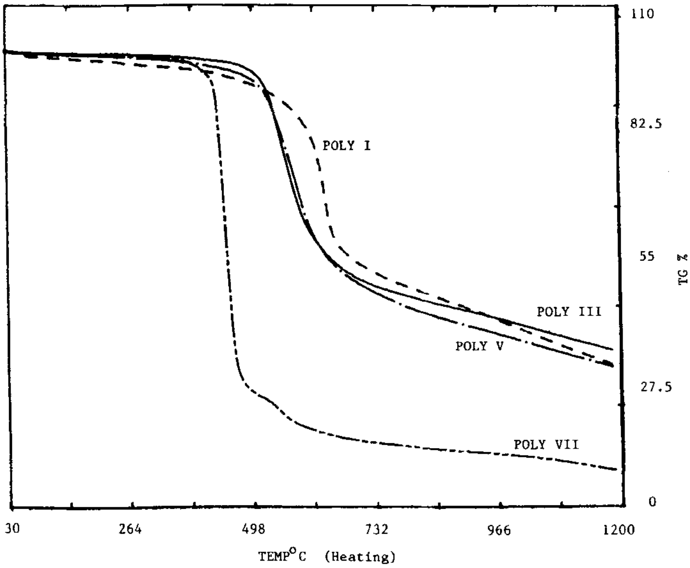


FIGURE 6 TGA curves of the linear polyimides under an argon atmosphere.

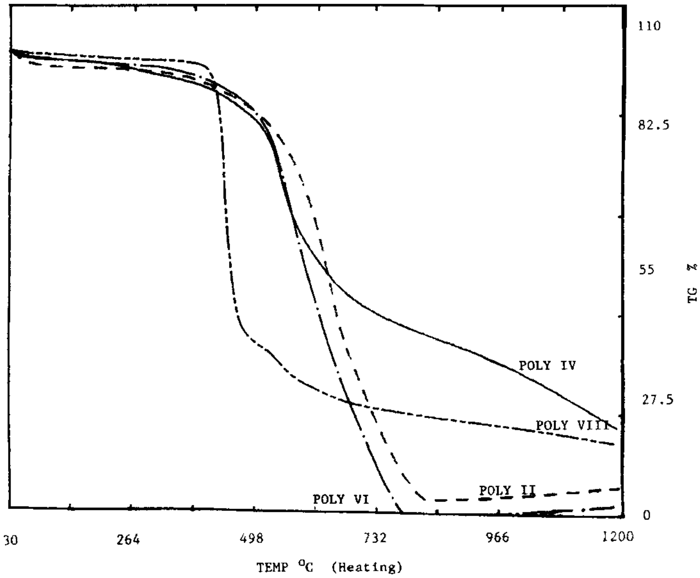


FIGURE 7 TGA curves of radially oriented polyimides under an argon atmosphere.

TABLE III Decomposition temperatures of the polyimides

Polyimide	*Decomposition temperature* °C					
	Onset		5% *Wt. loss*		10% *Wt. loss*	
	Argon	*Air*	*Argon*	*Air*	*Argon*	*Air*
Linear I	405	381	494	443	572	505
Radial II	357	331	427	422	505	478
Linear III	454	452	508	505	534	529
Radial IV	338	349	401	411	477	496
Linear V	400	392	481	451	529	510
Radial VI	354	330	427	403	491	467
Linear VII	357	352	414	400	430	419
Radial VIII	363	354	416	405	427	424

air atmospheres are presented in Table III. In general, the linear polyimides are more thermally stable than the corresponding radially oriented polyimides.

Optical polarizing microscopy experiments were executed over temperatures ranging from room temperature to 300°C. Hot stage optical polarizing microscopy of linear and radially oriented polyimides indicated no melting transition up to 300°C, the temperature limit of the instrument. Birefringence was not observed within this temperature range.

Solubility and Inherent Viscosity

The introduction of hexafluoro groups and the bicyclic ring resulted in an improvement in the solubility of the linear and radially oriented polymeric systems containing these features. The polyimides containing the hexafluoro group, and polyimides containing the bicyclic ring as well as hexafluoro groups exhibit increased solubility in comparison to the polyimides I and II. The polyimides, which displayed an improvement in solubility, were found to be soluble at 2% w/v concentration in organic solvents and in strong acids at room temperature, Table IV. In general, the radially oriented polyimides were found to exhibit greater solubility relative to the corresponding linear polyimides suggesting that the polymer systems are not crosslinked.

The inherent viscosities are relatively low, and the viscosity measurements of the radially oriented polyimides were found to be approximately twice that of the corresponding linear polyimides.

Wide Angle X-ray Diffraction

The X-ray diffraction scans of the linear polyimide I and its three-dimensional analog, polyimide II, exhibit semicrystalline diffraction peaks; the other polymers show a broad halo indicative of amorphous nature, Figure 8. In the X-ray scan for linear polyimide, there are four

TABLE IV Solubility properties and inherent viscosity measurements of the polyimides[a]

Polyimide	$\eta_{\text{inh.}}$ dL/g	*TMU*	*THF*	*DMF*	*DMAc*	*DMSO*	*NMP*	H_2SO_4	*MSA*	*m-C*	*Py*	*TCE*
Linear IV	0.12[b]	− −	− −	− −	− −	− −	− −	+ +	+ −	− −	− −	− −
Radial V	0.18[b]	+ −	+ −	+ −	+ −	+ +	+ −	+ +	+ +	+ −	+ −	+ −
Linear VI	0.11[c]	+ +	+ −	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ −
Radial VII	0.22[c]	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ −
Linear VIII	0.17[c]	+ +	+ −	+ +	+ +	+ +	+ +	+ +	+ +	+ −	+ +	+ −
Radial IX	0.21[c]	+ +	+ −	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Linear X	0.16[c]	+ −	− −	+ −	+ −	+ −	+ −	+ +	+ −	− −	+ −	+ −
Radial XI	0.24[c]	+ −	+ −	+ −	+ −	+ +	+ −	+ +	+ +	+ +	+ +	+ −

+ +, Soluble; + −, partially soluble; − −, insoluble.

[a] Solubility measurements at 2% w/v concentrations at room temperature; [b] inherent viscosity measured in concentrated sulfuric acid at 30°C; [c] inherent viscosity measured in dimethyl sulfoxide at 30°C; TMU, tetramethylurea; THF, tetrahydrofuran; DMF, dimethylformamide; DMAc, dimethylacetamide; DMSO, dimethyl sulfoxide; NMP, N-methyl-2-pyrrolidinone; MSA, methane sulfonic acid; *m*-C, *m*-cresol; Py, pyridine; TCE, 1,1,2,2-tetrachloroethane.

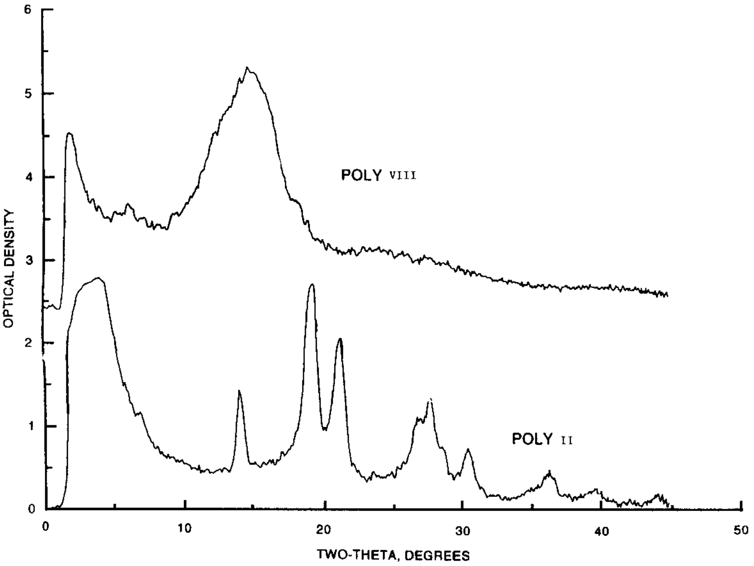


FIGURE 8 X-ray diffraction scans of polyimide II (semicrystalline) and polyimide VIII (amorphous).

prominent peaks, at 4° (*d*-spacing of 12.7 Å), 14° (*d*-spacing of 6.24 Å) and two centered at 20° (*d*-spacing of 4.62 and 4.20 Å). The crystal structure for this polymer has not yet been determined; however, preliminary data indicate that the peak at 4°, with a *d*-spacing of 12.7 Å, is due to the layer lines corresponding to the ordering of the chemical repeat units along the chain axis. The radially oriented polyimide II displays *d*-spacings identical to that of linear polyimide I. Efforts to determine the crystal packing of these polymers are ongoing.

Acknowledgments

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