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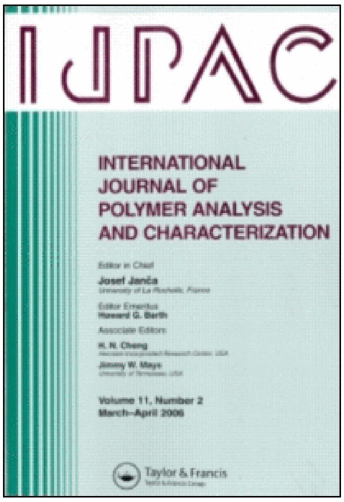

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Characterization of High-Performance Polyimides Containing the Bicyclo[2.2.2]oct-7-ene Ring System

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Characterization of High-Performance Polyimides Containing the Bicyclo[2.2.2]oct-7-ene Ring System

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Abstract: Polyamic acids and polyimides were synthesized by the polycondensation of bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride with 1,4-phenylenediamine, 1,3-phenylenediamine, 3,3′-dimethyl-4,4′-diaminobiphenyl diamine (*o*-tolidine), and 2,2′-bis(trifluoromethyl)benzidine. Thermogravimetric analysis indicates that the corresponding polyamic acids and polyimides were stable up to approximately 450°C under argon and air. Thermal and thermo-oxidative stability was higher for polyimides derived from disubstituted biphenyl moieties (CF_3 or CH_3) and bicyclic ring systems. The polymers exhibited enhanced solubility in organic solvents such as dimethyl sulfoxide, N,N-dimethylacetamide, and N,N-dimethylformamide. The polymers with high aromatic character tend to exhibit decreased solubility. X-ray data indicated that the polyamic acids are amorphous.

Keywords: Bicyclo[2.2.2]oct-7-ene; polyimide; polyamic acid

INTRODUCTION

Polyimides are a very important class of polymers that display outstanding thermo-oxidative stability as well as excellent mechanical and

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electrical properties. In spite of these excellent properties, they are very difficult to process (fabrication of films and fibers) due to their poor solubility in common solvents, the high processing temperature, and the evolution of volatiles during imidization. The low solubility of these polymers in organic and inorganic solvents and their high melting transitions are due essentially to the rigidity of the aromatic ring system, which results in large van der Waals forces between individual polymer molecular chains. Different approaches have been used to improve solubility and reduce melting transition of polyimides without destroying the high-performance properties of the polymers, especially thermal and thermal oxidative stability.[1–4] Efforts to increase the solubility of rodlike polymers include some structural modifications, such as the use of bulky substituents, kinks, and crank shaft, the introduction of randomly spaced semi-flexible chain fragments, the replacement of phenyl ring in the polymer system, and the use of non-coplanar biphenyl moieties.

Wholly aromatic polyimides exhibit high thermal and thermo-oxidative stability but also exhibit a high degree of intractability due to high π-electron density. In order to improve the processability of these polymers, a six-membered ring, such as bicyclo[2.2.2]oct-7-ene, which is a precursor to the aromatic ring system, can be used. The aromatic ring system and bicyclo[2.2.2]oct-7-ene ring system are found to be similar in linearity, geometry, and polarizability.[5,6] Polymers derived from bicyclo[2.2.2]oct-7-ene ring system are expected to be more processable due to a reduction in the symmetry of the polymer backbone and a reduction in the π-electron density of the system. For example, Polk et al.[7] used bicyclic ring systems in the synthesis of homopolyesters that exhibited liquid crystalline properties. Harruna and Polk[8] used a disubstituted bicyclic ring as a precursor to an aromatic ring system in the synthesis of high-performance polyamides.

Here, we report on the characterization of polyimides containing the bicyclo[2.2.2]oct-7-ene ring prepared by the substitution of an aromatic anhydride with a bicyclic type anhydride in combination with disubstituted diamines. The effects of the bicyclo[2.2.2]oct-7-ene ring system and the effects of the methyl (CH_3) and trifluoromethyl (CF_3) substitutents on thermal stability, liquid crystallinity, and solubility were studied.

INSTRUMENTATION AND MEASUREMENTS

Proton and carbon-13 nuclear magnetic resonance spectra were obtained in deuterated dimethyl sulfoxide (DMSO)-d_6 or deuterated sulfuric acid (D_2SO_4) with a Bruker WM-250 spectrometer. Solid state carbon-13 nuclear magnetic resonance (NMR) spectra were obtained with a Bruker ARX-400 and a Bruker AM-4000 spectrometer with a Silicon Graphics

INDY computer. Solutions were prepared using tetramethylsilane (TMS) as internal standard. Infrared spectra were performed on a Nicolet Omicon Fourier transform-infrared (FTIR) spectrometer, using KBr pellets. X-ray scattering patterns were obtained using the Philips X'Pert MPD X-ray defractometer.

Thermogravimetric analyses (TGA) were performed on a Seiko Scientific Instruments (SSI) TGA/DTA 220 thermogravimetric analyzer. Open platinum pans were used as reference and sample holders. Scans were run at 10°C/min under argon and air. Differential scanning calorimetry (DSC) data were obtained on a Seiko Scientific Instruments (SSI) DSC 220 differential scanning calorimeter, under argon and air. DSC curves were obtained at a heating rate of 10°C/min using sealed aluminum reference and sample pans. Transitions were taken a peak minima (endotherm) and peak maxima (exotherm). Visual observations of thermal transitions under cross-polarized light were made using the Laborlux Pol 12 polarizing optical microscope equipped with a heating stage.

Inherent viscosity measurements were obtained at 30°C with concentrations of 0.5 g/100 mL of polymer in DMSO or concentrated sulfuric acid. Solubility tests were determined at room temperature.

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RESULTS AND DISCUSSION

The structure of the polymers is presented in Figure 1. Elemental analysis data are presented in Table I. The infrared data of the polyamic acids and the corresponding polyimides are summarized in Tables II and III, respectively. The proton NMR data of the polymers are presented in Table IV.

The carbon-13 NMR spectrum of AI exhibits chemical shifts at δ 28.2 corresponding to the bridge head carbons, and the chemical shifts from δ 37.8 to δ 41.0 ppm correspond to the tertiary carbons of the bicyclic ring system. The peaks from δ 129.1 to δ 131.7 ppm correspond to the bridge carbon and to the unsubstituted aromatic carbon atoms. The chemical shift at δ 134.7 ppm indicates the equivalent substituted aromatic carbon atoms. The chemical shifts from δ 151.0 to δ 168.3 ppm correspond to the carbons of the carbonyls of the imide, amide, and carboxylic moieties.

The carbon-13 spectrum of AII shows a chemical shift at δ 34.8 corresponding to the bridge head carbon atoms, a chemical shift at δ 34.8 corresponding to the bridge head carbon atoms, and a chemical shift at δ 42.99 ppm corresponding to the tertiary carbons of the bicyclic ring system. The chemical shifts from δ 128.6 to δ 130.0 correspond to the aromatic ring unsubstituted carbon atoms, the chemical shift at δ 132.2

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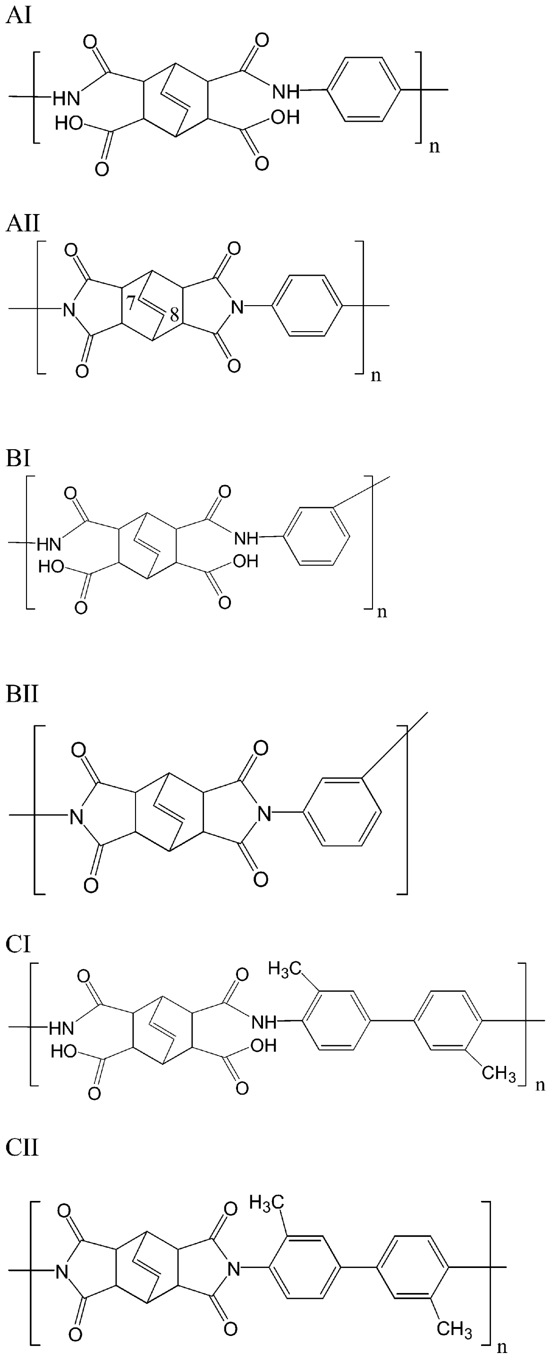
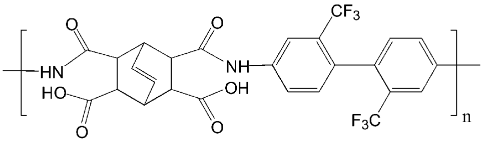
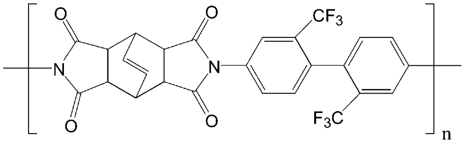


Figure 1. Structure of polymers.

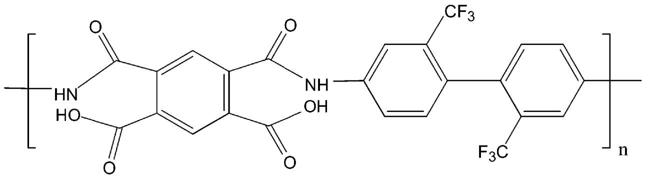
DI



DII



EI



EII

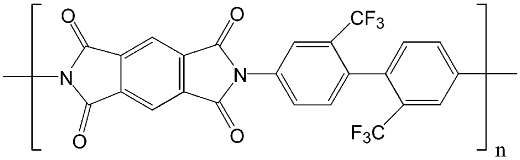


Figure 1. Continued.

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corresponds to the carbon-carbon double bond carbon atoms, and the chemical shift at δ 176.9 ppm corresponds to the carbon atom of the imide carbonyl (C=O).

The carbon-13 NMR spectrum of BI exhibits a chemical shift at δ 28.7 corresponding to the bridge head carbons of the bicyclic ring system; chemical shifts at δ 37.8, δ 34.8, and δ 43.77 ppm correspond to the tertiary carbons of the bicyclic ring system. The peaks at δ 126.2, δ 128.3, and δ 129.9 ppm correspond to the bridge carbons and to the unsubstituted aromatic carbon atoms, respectively. The chemical shift of the substituted carbon of the aromatic ring is observed at δ 131.8 ppm of the carbon-13 spectrum. The chemical shifts from δ 168.0 to δ 177.0 ppm correspond to the carbonyl carbons of the imide, amide, and carboxylic moieties.

Table I. Elemental analysis data of the polyamic acids and polyimides

	Theoretical %				Found %			
Polymers	C	H	N	F	C	H	N	F
AI	63.9	4.17	8.28	—	63.1	4.48	8.04	—
AII	67.5	3.78	8.74	—	66.3	3.99	8.77	—
BI	63.9	4.17	8.28	—	63.1	4.69	9.02	—
BII	67.5	3.78	8.74	—	66.7	3.95	8.69	—
CI	70.6	5.01	6.33	—	70.4	5.07	6.07	—
CII	73.6	4.75	6.61	—	72.9	4.99	6.72	—
DI	56.7	2.93	5.09	—	57.3	3.39	4.75	—
DII	58.6	2.65	5.26	21.4	57.2	2.31	5.36	20.5
EI	55.4	1.94	5.38	21.9	53.3	2.43	5.35	20.7
EII	57.4	1.61	5.58	22.7	56.2	2.47	5.12	22.5

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The carbon-13 NMR spectrum of BII shows a chemical shift at δ 34.3 corresponding to the bridge head carbon atoms of the bicyclic ring system, and a chemical shift at δ 43.6 ppm corresponding to the tertiary carbons of the bicyclic ring system. The chemical shifts at δ 126 and δ 139.0 correspond to the unsubstituted carbon atoms of the aromatic ring system. The chemical shift at 134.4 observed in the spectrum corresponds to the bridge carbons, and the chemical shift from δ 170.1 to δ 177.4 ppm corresponds to imide, carboxylic, and amide carbonyl carbon atoms.

The carbon-13 NMR spectrum of CI shows a chemical shift at δ 18.3 ppm corresponding to the methyl carbon atoms. The chemical shifts

Table II. Infrared absorption peak assignments of the polyamic acids

Functionality	Energy/cm^{-1}	Assignments
N–H	3499–2637	Amide
O–H	3499–2637	Carboxylic
C=O	1872–1878	Anhydride
C=O	1788–1782	Imide
C=O	1726–1729	Imide
C=O	1710–1716	Carboxylic
C=O	1690–1700	Amide
C=C	1604–1620	Bridge
N–C–O	1499–1512	Imide
C–N	1374–1378	Imide
C–F	1100–1200[a,b]	Trifluoromethyl

[a] Infrared C–F absorption of polyamic acid DI.
[b] Infrared C–F absorption of polyamic acid EI.

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Table III. Infrared absorption peak assignments of the polyimides

Functionality	Energy/cm^{-1}	Assignments
N–H	3592–3200	Amide
O–H	3592–3200	Carboxylic
C–H	3100–2631	Methyl
C=O	1788–1782	Imide
C=O	1722–1729	Imide
C=O	1710–1716	Carboxylic
C=O	1690–1700	Amide
C=C	1600–1617	Bridge
N–C–O	1492–1512	Imide
C–N	1374–1378	Imide
C–F	1100–1200[a,b]	Trifluoromethyl

[a] Infrared C–F absorption of polyimide DII.
[b] Infrared C–F absorption of polyimide EII.

from δ 30 to δ 50.0 ppm correspond to the bridge head and tertiary carbons of the bicyclic ring system. The chemical shifts from δ 120.0 to δ 135.0 ppm correspond to the bridge and the unsubstituted carbon atoms of the aromatic ring system. The substituted carbon of the aromatic ring is observed at δ 139.0 ppm. The peaks from δ 170.0 to δ 182.0 ppm correspond to the carbonyl of the imide, amide, and carboxylic moieties.

The carbon-13 NMR spectrum of CII shows a chemical shift at δ 19.4 ppm corresponding to the methyl carbon atoms. The chemical shift at δ 34.6 corresponds to the bridge head carbons of the bicyclic ring, while the chemical shift at δ 44.3 ppm corresponds to the tertiary carbon atoms of the bicyclic ring. The peaks from δ 120.0 to δ 149.0 ppm correspond to the overlapping of the chemical shifts of the unsubstituted carbons of the aromatic ring and the carbons of the double bond in the bicyclic ring system. The chemical shift from δ 170.2 to δ 176.7 ppm corresponds to the carbon of the imide, carboxylic, and amide carbonyls.

The carbon-13 spectrum of DI shows a chemical shift from δ 29.9 to δ 48.2 ppm corresponding to the bridge head carbons and the tertiary carbons of the bicyclic ring system. The peaks observed from δ 100.0 to δ 150.0 ppm correspond to the overlapping of the chemical shifts of the unsubstituted, substituted, trifluoromethyl carbon atoms of the aromatic ring system and the bridge carbons of the bicycle ring system. The chemical shifts from δ 165.0 to δ 180.0 ppm correspond to the carbons of the imide, amide, and carboxylic carbonyls.

The carbon-13 spectrum of DII shows a chemical shift at $\sim\delta$ 30.0 corresponding to the bridge head carbon atoms of the bicyclic ring system; the peaks from δ 125.6 to δ 136.6 ppm correspond to the overlapping

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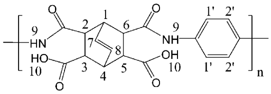
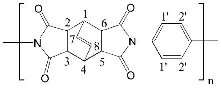
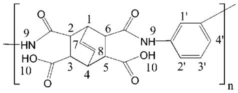
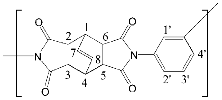
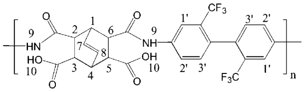
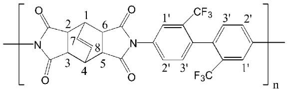
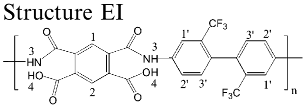
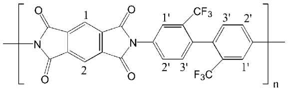
Table IV. Proton NMR data of polymers

Polymer	Proton number	Chemical shift assignment (ppm)
Structure AI	5, 6	3.3
	1, 4	3.5
	9	5.3
	7, 8	6.3
	1′, 2′	7.3
	Bicyclic exo, endo	6.5, 6.7
	2, 3	7.4, 7.6
	10	10.1
Structure AII	2, 3, 5, 6	1.5
	7, 8	4.0
	1′, 2′	8.7
	1, 4	3.5
Structure BI	2, 3, 5, 6	3.5
	1, 4	3.7
	9	5.3
	7, 8	6.3
	1′	6.1
	2′	6.9
	3′	7.2
Structure BII	2, 3, 5, 6	3.6
	1, 4	3.7
	7, 8	7.5
	1′, 2′, 3′, 4′	8.7
Structure DI	2, 3, 5, 6	3.5
	1, 4	3.6
	9	5.7
	7, 8	6.4
	1′, 2′, 3′	7.6–7.8
Structure DII	2, 3, 5, 6	3.5
	1, 4	3.6
	7, 8	6.4
	1′, 2′, 3′	7.6–7.8
Structure EI	3	5.8
	1–3′	7.8–8.6
	4	10.8
Structure EII		
	1–3′	7.3–8.5

Due to intractability of polymers CI and CII, solution NMR was not possible for these samples.

of the chemical shifts of the substituted aromatic carbon atoms, the carbon of the bridge of the bicyclic ring, and the carbons of the trifluoromethyl groups. The chemical shift at δ 177.3 corresponds to the carbon of the imide carbonyl.

The carbon-13 NMR spectrum of EI shows a broad chemical shift from δ 112 to δ 140 ppm corresponding to the overlapping of the chemical shifts of the aromatic and trifluoromethyl carbon atoms. The chemical shifts from δ 160 to δ 170 ppm correspond to the overlapping of the chemical shifts of the imide, amide, and carboxylic carbon atoms.

The carbon-13 NMR spectrum of EI shows a broad chemical shift from δ 115 to δ 142 ppm corresponding to the overlapping of the chemical shifts of the aromatic and trifluoromethyl carbon atoms. The chemical shifts at δ 170 ppm correspond to the overlapping of the chemical shifts of the imide carbon atom.

Table V summarizes the solubility of the polyamic acids and polyimides in different organic and inorganic solvents at room temperature and their viscosities. The solubility data show that 1,4-phenylenediamine and 1,3-phenylenediamine containing polyamic acids, AI, BI, and corresponding polyimides, AII, BII, were generally soluble in corrosive solvents such as concentrated sulfuric acid and methane sulfonic acid (MSA). In general, 1,4- and 1,3-phenylene containing polyamic acids and the corresponding polyimides were found to be in organic solvents,

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Table V. Solubility properties and inherent viscosity measurements of the polyamic acids and the polyimides

	Inherent viscosity	Solubility							
Polymer	dL/g	NMP	DMAc	DMF	DMSO	H_2SO_4	MSA	TMU	Acetone
AI	0.2^a	+−	−	+−	+	+	+	−	−
AII	0.3^a	+−	+−	−	+−	+	+	+−	−
BI	0.3^a	+−	−	+	+	+	+	−	−
BII	0.4^a	−	+−	−	+−	+	+	+−	−
CI	0.3^a	−	−	−	−	+	+−	−	−
CII	0.4^a	−	−	−	−	+	+	−	−
DI	0.2^b	+	+	+	+	+	+	+	+
DII	0.8^b	+	+	+	+	+	+	+	+
EI	0.5^b	+	+	+	+	+	+	+	+
EII	0.7^b	+−	+−	+	+−	+	+	+−	+−

[a] Viscosities measured in concentrated sulfuric acid.

[b] Viscosities measured in dimethyl sulfoxide (DMSO).

(+), soluble; (+−), partially soluble; (–), insoluble; NMP, 1-methyl-2-pyrrolidinone; DMAc, dimethylacetamide; DMF, dimethylformamide; MSA, methane sulfonic acid; TMU, tetramethylurea.

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such as dimethyl sulfoxide (DMSO). Solubility results indicate that the polyamic acid CI and the corresponding polyimide CII were soluble in corrosive solvents, such as concentrated sulfuric acid and MSA. Polyamic acids DI and EI and polyimide DII were soluble in all the solvents that were tested. Polyimide EII was partially soluble in all the solvents that were tested. The decreased solubility of EI is attributed to the presence of 1,2,4,5-benzene tetracarboxylic acid dianhydride, increasing the aromatic character of the polymer. The increased solubility of polyamic acids DI and EI and polyimide DII is attributed to the flexibility of the polymer backbone due to the non-coplanar character of the diamine used in the polymerization. Also, the electron-withdrawing properties of the trifluoromethyl group reduced the intractability of these polymers.

Table VI. Thermoanalysis data of polymers

	Thermal analysis data	
Polymer	Argon, °C	Air, °C
AI	407 T_d[1]	350
	408 T_d[2]	397
AII	421 T_d[1]	400
	460 T_d[2]	422
BI	409 T_d[1]	400
	401 T_d[2]	400
BII	415 T_d[1]	390
	456 T_d[2]	393
CI	Not observed T_d[1]	Not observed
	462 T_d[2]	490
CII	Not observed T_d[1]	Not observed
	448 T_d[2]	501
DI	T_g 203	201
	T_d[1] 400	400
	414 T_d[2]	480
DII	T_m 386	324
	Not observed	T_g 231
	T_d[2] 425	494
EI	T_g 233	234
	T_d[1] 401	400
	T_d[2] 602	581
EII	T_g 184	184
	T_d[2] 363	393

[1] Decomposition transitions measured using DSC.

[2] Decompostion transitions measured using TGA.

[3] Formation of blue and yellow birefringence fluid observed under hot stage optical polarizing microscope.

Table VII. Morphology data of the polyamic acids and the polyimides

Polymer	Morphology
AI	Amorphous
AII	Semicrystalline
BI	Amorphous
BII	Semicrystalline
CI	Amorphous
CII	Semicrystalline
DI	Amorphous
DII	Crystalline
EI	Amorphous
EII	Amorphous

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The observed low inherent viscosities suggest low molecular weights. The slight difference in inherent viscosities of polyamic acids AI, BI, and CI versus the corresponding polyimides AII, BII, and CII indicated that no significant changes in the degree of polymerization occurred in the thermal conversion from polyamic acids to the polyimides. Higher inherent viscosities were observed for polyimides DII and EII derived from 2,2′-bis(trifluoromethyl)benzidine, suggesting higher molecular weights.

Thermal analysis data of the polymers are presented in Table VI. The results indicate that in general, the polyimides derived from disubstituted biphenyl moieties (CF_3 or CH_3) and bicyclic ring systems exhibited high thermo-oxidative stability.

The morphology of the polyamic acids and the corresponding polyimides is summarized in Table VII. The data show that in general the polyimides are more ordered than the corresponding polyamic acid.

SUMMARY

Polyimides derived from unsubstituted phenyl moieties and bicyclo[2.2.2]oct-7-ene rings exhibited enhanced solubility compared to wholly aromatic polyimides while maintaining high thermal stability. Polyimides containing 2,2-disubstituted biphenyl moieties with trifluoromethyl groups (CF_3) exhibited enhanced solubility over those derived from 3,3′-disubstituted biphenyl moieties with methyl (CH_3) groups. Thermal and thermo-oxidative stability was higher for polyimides derived from disubstituted biphenyl moieties (CF_3 or CH_3) and bicyclic ring systems. Polymers with biphenyl moieties substituted in the 2,2′ positions with trifluoromethyl groups (CF_3) exhibited higher crystalline order than polymers substituted in the 3,3′ position with methyl groups (CH_3).

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