Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Characterization of High Temperature Polyimides from Bicyclic Dianhydrides

Ernest V. Pascoe[a]; Issifu I. Harruna[a]
[a] Department of Chemistry, Clark Atlanta University, Atlanta, Georgia, USA

To cite this Article Pascoe, Ernest V. and Harruna, Issifu I.(2003) 'Synthesis and Characterization of High Temperature Polyimides from Bicyclic Dianhydrides', Journal of Macromolecular Science, Part A, 40: 9, 915 — 932

To link to this Article: DOI: 10.1081/MA-120023527

URL: http://dx.doi.org/10.1081/MA-120023527

JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. A40, No. 9, pp. 915–932, 2003

Synthesis and Characterization of High Temperature Polyimides from Bicyclic Dianhydrides

Ernest V. Pascoe and Issifu I. Harruna*

Department of Chemistry, Clark Atlanta University, Atlanta, Georgia, USA

ABSTRACT

Polyimides were synthesized from bicylic dianhydrides and diamines. The bicyclic monomers used were bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCDA), 1,4,7,8-tetrabromobicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride, and 1,4,7,8-tetrachlorobicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride. The diamines used were benzidine, 4,4′-diaminodiphenyl ether, 4,4′-(hexafluoroisopropylidene)dianiline and 4,4′-(1,4-phenylenedioxy)dianiline. Each dianhydride was polycondensed with each of the diamines in *N*-methyl pyrrolidinone (NMP) at elevated temperatures. The polymers were characterized by means of IR and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, solubility and thermal analysis such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Thermogravimetric analysis studies indicate that the polymers were all stable to above 320°C. Most of the polymers were found to be soluble in highly polar solvents such as dimethyl sulfoxide (DMSO), NMP, dimethyl acetamide (DMAc) as well as concentrated sulfuric acid. Thermal studies of the behavior of the bicyclic components of the polyimides were carried out by the use of low molecular weight imide dimers. The results obtained indicate that the bicyclic ring system undergoes a thermal retro Diels-Alder reaction thus separating into two fragments.

---

*Correspondence: Issifu I. Harruna, Department of Chemistry, Clark Atlanta University, Atlanta, GA 30314, USA; Fax: 404-880-6890; E-mail: iharruna@cau.edu.

DOI: 10.1081/MA-120023527
1060-1325 (Print); 1520-5738 (Online)
www.dekker.com

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Key Words: Polyimides; Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydrides; Degradation; Retro Diels-Alder reaction.

INTRODUCTION

Aromatic heterocyclic polyimides such as Dupont's Kapton® and General Electric's Ultem® are important because of their high thermal stability, mechanical strength, chemical resistance, and good electrical properties.[1–17] Industrially, they often find application as engineering super plastics where they are used in place of materials such as iron and steel.

Despite their many desirable properties, wholly aromatic polyimides are very difficult to process into fibers and films due to their poor solubility in common solvents and their high melt temperatures. The high thermal stability and poor solubility of wholly aromatic polyimides is due to the presence of the aromatic rings along the polymer backbone. Processing of polymers is generally carried out by melt or solution techniques. It is therefore important for these polymers to be in solution or in the stable molten state to enhance processing. Since high temperature polyimides generally show great solvent resistance and have high melt temperatures, sometimes even decomposing without melting, low cost processing techniques are lacking.

Various methods have been reported for the synthesis of aromatic polyimides but the most common is the solution polycondensation of a diamine and a dianhydride in an appropriate solvent.[18] Intense synthetic efforts have been devoted to overcoming the problems experienced in the processing of high temperature polyimides. One approach is to produce more soluble polyimides that still retain the sought-after properties associated with these polymers. Several approaches, often used in combination, have been used to accomplish this objective. These include random copolymerization, introduction of kinks or bends in the polymer chain, asymmetric substitution, and the inclusion of randomly spaced flexible chain segments. A lot of effort has been directed towards improving the solubility of polyimides by introducing bulky pendent groups into the backbone and increasing flexibility along the chain of the polymer.[19–21] The fluorinated dianhydride monomer, hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride) has been widely studied because it gives highly soluble polyimides while exhibiting good thermal stability.[22] It has also been reported that the use of noncoplanar[23,24] and bulky diamines[25,26] can improve the solubility of polyimides when employed as monomers. Also, noncoplanar dianhydrides have been shown to improve solubility.[27]

Polyimides derived from cyclic dianhydrides show good solubility in organic solvents while still maintaining good thermal stability.[28] Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCDA) along with 1,4,7,8-tetrabromobicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride and 1,4,7,8-tetrachlorobicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride were therefore selected as monomers to study. These bicyclic systems were chosen because the rigid nature of the bicyclic ring would ensure that polymers synthesized from these monomers display high performance properties such as, thermal stability comparable to the wholly aromatic form, while being sufficiently soluble for processing to be feasible.

EXPERIMENTAL

Materials

The monomers, 1,4,7,8-tetrabromobicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (**IV**) and 1,4,7,8-tetrachlorobicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (**V**) were synthesized from tetrabromothiophene-1,1-dioxide and tetrachlorothiophene-1,1-dioxide, respectively, and two equivalents of maleic anhydride. The dioxides, tetrabromothiophene-1,1-dioxide and tetrachloro-1,1-dioxide were obtained from the oxidation of tetrabromothiophene and tetrachlorothiophene, respectively. Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride, maleic anhydride, tetrabromothiophene, tetrachlorothiophene, 57–86% 3-chloroperoxybenzoic acid and the solvents, 1,2-dichloroethane, bromobenzene, *N*-methyl pyrrolidinone (NMP), carbon tetrachloride, and hexane were obtained commercially. The amines, benzidine, 4,4′-diaminodiphenyl ether, 4,4′-(hexafluoroisopropylidene)dianiline, 4,4′-(1,4-phenylenedioxy)dianiline, and aniline were also obtained commercially.

The monomers were purified by recrystalization and sublimation. Solvents were freshly distilled and stored over molecular sieves.

Measurements

Infrared spectra were obtained using a Nicolet Omnicon FTIR spectrometer. The samples were prepared by grinding a small portion into a pellet with KBr. ^{1}H nuclear magnetic resonance (NMR) were obtained in deuterated dimethylsulfoxide (DMSO) using a Bruker WM-250 spectrometer while solid state ^{13}C NMR were obtained using a Bruker DSX 300 spectrometer. ^{1}H NMR were referred to tetramethylsilane (TMS) at 0.00 ppm. Mass spectra were obtained using the Hewlett Packard Gas Chromagraph/Mass Spectrum Series 5972. Elemental analysis data were provided by the Atlantic Microlab, Inc., Atlanta, GA.

Thermogravimetric analysis data were determined in nitrogen atmosphere with a TA Instruments SDT 2960 simultaneous DTA–TGA thermogravimetric analyzer. Open platinum or ceramic pans were used as both reference and sample holders and a heating rate of $10^\circ\text{C min}^{-1}$ was employed. Differential scanning calorimetry (DSC) was performed on a Seiko Scientific Instrument (SSI) DSC 220 differential scanning calorimeter. Transitions were taken as peak minima (endotherm) and peak maxima (exotherm). Differential scanning calorimetric curves were obtained from samples placed into sealed aluminum sample pans. Empty sealed aluminum pans were used as references. The heating rate was $10^\circ\text{C min}^{-1}$. Melting points of the monomers and intermediates were determined using the Melt-temp capillary melting apparatus. Lyotropic behavior was studied using a Leitz polarizing optical microscope.

Solubility studies were carried as follows: A powdered polymer sample (5–10 mg) was placed in a test tube to which approximately 5 mL of the test solvent was added. The tube was then heated to the boiling point of the solvent but not above 180°C and left to stand overnight at room temperature. Solubility was visually determined.

Inherent viscosity was measured at 30°C with a calibrated Cannon-Fenske viscometer at a concentration of 0.5 g/100 mL of polymer in NMP or concentrated sulfuric acid. Decomposition studies on the model compounds (imide dimers) were carried out in the following manner. A powdered sample of the dimer (0.25 g) was placed in a two-necked 10 mL distillation flask equipped with a nitrogen inlet tube, sitting in a heating mantle filled with sand. The flask was connected to a 10 mL two-necked collecting flask via a still body (condenser). The still body was equipped with a water inlet and outlet along with a vacuum outlet. The two-necked collecting vessel, which was clamped inside a dewar filled with liquid nitrogen, was equipped with an outlet to a drying tube and bubbler. The sample was slowly heated to 400°C while maintaining a steady water flow, a slow nitrogen flow, and a gentle vacuum. The fragments that were collected in the collecting vessel were then allowed to cool, dissolved in acetone, and analyzed by GC–Mass spectroscopy.

Monomers Synthesis

The monomers **IV** and **V** were synthesized from tetrabromothiophene and tetrachlorothiophene, respectively. The thiophenes were first oxidized to the thiophene dioxides and then made to undergo a double Diels-Alder reaction with two equivalents of maleic anhydride. The thiophenes were converted to thiophene dioxides by the procedure outlined by Raasch.[30] Conversion of the thiophene dioxides to the bicyclic dianhydrides was performed according to the procedure reported by Melles.[31]

Tetrabromothiophene-1,1-dioxide (I)

Tetrabromothiophene (45.00 g, 0.1126 moles) was refluxed with 57–86% 3-chloroperoxybenzoic acid (84.00 g) in 1,2-dichloroethane (750 mL) in a 2 L three-necked round-bottom flask equipped with a condenser. The reaction was refluxed for approximately 5 days. The solution was then cooled and the 3-chlorobenzoic acid that had precipitated was filtered off. The filtrate was then washed twice with a 5% sodium bicarbonate solution, dried with magnesium sulfate and treated with decolorizing charcoal. The solution was rotorvaporated to dryness and the residue recrystalized from carbon tetrachloride to give tetrabromothiophene-1,1-dioxide. Yield 25.9 g (53.3%), mp = 202–204°C (Lit.[30] 201–202°C). Infrared spectrum (KBr): 1578 and 1539 cm^{-1} (conjugated C=C), 1341 cm^{-1} (SO_2). Anal. Calcd for $C_4Br_4O_2S$: C, 11.12; Br, 74.03; S, 7.43. Found: C, 11.29; Br, 73.81; S, 7.38.

Tetrachlorothiophene-1,1-dioxide (II)

This compound was synthesized in a manner similar to compound **I**. Yield 42.0%, mp = 89–90°C (Lit.[30] 90–91°C). Infrared spectrum (KBr): 1604 and 1565 cm^{-1} (conjugated C=C), 1348 cm^{-1} (SO_2). Anal. Calcd for $C_4Cl_4O_2S$: C, 18.92; Cl, 55.84; S, 12.63. Found: C, 19.02; Cl, 55.96; S, 12.74.

1,4,7,8-Tetrabromobicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic Dianhydride (IV)

Tetrabromothiophene-1,1-dioxide (2.00 g, 0.0046 moles) was refluxed with maleic anhydride (0.91 g, 0.0093 moles) in a 100 mL three-necked round-bottom flask containing bromobenzene (25 mL) as the solvent. The solution was refluxed for approximately 5 days and then cooled to room temperature. The crystallized product, 1,4,7,8-tetrabromobicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride was then filtered and dried at 150°C under vacuum. Yield 1.14 g (44.0%), mp = 353–354°C. Infrared spectrum (KBr): 1863 and 1785 cm^{-1} (C═O). ^{1}H NMR (250 MHz, DMSO-d_6): δ 4.22 ppm (protons on the carbon α to the C═O). Mass spectrum m/z 560 [M^+], Anal. Calcd for $C_{12}H_4Br_4O_6$: C, 25.56; H, 0.71; Br, 56.69. Found: C, 26.26; H, 0.75; Br, 55.54.

1,4,7,8-Tetrachlorobicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic Dianhydride (V)

This compound was synthesized in a manner similar to compound **IV**. Yield: 41.8% mp = 344–345°C. Infrared spectrum (KBr): 1886 and 1802 cm^{-1} (C═O). ^{1}H NMR (250 MHz, DMSO-d_6): δ 4.32 ppm (protons on the carbon α to the C═O). Mass spectrum m/z 384 [M^+], Anal. Calcd for $C_{12}H_4Cl_4O_6$: C, 37.34; H, 1.04; Cl, 36.74. Found: C, 38.01; H, 1.14; Cl, 35.80.

Polymer Synthesis

Polymer **VIa**

A thoroughly dried 500 mL three-necked round-bottom flask was equipped with a magnetic stir bar, a nitrogen inlet tube, a reflux condenser with a drying tube, a thermometer and a bubbler, and the apparatus flushed with nitrogen. Benzidine (2.97 g, 0.0161 moles) was dissolved in anhydrous NMP (70 mL) with stirring while maintaining the nitrogen flow. A solution of BCDA (4.00 g, 0.0161 moles) in NMP (70 mL) was rapidly injected into the reaction flask. The mixture was stirred at 0°C for 1 h, slowly heated to 30–35°C and maintained for 24 h, and finally heated to 180°C and maintained for an additional 24 h. The reaction mixture was then precipitated in water, washed with ethanol and then extracted with acetone in a Soxhlet extractor for 48 h. The product was dried at 100°C for 24 h. Yield 6.29 g (98.6%), mp = 438°C dec. Infrared spectrum (KBr): 1789 cm^{-1} (imide C═O symmetrical stretching), 1716 cm^{-1} (imide C═O asymmetrical stretching), 1508 cm^{-1} (benzene C═C stretching), 1387 cm^{-1} (C—N stretching). ^{13}C-NMR (300 MHz, solid state): δ 33.43 ppm (bicyclic ring, C-1,4), 42.11 ppm (bicyclic ring, C-2,3,5,6), 125–130 ppm (benzene, C-2′-4′), 138.87 ppm (benzene, C-1′); 175.61 ppm (C═O, C-9,10,11,12).

Polymer **VIb**

This polymer was synthesized in a manner similar to polymer **VIa** mp = 435°C dec. Infrared spectrum (KBr): 1782 cm^{-1} (imide C═O symmetrical stretching), 1712 cm^{-1} (imide C═O asymmetrical stretching), 1502 cm^{-1} (benzene C═C stretching), 1390 cm^{-1} (C—N stretching). ^{13}C-NMR (300 MHz, solid state): δ 33.02 ppm (bicyclic ring, C-1,4), 42.62 ppm (bicyclic ring, C-2,3,5,6), 120–137 ppm (benzene, C-1′-3′); 176.44 ppm (C═O, C-9,10,11,12).

Polymer **VIc**

This polymer was synthesized in a manner similar to polymer **VIa** mp = 427°C dec. Infrared spectrum (KBr): 1782 cm^{-1} (imide C=O symmetrical stretching), 1716 cm^{-1} (imide C=O asymmetrical stretching), 1624 and 1525 cm^{-1} (benzene C=C stretching), 1380 cm^{-1} (C—N stretching). ^{13}C-NMR (300 MHz, solid state): δ 33.44 ppm (bicyclic ring, C-1,4), 43.09 ppm (bicyclic ring, C-2,3,5,6), 120–135 ppm (benzene, C-1′-5′), 175.79 ppm (C=O, C-9,10,11,12).

Polymer **VId**

This polymer was synthesized in a manner similar to polymer **VIa** mp = 433°C dec. Infrared spectrum (KBr): 1789 cm^{-1} (imide C=O symmetrical stretching), 1720 cm^{-1} (imide C=O asymmetrical stretching), 1620 and 1498 cm^{-1} (benzene C=C stretching), 1390 cm^{-1} (C—N stretching). ^{13}C-NMR (300 MHz, solid state): δ 34.37 ppm (C-1,4), 42.16 (C-2,3,5,6), 110–135 ppm (C-1′-3′,6′), 145–160 ppm (C-4′,5′), 176.16 ppm (C-9,10,11,12). Anal. Calcd for $C_{30}H_{20}N_2O_6$: C, 71.41; H, 4.00; N, 5.57. Found: C, 69.14; H, 4.43; N, 6.25.

Polymer **VIIa**

This polymer was synthesized in a manner similar to polymer **VIa** mp = 379°C dec. Infrared spectrum (KBr): 1795 cm^{-1} (imide C=O symmetrical stretching), 1729 cm^{-1} (imide C=O asymmetrical stretching), 1545 and 1506 cm^{-1} (benzene C=C stretching), 1381 cm^{-1} (C—N stretching). ^{13}C-NMR (300 MHz, solid state): δ 50.35 ppm (bicyclic ring, C-2,3,5,6), 120–135 ppm (benzene, C-1′-4′), 168.84 ppm (C=O, C-9,10,11,12).

Polymer **VIIb**

This polymer was synthesized in a manner similar to polymer **VIa** mp = 351°C dec. Infrared spectrum (KBr): 1789 cm^{-1} (imide C=O symmetrical stretching), 1729 cm^{-1} (imide C=O asymmetrical stretching), 1545 and 1505 cm^{-1} (benzene C=C stretching), 1394 cm^{-1} (C—N stretching). ^{13}C-NMR (300 MHz, solid state): δ 50.92 ppm (bicyclic ring, C-2,3,5,6), 110–135 ppm (benzene, C-1′-3′), 171.71 ppm (C=O, C-9,10,11,12).

Polymer **VIIc**

This polymer was synthesized in a manner similar to polymer **VIa** mp = 352°C dec. Infrared spectrum (KBr): 1795 cm^{-1} (imide C=O symmetrical stretching), 1736 cm^{-1} (imide C=O asymmetrical stretching), 1618 and 1525 cm^{-1} (benzene C=C stretching), 1381 cm^{-1} (C—N stretching). ^{13}C-NMR (300 MHz, solid state): δ 51.00 ppm (bicyclic ring, C-2,3,5,6), 120–140 ppm (benzene, C-1′-5′), 169.77 ppm (C=O, C-9,10,11,12).

Polymer **VIId**

This polymer was synthesized in a manner similar to polymer **VIa** mp = 357°C dec. Infrared spectrum (KBr): 1802 cm^{-1} (imide C=O symmetrical stretching), 1736 cm^{-1} (imide C=O asymmetrical stretching), 1631 and 1499 cm^{-1} (benzene C=C stretching), 1394 cm^{-1} (C—N stretching). ^{13}C-NMR (300 MHz, solid state): δ 51.39 ppm (bicyclic ring, C-2,3,5,6), 115–135 ppm (benzene, C-1′-3′,6′), 145–160 ppm (benzene, C-4′,5′), 169.71 ppm (C=O, C-9,19,11,12).

Polymer **VIIIa**

This polymer was synthesized in a manner similar to polymer **VIa** mp = 365°C dec. Infrared spectrum (KBr): 1802 cm^{-1} (imide C=O symmetrical stretching), 1736 cm^{-1} (imide C=O asymmetrical stretching), 1506 cm^{-1} (benzene C=C stretching), 1381 cm^{-1} (C—N stretching). ^{13}C-NMR (300 MHz, solid state): δ 50.11 ppm (bicyclic ring, C-2,3,5,6), 120–135 ppm (benzene, C-1′-4′), 169.44 ppm (C=O, C-9,10,11,12).

Polymer **VIIIb**

This polymer was synthesized in a manner similar to polymer **VIa** mp = 362°C dec. Infrared spectrum (KBr): 1790 cm^{-1} (imide C=O symmetrical stretching), 1726 cm^{-1} (imide C=O asymmetrical stretching), 1649 and 1509 cm^{-1} (benzene C=C stretching), 1390 cm^{-1} (C–N stretching). ^{13}C-NMR (300 MHz, solid state): δ 51.05 ppm (bicyclic ring, C-2,3,5,6), 110–135 ppm (benzene, C-1′-3′), 168.90 ppm (C=O, C-9,10,11,12).

Polymer **VIIIc**

This polymer was synthesized in a manner similar to polymer **VIa** mp = 324°C dec. Infrared spectrum (KBr): 1796 cm^{-1} (imide C=O symmetrical stretching), 1726 cm^{-1} (imide C=O asymmetrical stretching), 1684 and 1523 cm^{-1} (benzene C=C stretching), 1390 cm^{-1} (C—N stretching). ^{13}C-NMR (300 MHz, solid state): δ 51.24 ppm (bicyclic ring, C-2,3,5,6), 120–140 ppm (benzene, C-1′-6′), 169.92 ppm (C=O, C-9,10,11,12).

Polymer **VIIId**

This polymer was synthesized in a manner similar to polymer **VIa** mp = 330°C dec. Infrared spectrum (KBr): 1796 cm^{-1} (imide C=O symmetrical stretching), 1740 cm^{-1} (imide C=O asymmetrical stretching), 1621 and 1495 cm^{-1} (benzene C=C stretching), 1382 cm^{-1} (C–N stretching). ^{13}C-NMR (300 MHz, solid state): δ 51.56 ppm (bicyclic ring, C-2,3,5,6), 110–135 ppm (benzene, C-1′-3′,6′), 145–160 (benzene, C-4′,5′), 169.74 ppm (C=O, C-9,10,11,12).

Synthesis of Model Compounds

N,*N*′-Diphenylbicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboximide (**IX**)

A thoroughly dried 500 mL three-necked round-bottom flask was equipped with a magnetic stir bar, a nitrogen inlet tube, a reflux condenser with a drying tube, a Dean Stark trap, a thermometer and a bubbler, and the apparatus flushed with nitrogen. Aniline (2.94 mL, 0.0322 moles) was added to anhydrous NMP (70 mL) in the flask with stirring while maintaining the nitrogen flow. A solution of BCDA (4.00 g, 0.0161 moles) in NMP (70 mL) was rapidly injected into the reaction flask. The mixture was stirred at 0°C for 1 h, slowly heated to 30–35°C and maintained for 24 h, and finally heated to 180°C and maintained for an additional 24 h. The reaction mixture was then precipitated in water and filtered. The product was then dried at 100°C for 24 h. Yield 6.38 g (99.4%). mp = 374°C dec. Infrared spectrum (KBr): 1782 cm^{-1} (imide C=O symmetrical stretching), 1716 cm^{-1} (imide C=O asymmetrical stretching), 1604 and 1499 cm^{-1} (benzene C=C stretching), 1394 cm^{-1} (C—N stretching). ^1H NMR (250 MHz, DMSO-d_6): δ 3.42 ppm (4H, H-2,3,5.6), 3.53 ppm (2H, H-1,4), 6.31 pmm (2H, H-7,8), 7.16 ppm (4H, d, H-2′), 7.40 ppm (2H, d, H-4′), 7.46 ppm (4H, dd, H-3′). Mass spectrum *m*/*z* 398 [M^+].

N,*N*′-Diphenyl-1,4,7,8-tetrabromobicyclo[2.2.2]oct-7-ene-
2,3,5,6-carboximide (**X**)

This model compound was synthesized in a manner similar to model compound **IX** mp = 350°C dec. Infrared spectrum (KBr): 1789 cm^{-1} (imide C=O symmetrical stretching), 1736 cm^{-1} (imide C=O asymmetrical stretching), 1552 and 1506 cm^{-1} (benzene C=C stretching), 1394 cm^{-1} (C—N stretching). ^1H NMR (250 MHz, DMSO-d_6): δ 4.00 ppm (4H, H-2,3,5.6), 7.11 ppm (4H, d, H-2′), 7.46 ppm (2H, d, H-4′), 7.54 ppm (4H, dd, H-3′).

N,*N*′-Diphenyl-1,4,7,8-tetrachlorobicyclo[2.2.2]oct-7-ene-
2,3,5,6-carboximide (**XI**)

This model compound was synthesized in a manner similar to model compound **IX** mp = 353°C dec. Infrared spectrum (KBr): 1795 cm^{-1} (imide C=O symmetrical stretching), 1736 cm^{-1} (imide C=O asymmetrical stretching), 1585 and 1506 cm^{-1} (benzene C=C stretching), 1387 cm^{-1} (C—N stretching). ^1H NMR (250 MHz, DMSO-d_6): δ 4.03 ppm (4H, H-2,3,5.6), 7.11 ppm (4H, d, H-2′), 7.48 ppm (2H, d, H-4′), 7.55 ppm (4H, dd, H-3′).

RESULTS AND DISCUSSION

Monomers

The monomers, 1,4,7,8-tetrabromobicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (**IV**) and 1,4,7,8-tetrachlorobicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (**V**), were synthesized by the oxidation of tetrabromothiophene and tetrachlorothiophene with 3-chloroperoxybenzoic acid in 1,2-dichloroethane[30] to the corresponding dioxides, tetrabromothiophene-1,1-dioxide (**I**) and tetrachlorothiophene-1,1-dioxide (**II**), respectively (Sch. 1). A very strong oxidizing agent such as 3-chloroperoxybenzoic acid was required for this process. Tetrabromothiophene-1,1-dioxide (**I**) and tetrachlorothiophene-1,1-dioxide (**II**) were then used to synthesize 1,4,7,8-tetrabromo-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (**IV**) and 1,4,7,8-tetrachloro-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (**V**).

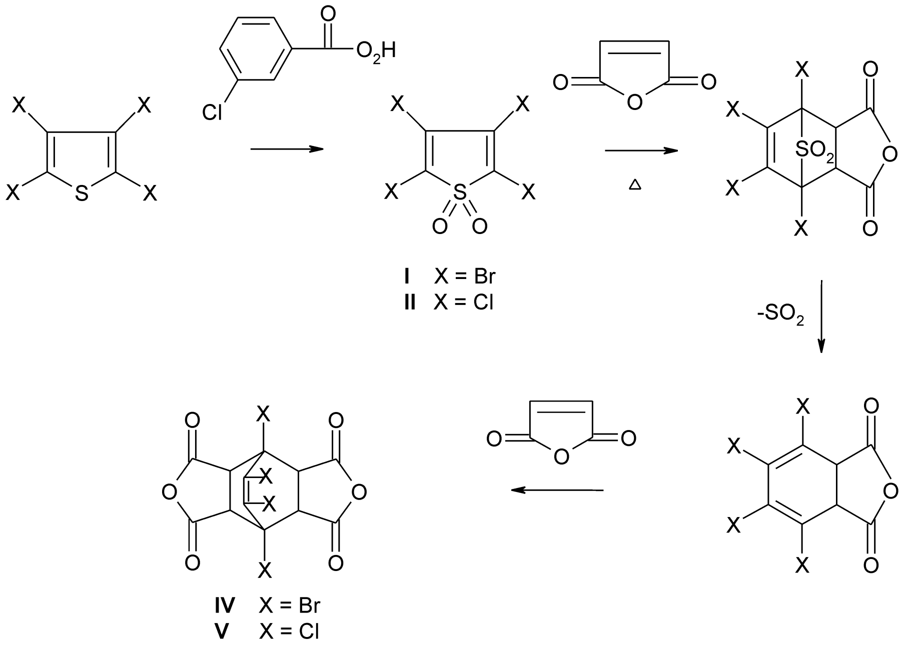
The synthesis of the bicyclic monomers occurs in three steps. The reaction requires refluxing in bromobenzene for approximately 5 days for useful yields to be achieved. In the first step, the dioxide reacts with one equivalent of maleic anhydride to produce an unstable bicyclic intermediate that thermally decomposes, losing sulfur dioxide to form a cyclic diene. In the final step, the diene reacts with another equivalent of maleic anhydride to produce the bicyclic monomer.

The melting points for **I** and **II** were found to be 202–204°C and 89–90°C, respectively. These values are consistent with those observed in the literature.[30]

The IR analyses of **I** show stretching due to the conjugated C=C at 1578 and 1539 cm^{-1} while that for the SO_2 is observed at 1341 cm^{-1}. Similarly for **II** conjugated C=C stretches appear at 1604 and 1565 cm^{-1} and that for the SO_2 at 1348 cm^{-1}.

The IR analyses of **V** show strong stretches due to the carbonyl C=O at 1886 and 1802 cm^{-1}. The carbonyl stretches for **IV** appear at 1863 and 1785 cm^{-1}. The chemical shift for the hydrogen in **IV** occurs at δ 4.22 ppm while that for **V** appear at δ 4.32 ppm.

The mass spectrum of **V** shows the presence of the molecular ion (m/z) peak at 384 [M^+] consistent with theoretical calculations. Similarly, the molecular ion (m/z) peak of **IV** shows up at 560 [M^+].



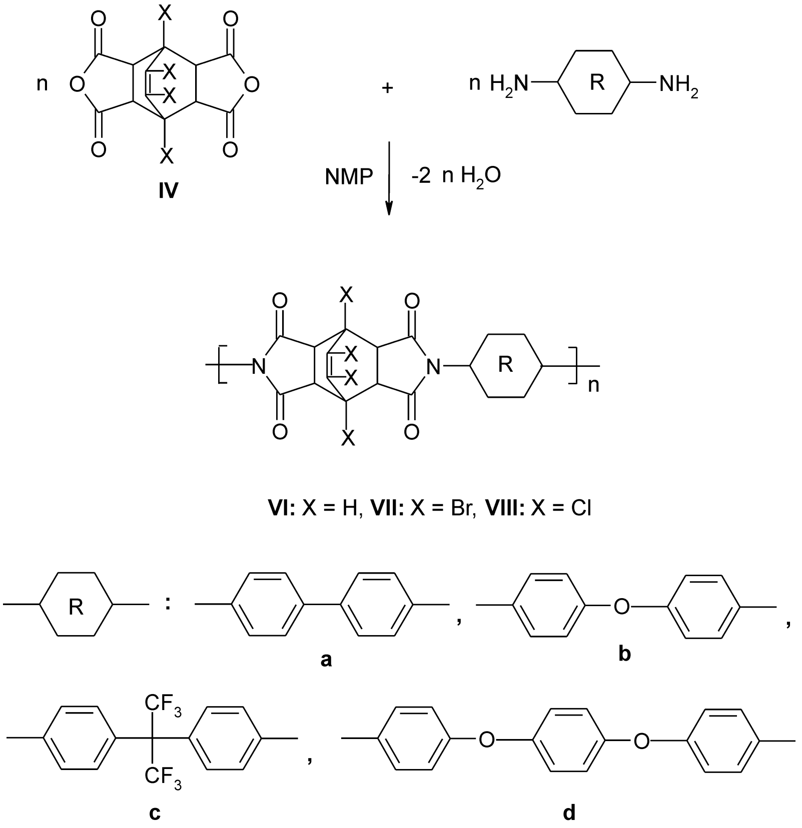
Scheme 1. Synthetic route to **IV** and **V**.

Polymers

Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (**III**), 1,4,7,8-tetrabromo-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (**IV**), and 1,4,7,8-tetrachloro-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (**V**) were utilized with selected diamines to synthesize bicyclic polyimides as illustrated by Sch. 2. The syntheses were carried out by the conventional method of condensation to the polyamic acid (which was not isolated) and then to the polyimide at elevated temperatures.

Imidization was confirmed by the characteristic imide peaks at 1782–1802 cm^{-1} (imide C=O symmetrical stretching), 1712–1740 cm^{-1} (imide C=O asymmetrical stretching), and 1381–1394 cm^{-1} (C—N stretching). Stretching associated with the benzene ring appears between 1495 and 1684 cm^{-1}.

The C=C of the ethylene bridge is not observed because it is overlapped by the imide signal. The data obtained shows a general pattern where the signals of each functional group for the polyimides made from the tetrahalogenated monomers, **IV** and **V** occur at higher frequencies compared to that of the corresponding polyimide made from BCDA (**III**).



Scheme 2. Synthetic route to the bicyclic polymers.

The solid state ^{13}C NMR analyses of **VIa** show signals for the carbons of the cyclohexane ring appearing between 30 and 60 ppm, while that for the benzene ring occur at 110–160 ppm and that for the carbonyl carbons at 165–180 ppm.

The inherent viscosities of the polymers were analyzed using NMP and concentrated sulfuric acid as the solvents (Table 1). The general trend was that the polymers (**VIa**–**VIb**) synthesized from the bicyclic dianhydride, **III** (which lacks halogens) gave higher viscosity values than the others. Within each group, those polymers synthesized from the more flexible diamines gave higher viscosities. The viscosities observed were within the same general range as those observed in literature for bicyclic polyimides.[29]

The T_g endotherms in general were weak and were only observed in polymers **VIb** (356°C) and **VIId** (377°C). The absence of T_g endotherms, and their weak nature when observed, is due to the rigid nature of the polymers. All the bicyclic polymers decomposed without melting (Table 1). Figure 1 shows general TGA curves for the polymers. The onset of decomposition characteristically is above 400°C for the **VIa**–**VId** series but below 400°C (324–380°C) for those from the halogenated bicyclic dianhydrides. The lower onset of decomposition in the latter is due to the presence of the halogens on the bicylic ring.

Attempts to aromatize the bicyclic ring of the polymers with the use of aromatic catalyst such as $ZnCl_2$ and K_2CO_3 were unsuccessful.

Lyotropic fluid formation was not observed in the bicyclic polymers up to concentrations of 10% weight to volume observed using a Leitz polarizing optical microscope.

Table 2 shows the solubility results of the bicyclic polymers in some common solvents. All the polymers were soluble in concentrated sulfuric acid. The polymers in general exhibit good solubility in polar high boiling point organic solvents such as 1-methyl-2-pyrrolindinone (NMP), DMSO, and dimethylacetamide (DMAc). The polymers made from the same diamine showed similar solubility properties. When polymer

Table 1. Characteristics of the polyimides.

Polymers	$\eta_{inh}{}^{b}$ (dL g^{-1})	T_d (°C)
VIa[a]	0.22	438
VIb	0.70	435
VIc	0.36	427
VId	0.50	433
VIIa[a]	0.35	379
VIIb	0.26	351
VIIc	0.26	352
VIId	0.42	357
VIIIa[a]	0.13	365
VIIIb	0.47	362
VIIIc	0.29	324
VIIId	0.21	330

[a] The solvent used for the viscosity study of these polymers was sulfuric acid. For the other polymers the solvent used was NMP.
[b] Measured at a concentration of 0.5 g dL^{-1} at 30°C.

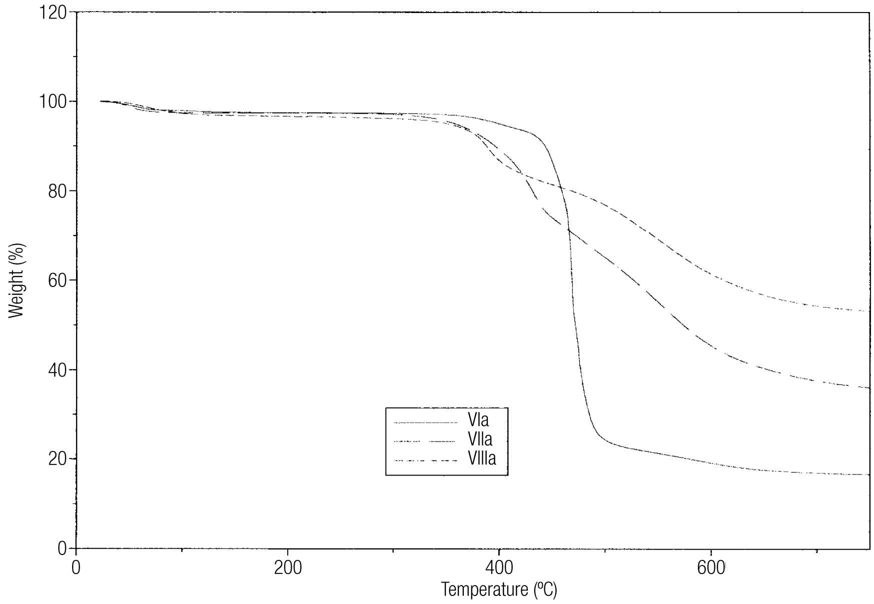


Figure 1. Thermogravimetric analysis thermograms of **VIa**, **VIIa**, and **VIIIa**.

synthesized from **III** and a particular diamine was soluble in a certain solvent, then the corresponding polymers made from **IV** and **V** and that diamine were also soluble in that solvent. This suggests that the polarity of the halogens on the bicyclic ring did not significantly alter the solubility of these polymers. The solubility of the polymers suggest solution techniques, as a processing option.

Table 2. Solubility properties of bicyclic polymers.

	H_2SO_4	NMP	DMSO	DMAc	THF	Methanol	Ethanol
VIa	++	−−	−−	−−	−−	−−	−−
VIb	++	++	++	++	−−	−−	−−
VIc	++	++	++	++	+−	−−	−−
VId	++	++	++	++	−−	−−	−−
VIIa	++	−−	−−	−−	−−	−−	−−
VIIb	++	++	++	++	−−	−−	−−
VIIc	++	++	++	++	+−	−−	−−
VIId	++	++	++	++	−−	−−	−−
VIIIa	++	−−	−−	−−	−−	−−	−−
VIIIb	++	++	++	++	−−	−−	−−
VIIIc	++	++	++	++	+−	−−	−−
VIIId	++	++	++	++	−−	−−	−−

Note: (++), soluble; (+−), partially soluble; (−−), insoluble; H_2SO_4, sulfuric acid; NMP, *N*-methyl pyrrolindinone; DMSO, dimethyl sulfoxide; DMAc, dimethylacetamide; THF, tetrahydrofuran; MeOH, methanol; and EtOH, ethanol.

Dimers

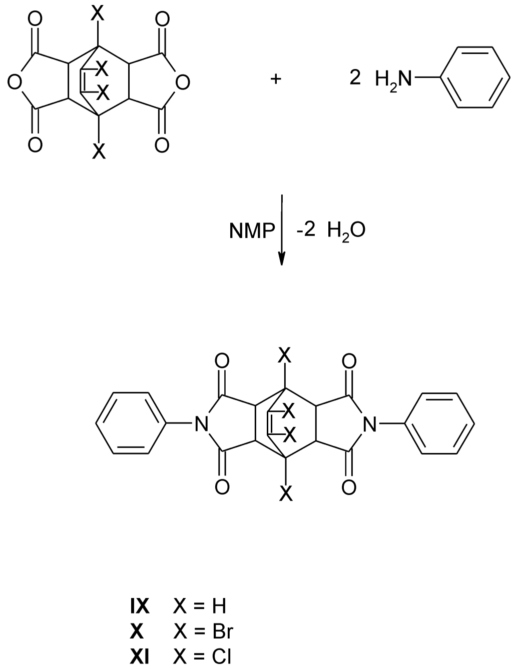
To evaluate the decomposition process of the bicyclic ring three dimers, **IX**, **X**, and **XI** were synthesized as illustrated in Sch. 3. The diimides were used as model compounds for this investigation because they are electronically similar to the polymers and are expected to give cleaner and more easily analyzed fragments in thermal studies. The synthesis of the dimer was carried out by a similar method to that of the polymers.

For the dimers, the symmetrical stretching of the imide shows up at 1782–1796 cm^{-1} in accordance with theory. The asymmetrical stretch is observed at 1716–1736 cm^{-1} and the C—N bond appears at 1387–1394 cm^{-1} while the C=C stretches of the benzene ring are observed at 1499–1604 cm^{-1}.

For the dimer **IX**, the hydrogens of C2,3,5, and 6 give a chemical shift at δ 3.42 ppm in ^1H NMR (250 MHz, DMSO-d_6) studies. The chemical shift of the hydrogens of C1 and C4 appear at 3.53 ppm while that for those protons located on the bridge carbons, C7 and 8, appeared at 6.31 ppm. The hydrogen of the benzene ring appears at δ 7.16–7.46 ppm. The results obtained were consistent with that found in the literature.[5] For the dimers **X** and **XI** the protons of C2,3,5, and 6 are observed at δ 4.00 ppm and 4.03 ppm, respectively. For **X** and **XI**, the protons of the benzene ring show chemical shifts in the range 7.11–7.55 ppm.

The dimer **IX** shows a molecular ion (*m*/*z*) peak at 398, consistent with theoretical calculations of the molecular weight.

Table 3 gives a list of all the fragments obtained from the thermal decomposition of the dimers. Schemes 4 and 5 show the retro Diels-Alder pathway for the decomposition.

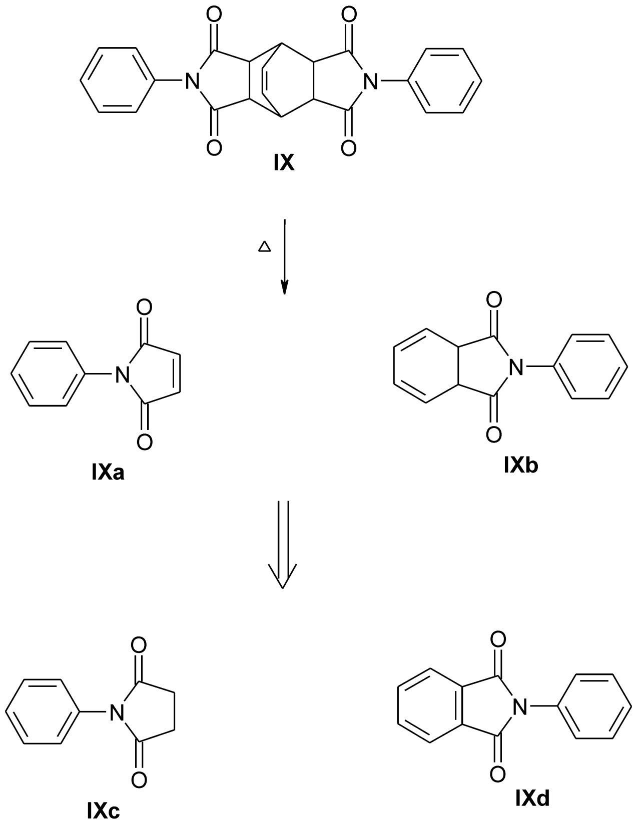


IX X = H
X X = Br
XI X = Cl

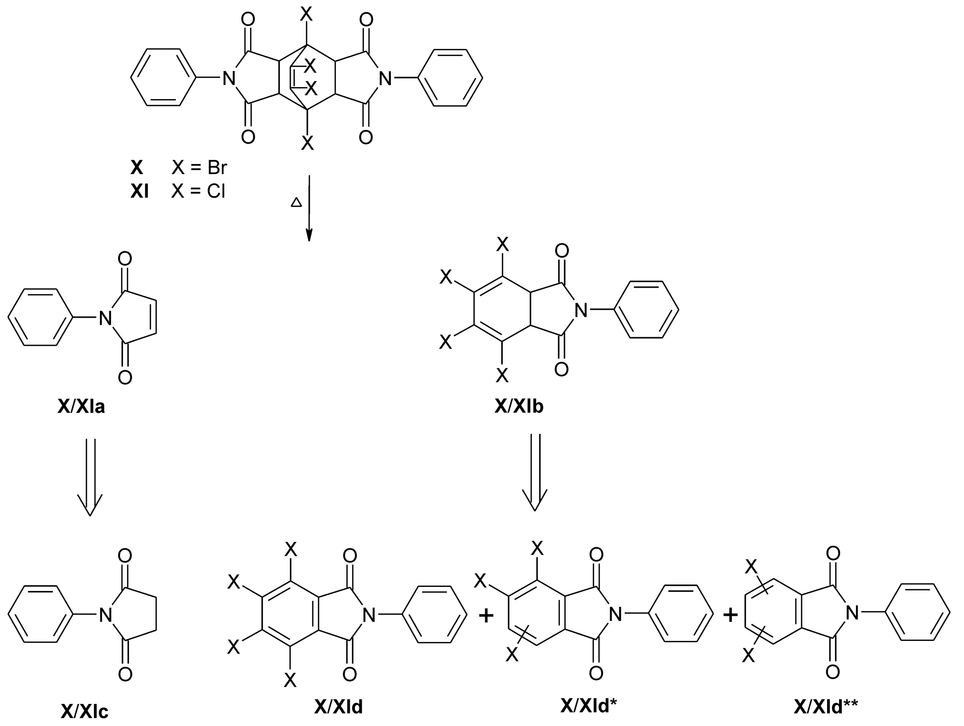
Scheme 3. Synthetic route to the dimers **IX**, **X**, and **XI**.

Table 3. GC–Mass spectroscopy data for the dimers after thermal treatment.

Dimers	Signals				
IX					
GC (min)	10.11	11.15	13.18	23.94	
Molecular ion (m/z) peak	173	175	223	398	
Fragment	**IXa**	**IXc**	**IXd**	**IX**	
X					
GC (min)	10.25	11.09	15.56	17.37	
Molecular ion (m/z) peak	173	175	379	457	
Fragment	**Xa**	**Xc**	**Xd****	**Xd***	
XI					
GC (min)	10.22	11.37	14.84	15.42	16.50
Molecular ion (m/z) peak	173	175	291	325	359
Fragment	**XIa**	**XIc**	**XId****	**XId***	**XId**



Scheme 4. Decomposition of **IX** by a retro Diels-Alder reaction.



Scheme 5. Decomposition of **X** and **XI** by a retro Diels-Alder reaction.

The fragments obtained and reported in Table 3 were consistent with the retro Diels-Alder reaction. For the dimer **IX**, the presence of **IXa**, **IXc**, and **IXd** were all detected but the diene **IXb** was not. The retro Diels-Alder process is supported by previous studies.[5] For the dimer **X**, fragments corresponding to **Xa**, **Xc** were observed.

The tetrahalogenated fragment, **Xd** was not seen. Halogen loss from **Xb** through dehydrohalogenation and halogen substitution leads to the tri and dihalogenated derivatives **Xd*** and **Xd**** (Sch. 5). In the case of the dimer **XI**, the presence of **XIa** and **Xc** were observed. A fragment corresponding to **XId** along with the tri and dihalogenated fragments were also detected. All the fragments containing halogens showed M, M + 2, M + 4 etc., patterns that were consistent with theory.

CONCLUSION

Polyimides containing the bicyclo[2.2.2]oct-7-ene ring system were successfully synthesized from bicyclic dianhydrides (bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride, 1,4,7,8-tetrabromobicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride and 1,4,7,8-tetrachlorobicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride) with selected diamines (benzidine, 4,4′diaminodiphenyl ether, 4,4′-(hexafluoroisopropylidene)dianiline or 4,4′-(1,4-phenylenedioxy)dianiline).

The halogenated dianhydrides were synthesized by the oxidation of the respective tetrahalogenated thiophene to the thiophene dioxide, followed by a double Diels-Alder reaction with two equivalents of maleic anhydride to obtain the dianhydrides.

These polymers showed good thermal stability ranging between 324°C and 437°C. The polyimides synthesized from BCDA (**VIa**–**VId**) in general showed greater thermal stabilities than those from the tetrabromobicyclo dianhydride (**VIIa**–**VIId**) and the tetrachlorobicyclo dianhydride (**VIIIa**–**VIIId**). Glass transition temperatures were not observed for most of the polymers due to the rigid nature of the polymer chain.

Solubility studies of the polymers indicate that they are soluble in polar organic solvents such as NMP, DMSO, and DMAc. This suggests solution techniques as a processing option.

Thermal analysis carried out with model compounds indicated that the bicyclic moiety undergoes a thermal retro Diels-Alder reaction in which the ring separates into two components.

REFERENCES

1. Inoue, T.; Kakimoto, M.; Imai, Y. First observation of a thermotropic liquid crystal in a simple polyimide derived from 1,11-diaminoundecane and 4,4″-therphenyltetracarboxylic acid. Macromolecules **1995**, *28*, 6368–6370.
2. Facinelli, J.V.; Gardener, S.L.; Dong, L.; Sensinich, C.L.; Davis, R.M.; Riffle, J.S. Controlled molecular weight polyimides from poly(amic acid) salt precursors. Macromolecules **1996**, *29*, 7342–7350.
3. Perry, R.J.; Tunney, S.E.; Wilson, B.D. Polyimide formation through the palladium-mediated carbonylation and coupling of bis(o-iodo amides) and diamines. Macromolecules **1996**, *29*, 1014–1020.
4. Koning, C.E.; Teuwen, L.; De Plaen, A. Enhancement of the crystallinity of a thermoplastic polyimide. Polymer **1996**, *37* (25), 5619–5625.
5. Itamura, S.; Yamada, M.; Tamura, S.; Matsumoto, T.; Kurosaki, T. Soluble polyimides with polyalicyclic structures. 1. Polyimides from bicyclo[2.2.2]oct-7-ene-2-exo,3-exo,5-exo,6-exo-tetracarboxylic-2,3:5,6-dianhydrides. Macromolecules **1993**, *26*, 3490–3493.
6. Galia, M.; Monte, D.; Serra, A.; Mantecon, A.; Cadiz, V. Modification of DGEBA with diimide-diacids derived from bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride and crosslinking study. J. Appl. Polym. Sci. **1996**, *60*, 2177–2183.
7. Wantanabe, Y.; Sakai, Y.; Ueda, M.; Oishi, Y.; Mori, K. Synthesis of wholly alicyclic polyimides from N-silylated alicyclic diamines. Chem. Lett. **2000**, *5*, 450–451.
8. Meador, M.A.B.; Johnston, J.C. Oxidative degradation of nadic-end-capped polyimides. 2. Evidence for reactions occurring at high temperatures. Macromolecules **1997**, *30*, 3215–3223.
9. Kreuz, J.A.; Hsiao, B.S.; Renner, C.A.; Goff, D.L. Crystalline homopolyimides and copolyimides derived from 3,3′,4,4′-biphenyltetracarboxylic dianhydride/1,3-bis(4-aminophenoxy)benzene/1,12-dodecanediamine. 1. Materials, preparation and characterization. Macromolecules **1995**, *28*, 6926–6930.
10. Liu, J.; Gao, Y.; Wang, F.; Wu, M. Preparation and characteristics of nonflammable polyimide materials. J. Appl. Polym. Sci. **2000**, *75*, 384–389.

11. Liu, Y.; Hsiue, G.; Lan, C.; Kuo, J.; Jeng, R.; Chiu, Y. Synthesis, thermal properties, and flame retardancy of phosphorus containing polyimides. J. Appl. Polym. Sci. **1997**, *63*, 875–882.
12. Niume, K.; Nakamichi, K.; Takatuka, R.; Toda, F.; Ono, K.; Iwakura, Y. Heat-resistant polymers containing thianthrene analogs units. I. Polyimides. J. Polym. Sci., Part A: Polym. Chem. Ed. **1979**, *17*, 2371–2385.
13. Prema, S.; Srinivasan, M. Synthesis and characterization of polyimides containing heterocyclic units. J. Polym. Sci., Part A: Polym. Chem. Ed. **1988**, *26*, 1553–1560.
14. Niume, K.; Hiroshashi, R.; Toda, F.; Ono, K.; Hasagawa, M.; Iwakura, Y. Thermal and electrical properties of polyimides containing tricyclic fused rings. Polymer **1981**, *22*, 649–654.
15. Pinel, E.; Bas, C.; Neyertz, S.; Aberola, N.D.; Petiaud, R.; Mercier, R. Copolyimides with trifluoromethyl or methoxy substituents. NMR characterization. Polymer **2002**, *43*, 1983–1992.
16. Kuo, W.-J.; Hsiue, G.-H.; Jeng, R.J. Novel guest-host NLO poly(ether imide) based on a two-dimensional carbazole chromophore with sulfonyl acceptors. Macromolecules **2001**, *34*, 2373–2384.
17. Hao, J.; Tanaka, K.; Kita, H.; Okamoto, K.I. Synthesis and properties of polyimides from thianthrene-2,3,7,8-tetracarboxylic dianhydride-5,5,10,10-tetraoxide. J. Polym. Sci., Part A: Polym. Chem. Ed. **1998**, *36*, 485–494.
18. Park, S.K.; Park, S.Y.; Lee, C.J. Direct polymerization of aromatic diacid dimethyl esters with aromatic diamines II. Control of copolyimide chemical structure. Polymer **2000**, *41*, 433–440.
19. Harris, F.W.; Feld, W.A.; Lanier, L.H. Structure-solubility relationships in aromatic polyimides. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) **1976**, *17* (2), 353–358.
20. Imai, Y.; Malder, N.N.; Kakimoto, M. Synthesis and characterization of soluble polyimides from 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene and aromatic tetracarboxylic dianhydrides. J. Polym. Sci., Polym. Chem. Ed. **1984**, *22*, 2189–2196.
21. Arai, M.; Cassidy, P.E.; Farley, J.M. Copolyimidines. 2. Copoly(imidine-imides) from 3,5-dibenzylidenepyromellitide, 4,4′-diaminodiphenyl ether, and various dianhydrides. Macromolecules **1989**, *22*, 989–992.
22. Matsuura, T.; Hasuda, Y.; Nishi, S.; Yamada, N. Polyimide derived from 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl. 1. Synthesis and characterization of polyimides prepared with 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride or pyromellitic dianhydride. Macromolecules **1991**, *24*, 5001–5005.
23. Bateman, J.H.; Gordon, D.A. Soluble polyamide-imides derived from phenylindane diamines. U.S. Pat. 4,026,876, 1977.
24. Elsner, G. Residual stress and thermal expansion of spun-on polyimide films. J. Appl. Polym. Sci. **1987**, *34*, 815–828.
25. Jeong, H.; Oishi, Y.; Kakimoto, M.A.; Imai, Y. Synthesis and characterization of new soluble aromatic polyimides from 3,4-bis(4-aminophenyl)-2,5-diphenylfuran and aromatic tetracarboxylic dianhydrides. J. Polym. Sci., Polym. Chem. Ed. **1991**, *29*, 39–43.
26. Oishi, Y.; Ishida, M.; Kakimoto, M.; Imai, Y.; Kurosaki, T. Preparation and properties of novel soluble aromatic polyimides from 4,4′-diaminotriphenylamine and aromatic tetracarboxylic dianhydrides. J. Polym. Sci., Polym. Chem. Ed. **1992**, *30*, 1027–1035.

27. Falcigno, P.A.; Jasne, S.; King, M. Fully imidized soluble polyimides based on a novel dianhydride: 2,2′-dichloro-4,4′,5,5′-benzophenone tetracarboxylic dianhydride. J. Polym. Sci., Polym. Chem. Ed. **1992**, *30*, 1433–1441.
28. Suzuki, A.; Hojo, N. Preparation and properties of polyimides from bicyclo[2.2.2]oct-7-ene-2,3:5,6-tetracarboxylic dianhydrides and various diamines. J. Chem. Soc. Japan **1980**, *5*, 749–753.
29. Chun, B. Preparation and characterization of organic-soluble optically transparent polyimides from alicyclic dianhydride, bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride. Polymer **1994**, *35*, 4203–4208.
30. Raasch, M.S. Annelations with tetrachlorothiophene-1,1-dioxide. J. Org. Chem. **1980**, *45*, 856–867.
31. Melles, J.L. Reactions of thiophene dioxides. Rec. Trav. Chim. **1952**, *71*, 869–877.

Received January 15, 2003

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016