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Soluble Polyimides with Polyalicyclic Structure. 1. Polyimides from Bicyclo[2.2.2]oct-7-ene-2-*exo*,3-*exo*,5-*exo*,-6-*exo*-tetracarboxylic 2,3:5,6-Dianhydrides

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ABSTRACT: Bicyclo[2.2.2]oct-7-ene-2-*exo*,3-*exo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (**3a**) and its 1-methyl analogue (**3b**) were synthesized by a one-pot Diels–Alder (DA) reaction from maleic anhydride, and 4,5-dibromocyclohexane-1,2-dicarboxylic anhydride (**2a**) and 3-methyl-4,5-dibromocyclohexane-1,2-dicarboxylic anhydride (**2b**), respectively. Each tetracarboxylic dianhydride was also prepared directly without isolation of the bromine adduct (**2a** or **2b**) from the reaction product of bromine with 4-cyclohexene-1,2-dicarboxylic anhydride (**1a**) or 3-methyl-4-cyclohexene-1,2-dicarboxylic anhydride (**1b**). The polyimides prepared from **3a** and **3b** with aromatic diamines were soluble in aprotic and protic polar solvents and possessed molecular weights in the range from 1.6×10^4 to 4.6×10^4. The polyimide films were revealed to be almost colorless. Thermal gravimetric analysis gave an indication that these polyimides had good thermal stability with no significant weight loss up to approximately 360 °C. A thermal decomposition mechanism is proposed on the basis of GC–MS analysis on the pyrolyzed products of the model compounds **6a** and **6b**, and it is concluded that the decomposition in nitrogen was a consequence of the retro-DA reaction of polymer chains.

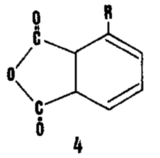
Introduction

Wholly aromatic polyimides such as Kapton are well known to exhibit high-temperature stability; however, the applications have been limited by poor solubility in organic solvents.[1,2] Recently, several techniques and/or monomers were developed to lend solubility to Kapton-type polyimides. It has been reported that employing noncoplanar[3–6] and bulky diamines such as polyphenylated diamine[7,8] makes Kapton-type polyimides soluble. In a like manner, noncoplanar dianhydrides are found to be effective in the improvement of solubility.[9] On the other hand, it was also demonstrated that solubility can be attained by using an aliphatic dianhydride such as 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride, although thermal stability is compromised.[10]

We expected that the introduction of polyalicyclic structure as an anhydride unit could improve the solubility of the polyimides with retention of excellent thermal stability due to the multibond and rigidity of the polyalicyclic structure. Up to now, the inter- or intramolecular Diels–Alder (DA) reaction has been well accepted as a versatile method for synthesizing organic compounds with ring structures.[11–19] With regard to the above points, the preparation of bicyclo[2.2.2]oct-7-ene-2-*exo*,3-*exo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (**3a**) was attempted from maleic anhydride and 3,5-cyclohexadiene-1,2-dicarboxylic anhydride (**4**), in order to produce polyimides that might be soluble without compromising thermal stability. During a synthetic study of the bicyclotetracarboxylic dianhydride, however, a conventional preparation of **4** from 4,5-dibromocyclohexane-1,2-dicarboxylic anhydride (**2a**) which is obtained by bromination of easily available 4-cyclohexene-1,2-dicarboxylic anhydride (**1a**) was not feasible, because **4** converted readily into phthalic anhydride (**5**) which may be more thermodynamically stable than the former. Alternative methods for preparing the dianhydride (**3a**) and its 1-methyl analogue (**3b**) have been reported so far.[20,21] However, those procedures involved many processes requiring highly skilled techniques and necessitated raw materials which are hardly available. These facts led us to develop a new method by a one-pot DA reaction for synthesizing the above-mentioned bicyclotetracarboxylic dianhydrides. This paper reports on the facile synthesis of two dianhydrides, **3a** and its 1-methyl analogue (**3b**), by the one-pot DA reaction and the synthesis and characterization of the polyimides obtained therefrom. Furthermore, the thermal decomposition mechanism of the polymers was investigated using a Curie point pyrolyzer–GC–MS.

Results and Discussion

The synthetic route to the bicyclic dianhydrides is illustrated in Scheme I. (1*R*,2*S*,3*R*)-3-Methyl-4-cyclohexene-1,2-dicarboxylic anhydride (**1b**) was prepared from the 1*S*,2*R*,3*R* isomer by base-catalyzed isomerization.[22] Brominations of **1a** and **1b** were carried out in ether at 2 °C to afford the corresponding bromine adducts, **2a** and 3-methyl-4,5-dibromohexane-1,2-dicarboxylic anhydride (**2b**). All of the compounds, **1b**, **2a**, and **2b**, were assumed to be racemic mixtures because they showed no optical activities. Bicyclo[2.2.2]oct-7-ene-2-*exo*,3-*exo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (**3a**) and its 1-methyl analogue (**3b**) were prepared by the reaction of each bromine adduct (**2a** or **2b**) with maleic anhydride *via* possible formation of a diene followed by the DA reaction, upon heating the reaction mixture at 200 °C for 15 h. Prior to the above experiment, though **2a** or **2b** was heated to assure the formation or existence of a diene (**4**) *via* dehydrobromination, nothing was separated but phthalic anhydride (**5**), probably due to higher thermodynamic stability of the latter. Therefore, it would be anticipated in the reaction path that, as soon as the bromine adducts (**2a** and **2b**) undergo thermal dehydrobromination and



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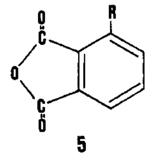

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Scheme I

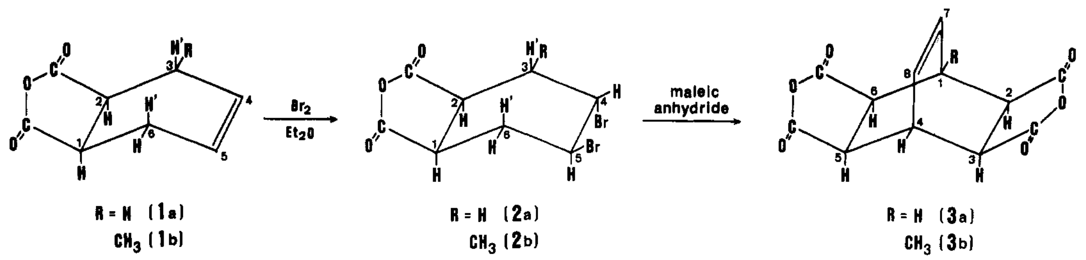
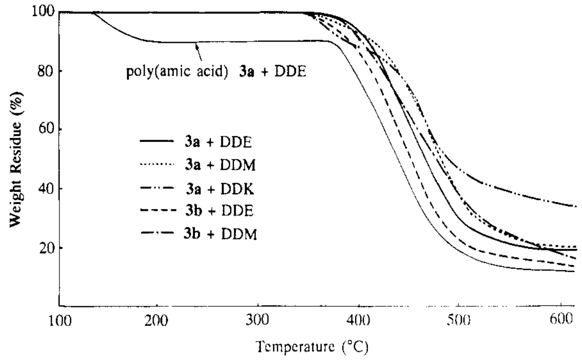


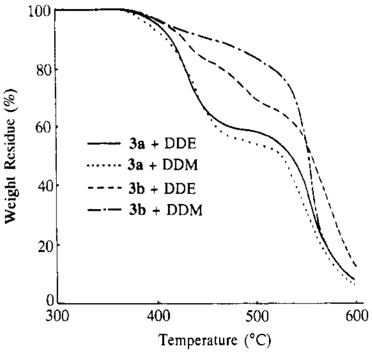
Table I. Polyimides from 3a, 3b, and Diamines[a]

dianhydride	diamine	$\bar{M}_n{}^b \times 10^4$	$T_5{}^c$ in air	$T_5{}^c$ in N_2	film
3a	DDE	1.9	330	415	flexible
3a	DDM	1.6	385	410	flexible
3a	DDK	2.3	350	365	brittle
3a	DDS	1.7	385	365	brittle
3b	DDE	4.1	400	395	flexible
3b	DDM	3.9	335	410	flexible
3b	DDK	2.7	350	365	brittle
3b	DDS	4.6	338	372	brittle

[a] Polymerization: diamine, 7.7 mmol; dianhydride, 8.1 mmol; pyridine, 0.84 mL; solvent (DMAc), 30 mL; room temperature; 8 h. Imidization: 240 °C; 1 h. [b] GPC (0.05 M DMF solution of LiBr), polystyrene standard. [c] 5% weight loss temperature by TGA with a heating rate of 5 °C/min.



(a) under nitrogen



(b) under air

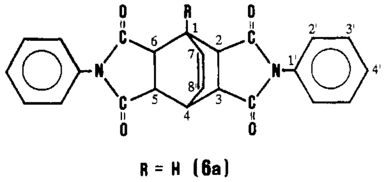
Figure 1. TGA profiles of polyimides from **3a**, **3b**, and diamines (a) under nitrogen and (b) under air.

diene (**4**) appears as a transient intermediate, the DA reaction with maleic anhydride takes place to afford **3a** and **3b**. Here, the bromine adduct can be concluded to work thermally as a precursor to the diene. The above compounds **3a** and **3b** were also synthesized from the reaction mixtures without isolation of **2a** and **2b** after reacting bromide with **1a** and **1b**, respectively, and maleic anhydride. These newly developed preparative methods of the dianhydrides by the one-pot DA reaction of the diene precursor with the dienophile, which are able to complete sequential reactions in one vessel, are shorter and simpler processes than those previously reported for the syntheses of **3a** and **3b**.[20,21]

Poly(amic acid)s were prepared by the reactions of **3a** and **3b** with 4,4′-diaminodiphenyl ether (DDE), 4,4′-diaminodiphenylmethane (DDM), 3,3′-diaminodiphenyl ketone (DDK), and 4,4′-diaminodiphenyl sulfone (DDS) in *N*,*N*-dimethylacetamide (DMAc) in the presence of pyridine at room temperature for several hours under a nitrogen atmosphere. Polymerizations proceeded homogeneously without gelation. These resulting poly(amic acid) solutions were heated to convert to the corresponding polyimides or after casting to form films, and then heated at 220 °C for 1 h to form these polyimides as films. All types of the obtained polyimides were soluble in aprotic polar solvents such as *N*,*N*-dimethylformamide (DMF), DMAc, *N*-methylpyrrolidone, and dimethyl sulfoxide and in protic solvents such as cresol and phenol. The polyimide films were almost colorless.

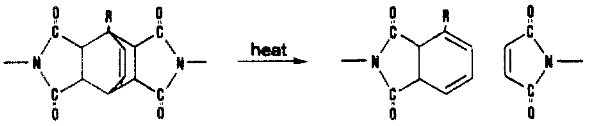
The molecular weights of the soluble polyimides were estimated by gel permeation chromatography (GPC) (0.05 M DMF solution of LiBr as an eluent) after calibration with standard polystyrenes, although their structures were somewhat different. Thermal behaviors of the polyimides under air and nitrogen streams were evaluated as a 5% weight loss temperature by thermogravimetric analysis (TGA) with a heating rate of 5 °C/min. The results together with film properties are listed in Table I. These polymers had molecular weights in the range from 1.6×10^4 to 4.6×10^4. Polyimide films from DDK and DDS were somewhat brittle, possibly due to high rigidity of the polymer chains. Thermogravimetric curves indicate that cyclization of poly(amic acid)s starts at over 100 °C and is complete at 200 °C and that all the polyimides possess good thermal stability with no significant weight loss up to approximately 360 °C in a nitrogen atmosphere (Figure 1).

The thermal decomposition mechanism was studied by analyzing the TGA profiles in detail and by examining the decomposition products of the model compounds **6a** and **6b** by means of pyrolysis capillary gas chromatography–mass spectrometry. As can be seen from Figure 1, the thermal decomposition behavior of the polyimides depends markedly on the atmosphere in which TGA was performed. In nitrogen, the samples decomposed at around 360 °C and underwent continuous weight loss up to 600 °C with about 20% residue, although the char yield of these polymers should be over 50–60% in an inert atmosphere on the basis of the carbon content of the polymers. The model compounds **6a** and **6b** were subjected to Curie point



R = H (**6a**)
CH₃ (**6b**)

Scheme II



pyrolysis (5 s, 590 °C, He atmosphere), and the volatile fragmentation products were fractionated, and then identified with mass spectrometry. The main product in each case was *N*-phenylmaleimide which could be formed by the retro-DA reaction of the model compounds, although other fragmentation products, diene compounds, were not detected probably because of their low volatility and/or formation of nonvolatile polymeric compounds. These results indicate that decomposition of the polyimides in nitrogen is affected by the retro-DA reaction which seems to occur around 360 °C regardless of the polymer from **3a** or **3b** (Scheme II). On the other hand, in air, there exists somewhat different behavior in the TGA profile between polyimides from **3a** and those from **3b** (Figure 1b). As concerns the polyimides from **3a**, the first onset of rapid weight loss around 360 °C is thought to be due to scission of polymer chains by the retro-DA reaction as described above, and then above 450 °C incorporation of an oxidative degradation of the polymer chain commences, which could restrain the rapid weight loss by the retro-DA reaction and result in rather slower weight loss. On the contrary, in the case of those from **3b**, an oxidation of the *exo*-ring methyl group is likely to occur easily, accompanying conversion of the retrogradable bicyclo[2.2.2]oct-7-ene unit to a structure which no more is affected by the retro-DA reaction. Consequently, the weight loss attributed to the retro-DA reaction cannot be observed in polyimides from **3b**, and the slower rate of weight loss is interpreted to be a concequence of the oxidative degradation rather than the retro-DA reaction.

Experimental Section

Materials and Instruments. The solvents were purified in the usual way prior to use. Pyridine was refluxed with CaH_2 and fractionally distilled. DDE and DDS were purified by recrystallization from methanol. DDK and DDM were recrystallized from ethyl acetate and benzene–hexane (1:1), respectively.

Melting points were measured with a Shimadzu DT-30 thermal analyzer. ^{1}H and ^{13}C NMR spectra were obtained at ambient temperature on a JEOL JNM-EX400WB spectrometer operating at 400 and 100 MHz, respectively. Proton and carbon signals in ^{1}H and ^{13}C NMR spectra were assigned in H,H-COSY, H,C-COSY, and NOESY (eliminating the J correlation) spectra. Signals were singlet where no multiplicity was shown. The internal standard was tetramethylsilane, and J values are given in hertz. Infrared spectra (KBr pellets) were recorded on a JASCO A-102 spectrophotometer. Mass spectra (EIMS) were measured using a Shimadzu GCMS-7000 mass spectrometer equipped with a direct ionization probe at an ionizing voltage of 70 eV. Elemental analyses were performed using a Perkin-Elmer CHN 2400 elemental analyzer. The molecular weight was analyzed using a JASCO 800 gel permeation chromatograph equipped with an RI detector and Shodex KD-80M columns in a 0.05 M DMF solution of LiBr at 50 °C; molecular weight calculations were made on the basis of polystyrene standards. Thermogravimetric analysis (TGA) was performed using a Shimadzu DT-30 thermal analyzer at a heating rate of 5 °C/min under an air or nitrogen stream.

Pyrolysis Capillary Gas Chromatography–Mass Spectrometry. The model compounds **6a** and **6b** were subjected to pyrolysis (JAI JHP-3 Curie point pyrolyzer; Curie point, 5 s, 590 °C, He atmosphere). The fragmentation products were separated on line using capillary gas chromatography (DELSI DI-200; column, OV-101, i.d. 0.25 mm, 25 m; carrier gas, He) and identified with mass spectrometry (JEOL Automass-20).

Monomer Synthesis. Racemic (1*R*,2*S*,3*R*)-3-Methyl-4-cyclohexene-1,2-dicarboxylic Anhydride (1b). A mixture of the racemic 1*S*,2*R*,3*R* isomer (230 g, 1.39 mol) and *N*,*N*-dibutylaniline (2.3 mL) was heated at 190 °C for 5 h. By fractional distillation of the reaction mixture a colorless fraction was collected (110.5–111.5 °C (2 mmHg), 83%): ^{1}H NMR ($CDCl_3$) δ 1.38 (3H, d, $J_{Me,3}$ = 7.3, CH_3), 2.24 (1H, dddd, $J_{6',1}$ = 7.8, $J_{6',4}$ = 3.4, $J_{6',5}$ = 2.9, $J_{6',6}$ = 15.6, H-6′), 2.52 (1H, qddd, $J_{3,Me}$ = 7.3, $J_{3,2}$ = 6.8, $J_{3,4}$ = 3.9, $J_{3,5}$ = 3.0, H-3), 2.73 (1H, ddd, $J_{6,1}$ = 2.5, $J_{6,5}$ = 6.3, $J_{6,6'}$ = 15.6, H-6), 3.29 (1H, dd, $J_{2,1}$ = 9.8, $J_{2,3}$ = 6.8, H-2), 3.43 (1H, ddd, $J_{1,2}$ = 9.8, $J_{1,6}$ = 2.6, $J_{1,6'}$ = 7.8, H-1); ^{13}C NMR ($CDCl_3$) δ 16.59 (CH_3), 23.59 (C-6), 29.83 (C-3), 40.78 (C-1), 45.01 (C-2), 127.19 (C-5), 134.80 (C-4), 171.63 (C=O), 174.39 (C=O); $[\alpha]^{25}_D$ = 0° (2.0% w/v, acetone).

Racemic (1*R*,2*S*,4*S*,5*S*)-4,5-Dibromohexane-1,2-dicarboxylic Anhydride (2a). Bromine (210 g, 1.31 mol) was added dropwise to the suspension of 4-cyclohexene-1,2-dicarboxylic anhydride (**1a**) (200 g, 1.31 mol) in 600 mL of ether with magnetic stirring at 2 °C, and stirring was allowed to continue for 4 h after the addition was completed. The resulting precipitate was filtered and washed with a small amount of ether. Recrystallization from cyclohexane gave white crystals (348 g, 81%): mp 141–142 °C; ^{1}H NMR ($CDCl_3$) δ 2.48 (1H, ddd, $J_{6,1}$ = 7.8, $J_{6,5}$ = 3.5, $J_{6,6'}$ = 15.4, H-6), 2.74 (1H, ddd, $J_{6',1}$ = 11.0, $J_{6',5}$ = 3.5, $J_{6',6}$ = 15.4, H′-6), 2.76 (1H, ddd, $J_{3,2}$ = 2.4, $J_{3,3'}$ = 16.4, $J_{3,4}$ = 3.8, H-3), 2.88 (1H, ddd, $J_{3',2}$ = 7.8, $J_{3',3}$ = 16.4, $J_{3',4}$ = 3.8, H′-3), 3.24 (1H, ddd, $J_{2,1}$ = 8.2, $J_{2,3}$ = 2.4, $J_{2,3'}$ = 7.8, H-2), 3.46 (1H, ddd, $J_{1,2}$ = 8.2, $J_{1,6}$ = 7.8, $J_{1,6'}$ = 11.0, H-1), 4.55 (1H, ddd, $J_{4,3}$ = 3.8, $J_{4,3'}$ = 3.8, $J_{4,5}$ = 3.8, H-4), 4.60 (1H, ddd, $J_{5,4}$ = 3.8, $J_{5,6}$ = 3.5, $J_{5,6'}$ = 3.5, H-5); ^{13}C NMR ($CDCl_3$) δ 25.38 (C-3), 27.71 (C-6), 36.19 (C-1), 36.59 (C-2), 46.42 (C-4), 47.59 (C-5), 171.27 (C=O), 171.74 (C=O); IR (KBr) 1850, 1785, 1430, 1350, 1230, 1202, 1170, 1098, 1071, 1033, 998, 961, 935, 900, 850, 830, 745, 710 cm^{-1}; $[\alpha]^{25}_D$ = 0° (2.0% w/v, acetone).

Bicyclo[2.2.2]oct-7-ene-2-*exo*,3-*exo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-Dianhydride (3a). The bromine adduct (**2a**) (2.0 g, 6.4 mmol) was heated with maleic anhydride (1.26 g, 12.8 mmol) at 200 °C for 15 h. After the reaction mixture was cooled, about 20 mL of acetone was added to it, and then the resulting slurry was heated under reflux for 1 h, after which it was filtered. The solid was recrystallized from acetonitrile, and a white crystalline product (1.12 g, 70%) was obtained: mp 356.0–356.5 °C; ^{1}H NMR (DMSO-d_6) δ 3.49 (2H, d, $J_{1,7}$ = $J_{4,8}$ = 3.4, H-1,4), 3.61 (4H, H-2,3,5,6), 6.38 (2H, dd, $J_{7,1}$ = $J_{8,4}$ = 3.4, $J_{7,8}$ = $J_{8,7}$ = 3.9, H-7,8); ^{13}C NMR (DMSO-d_6) δ 33.23 (C-1,4), 42.97 (C-2,3,5,6), 132.42 (C-7,8), 172.27 (C=O); IR (KBr) 1850, 1780, 1240, 1100, 933, 879 cm^{-1}; EIMS, *m*/*e* 243 (M+), 204, 176, 150, 132, 104, 78, 51, 44, 28, 26. Anal. Calcd for $C_{12}H_8O_6$: C, 58.07; H, 3.26. Found: C, 57.99; H, 3.16.

Racemic (1*R*,2*S*,3*S*,4*S*,5*S*)-3-Methyl-4,5-dibromohexane-1,2-dicarboxylic Anhydride (2b). As described above for the compound **2a**, **2b** was prepared from **1b**: yield 66%; mp 137–138 °C; ^{1}H NMR ($CDCl_3$) δ 1.35 (3H, d, $J_{Me,3}$ = 6.4, CH_3), 2.65 (1H, qdd, $J_{3,Me}$ = 6.4, $J_{3,2}$ = 11.4, $J_{3,4}$ = 3.2, H-3), 2.82 (1H, ddd, $J_{6,1}$ = 2.0, $J_{6,5}$ = 2.4, $J_{6,6'}$ = 16.1, H-6), 2.90 (1H, ddd, $J_{6',1}$ = 8.1, $J_{6',5}$ = 4.1, $J_{6',6}$ = 16.1, H-6′), 2.93 (1H, dd, $J_{2,1}$ = 8.6, $J_{2,3}$ = 11.4, H-2), 3.25 (1H, ddd, $J_{1,2}$ = 8.6, $J_{1,6}$ = 2.0, $J_{1,6'}$ = 8.1, H-1), 4.45 (1H, dd, $J_{4,3}$ = 3.2, $J_{4,5}$ = 3.3, H-4), 4.69 (1H, ddd, $J_{5,4}$ = 3.3, $J_{5,6}$ = 2.4, $J_{5,6'}$ = 4.1, H-5); ^{13}C NMR ($CDCl_3$) δ 18.37 (CH_3), 24.37 (C-6), 30.16 (C-3), 37.17 (C-1), 43.02 (C-2), 47.15 (C-5), 57.30 (C-4), 171.04 (C=O), 171.59 (C=O); IR (KBr) 1855, 1780, 1425, 1345, 1235, 1215, 1165, 1103, 1060, 982, 950, 915, 878, 810, 703 cm^{-1}; $[\alpha]^{25}_D$ = 0° (2.0% w/v, acetone). Anal. Calcd for $C_9H_{10}Br_2O_3$: C, 33.16; H, 3.09; Br, 49.03. Found: C, 33.16; H, 2.99; Br, 48.77.

1-Methyl-bicyclo[2.2.2]oct-7-ene-2-*exo*,3-*exo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-Dianhydride (3b). In the same manner as for compound **3a**, **3b** was obtained in 73% yield from maleic anhydride and **2b**: mp 273–274 °C; ^{1}H NMR (DMSO-d_6) δ 1.69 (3H, CH_3), 3.33 (2H, d, $J_{2,3}$ = $J_{6,5}$ = 8.8, H-2,6), 3.47 (1H, dd, $J_{4,5}$ = 3.2, $J_{4,8}$ = 5.9, H-4), 3.66 (2H, dd, $J_{3,2}$ = $J_{5,6}$ = 8.8, $J_{3,4}$ = $J_{5,4}$ = 3.2, H-3,5), 6.13 (1 H, d, $J_{7,8}$ = 8.3, H-7), 6.33 (1H, dd, $J_{8,4}$ = 5.9, $J_{8,7}$ = 8.3, H-8); ^{13}C NMR (DMSO-d_6) δ 18.40 (CH_3), 33.34 (C-4), 39.38 (C-1), 44.79 (C-3, C-5), 48.08 (C-2, C-6), 131.77 (C-8), 137.51 (C-7), 171.16 (C=O), 172.46 (C=O); IR (KBr) 1850, 1780, 1220, 1090, 925, 860 cm^{-1}; EIMS, *m*/*e* 262 (M+), 247, 223, 163, 149, 121, 105, 104, 77, 44, 28, 26. Anal. Calcd for $C_{13}H_{10}O_6$: C, 59.55; H, 3.84. Found: C, 59.72, H, 3.68.

One-Pot Method. The above compounds **3a** and **3b** were also synthesized directly from **1a** and **1b**, respectively, in 68-70% yield without isolating compounds **2a** and **2b**. To the reaction mixture prepared by allowing **1a** or **1b** to react with bromine in ether at 2 °C for several hours was added maleic anhydride, and then the mixture was heated at 200 °C for 19 h with distilling ether. After cooling, the resulting solid was treated with acetone as described above, and repeated recrystallization from acetonitrile gave white crystals (**3a** or **3b**).

Model Compound 6a. A mixture of **3a** (2.0 g, 8.1 mmol) and aniline (1.5 g, 16.2 mmol) in dioxane (20 mL) was refluxed for 4 h. After cooling, the resulting precipitate was filtered off and the solid was dissolved in acetic anhydride (20 mL). The solution was heated at reflux temperature for 3 h, and then it was poured into ether (100 mL). The crude material was recrystallized from acetonitrile/water: yield 67%; mp 350 °C dec; ^{1}H NMR (DMSO-d_6) δ 3.41 (4H, H-2,3,5,6), 3.54 (2H, d, $J_{1,7} = J_{4,8} = 2.4$, H-1,4), 6.31 (2H, d, $J_{7,1} = J_{8,4} = 2.4$, H-7,8), 7.16 (4H, d, $J_{2',3'} = 7.3$, H-2′), 7.40 (2H, d, $J_{4',3'} = 6.8$, H-4′), 7.46 (4H, dd, $J_{3',2'} = 7.3$, $J_{3',4'} = 6.8$, H-3′); ^{13}C NMR (DMSO-d_6) δ 33.92 (C-1,4), 42.39 (C-2,3,5,6), 126.75 (C-2′), 128.36 (C-4′), 128.82 (C-3′), 130.92 (C-7,8), 132.02 (C-1′); IR (KBr) 3050, 2950, 1770, 1702, 1590, 1490, 1380, 1300, 1187, 799, 745, 714, 691 cm^{-1}; EIMS *m/e* 398 (M+).

Model Compound 6b. As described above for compound **6a**, **6b** was prepared from **1b** and aniline and was recrystallized from acetonitrile/water: yield 71%, mp 251.4-252.2 °C; ^{1}H NMR (DMSO-d_6) δ 1.80 (3H, CH_3), 3.09 (2H, d, $J_{2,3} = J_{6,5} = 9.3$, H-2,6), 3.44 (2H, dd, $J_{3,2} = J_{5,6} = 9.3$, $J_{3,4} = J_{5,4} = 3.9$, H-3,5), 3.53 (1H, dd, $J_{4,3} = J_{4,5} = 3.9$, $J_{4,8} = 6.4$, H-4), 6.10 (1H, d, $J_{7,8} = 8.3$, H-7), 6.26 (1H, dd, $J_{8,4} = 6.4$, $J_{8,7} = 8.3$, H-8), 7.15 (4H, d, $J_{2',3'} = 7.3$, H-2′), 7.42 (2H, d, $J_{4',3'} = 7.3$, H-4′), 7.48 (4H, dd, $J_{3',2'} = 7.3$, $J_{3',4'} = 7.3$, H-3′); ^{13}C NMR (DMSO-d_6) δ 19.20 (CH_3), 33.74 (C-4), 39.43 (C-1), 43.76 (C-3,5), 47.46 (C-2,6), 126.85 (C-2′), 128.35 (C-4′), 128.82 (C-3′), 129.75 (C-8), 132.04 (C-1′), 135.92 (C-7), 175.44 (2,6-side C=O), 176.35 (3,5-side C=O); IR (KBr) 3060, 2930, 1770, 1710, 1493, 1380, 1310, 1222, 1190, 805, 750, 690 cm^{-1}; EIMS, *m/e* 412 (M+).

General Polymerization Procedure. The diamine (7.6 mmol) and pyridine (0.84 mL) were placed in a 30-mL three-necked flask containing DMAc (7.6 mL). A slow stream of nitrogen gas was maintained. The mixture was stirred magnetically until the diamine was dissolved. A small excess of the tetracarboxylic dianhydride (8.1 mmol) was then added into the clear solution over a 2-h period. After being stirred at room temperature for 6 h, the reaction solution was poured into acetone (300 mL). The precipitated poly(amic acid) was filtered off and dried at room temperature for 1 d under vacuum and at 240 °C for 5 h to effect cyclization to the polyimide.

Polyimide Films. The solid polyimides were dissolved in DMAc at a concentration of over 10–20% (w/w), and the solutions were cast onto plate glasses using a doctor blade set at 30 mils. Polyimide films were prepared by drying under vacuum at room temperature for 1 d and then heating in air at 240 °C for 1 h. The polyimide films were also obtained from poly(amic acid) solutions by heating the glass plates on which the poly(amic acid) solutions were cast at 240 °C for 1 h. Removal from the glass plates was aided by immersion in hot water.

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