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Soluble Polyimides with Polyalicyclic Structure. 3.[1] Polyimides from (4a*rH*,8a*cH*)-Decahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene-2*t*,3*t*,6*c*,7*c*-tetracarboxylic 2,3:6,7-Dianhydride

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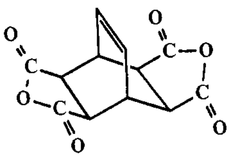
ABSTRACT: New ladder-rich and soluble polyimides with a polyalicyclic structure were prepared from conventional aromatic diamines and a novel tetracarboxylic dianhydride with a tetraalicyclic structure, (4a*rH*,8a*cH*)-decahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene-2*t*,3*t*,6*c*,7*c*-tetracarboxylic 2,3:6,7-dianhydride (3). The dianhydride (3) was sythesized by a Diels-Alder (DA) reaction of 2,5-norbornadiene with cyclopentadiene, followed by the Pd(0)-catalyzed tetrakismethoxycarbonylation, an ester exchange reaction, and then the dehydration reaction. The structure of 3 was determined using NMR and single crystal X-ray analysis. The polyimides obtained from 3 were soluble in polar aprotic and protic solvents and had molecular weights in the range 1.1×10^4 to 5.8×10^4 as $\bar{M}_n$. These polymers exhibited excellent thermal stability without significant weight loss up to 420 °C. The T_5's in nitrogen and in air were over 460 and 440 °C, respectively. The T_g's were over 250 °C except for the polyimide prepared from DDS as a diamine component. The polyimide films were found to be almost colorless. The films had a tensile modulus range of 1.71-2.30 GPa, a tensile strength range of 91-112 MPa, and an elongation range at break of 19-35%.

Introduction

Polyimides have been of great interest in engineering and microelectronics for a number of applications due to their unique property combinations.[2,3] Although exceptional thermal stability is complemented by excellent mechanical and electrical performance and dimensional stability over a wide range of temperatures, their insolubility in common organic solvents and their high glass and softening temperatures make these systems difficult to process and fabricate. Therefore, much effort has been concentrated on synthesizing soluble, tractable polyimides without sacrificing their desired properties. One of the successful approaches is to introduce pendant phenyl and alkyl groups[4-6] or fluorine, chlorine, phosphorus, etc.[7-11] into the polymer backbone. Another approach to enhance solubility and processability is to utilize alicyclic dianhydrides such as 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexane-1,2-dicarboxylic anhydride[12] or cyclobutane-1,2,3,4-tetracarboxylic dianhydride and its homologue,[13,14] though the thermal stability is significantly sacrificed probably due to the presence of either a carbon-carbon single bond in the former or a cyclobutane structure that is thermodynamically unstable in the latter. These results have made our research efforts focus on the adoption of a stable polyalicyclic dianhydride for the preparation of polyimides that were thermally stable and easier to process and fabricate. The introduction of a polyalicyclic unit into the polyimide backbone would facilitate less polymer-polymer interaction and less probability of main chain scission because of the presence of multibonds and, additionally, would increase main chain rigidity, which would be very advantageous for our goal.



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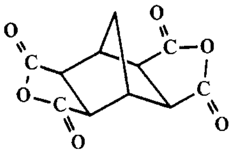

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In our first study,[15] bicyclo[2.2.2]oct-7-ene-2-*exo*,3-*exo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (4) has been synthesized by a one-pot Diels-Alder (DA) reaction. The polyimides prepared from the anhydrides and aromatic diamines were soluble and thermally stable; however, they might rank no more than medium among heat-resistant polymers. On the basis of GC-MS analyses of the pyrolyzed products of the model compounds, a thermal decomposition mechanism of the above-mentioned polyimides was offered in which a retro-DA reaction of the polymer backbone, which contained a potentially retrodegradable bicyclo[2.2.2]oct-7-ene structure, emerged at around 360 °C in a nitrogen atmosphere and, therefore, limited their heat durability below 360 °C. Most recently, we reported that a novel bialicyclic dianhydride, which would not be retrodegradable, bicyclo]2.2.1]heptane-2-*exo*,3-*exo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (5), was prepared[16] and that the polyimides obtained from 5 and aromatic diamines were recognized to possess both solubility in organic solvents and excellent thermal stability.[17] The present report relates the synthesis and the structure elucidation of a new ladder-rich tetracarboxylic dianhydride, (4a*rH*,8a$_c$H)-decahydro-1*t*,4*t*;5*c*,8*c*-dimethanonaphthalene-2*t*,3*t*,6*c*,7*c*-tetracarboxylic 2,3:6,7-dianhydride (3), and the synthesis and the characterization of soluble polyimides having a ladder-richer backbone obtained from the novel dianhydride (3) and conventional aromatic diamines.

Results and Discussion

Monomer Synthesis. The synthetic route of 3 is shown in Scheme 1. Prior to the methoxycarbonylation of (4a*rH*,8a*cH*)-1,4,4a,5,8,8a-hexahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene (1), 1 was prepared by a DA reaction of 2,5-norbornadiene with cyclopentadiene. Practically, 2,5-norbornadiene was allowed to react with cyclopentadiene in an autoclave by heating at 195 °C for 6 h. Upon fractional distillation of the reaction mixture, 1 was obtained as a colorless fraction (bp 60 °C/2 mmHg) in 31% yield. The detailed structure assignment of the NMRs are presented and identified in the Experimental

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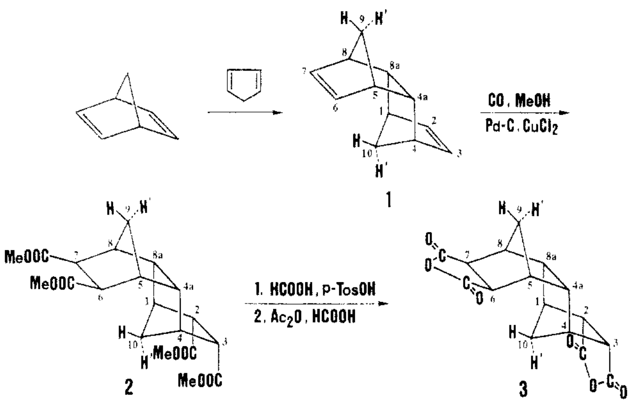
Scheme 1



Section. The palladium(0)-catalyzed tetrakismethoxycarbonylation of 1 was carried out according to our previous report[16] to produce tetramethyl (4a*rH*,4a*cH*)-decahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene-2*t*,3*t*,6*t*,7*t*-tetracarboxylate (2) in 35% yield (mp 169-170 °C). James and Stille have proposed a reaction mechanism of palladium(II)-catalyzed bismethoxycarbonylation of norbornene.[18] According to their mechanism, eventually, the two introduced methoxycarbonyl groups should have an *exo* configuration and result in norbornane-2-*exo*,3-*exo* dicarboxylate. The stereochemical assignments made using NMRs on 2 are coincident with Stille's proposal. (4a*rH*,8a*cH*)-Decahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene-2*t*,3*t*,6*c*,7*c*-tetracarboxylic 2,3:6,7-dianhydride (3) was prepared in 83% yield by an ester exchange reaction catalyzed by *p*-toluenesulfonic acid in formic acid, subsequently without isolation of (4a*rH*,8a*cH*)-decahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene-2*t*,3*t*,6*c*,7*c*-tetracarboxylic acid, followed by the dehydration reaction with acetic anhydride. The ^{1}H and ^{13}C NMR spectra of 3 in DMSO-d_6 are shown in Figure 1. H,H-COSY, H,H-NOESY (with elimination of the *J* correlation), and H,C-COSY experiments were run to confirm the assignments for the proton and carbon signals in the ^{1}H and ^{13}C NMR spectra (see Figures 2–4). X-ray crystal data for 3 were acquired from a colorless crystal obtained by slow evaporation of an acetic anhydride solution of 3 in air (Table 1). Refinement, described in the Experimental Section, results in the structure shown in Figure 5. Selected bond distances and bond angles are summarized in Tables 2 and 3, respectively, in which the atom labeling used is the same as in Figure 5. The structure is coincident with that deduced from the spectroscopic data. The anhydride (3) crystallizes in the space group $P2_1/c$ and has eight formula units in the unit cell.

The DA reaction of dimethyl bicyclo[2.2.1]hept-4-ene-2-*endo*,3-*endo*-dicarboxylate with cyclopentadiene gave dimethyl (4a*rH*,8a*cH*)-1,2,3,4,4a,5,8,8a-octahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene-2*c*,3*c*-dicarboxylate, and then the compound was converted to (4a*rH*,8a*cH*)-decahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene-2*c*,3*c*,6*c*,7*c*-tetracarboxylic 2,3:6,7-dianhydride in a manner similar to that mentioned above. The structure elucidation of these compounds accompanied by the stereochemistry and polyimides from the anhydride will be reported elsewhere in the near future.

Polymer Synthesis. The polyimides were prepared according to a previously reported procedure,[17] and the synthetic route of the polyimides from the anhydride (3) and the various aromatic diamines is illustrated in Scheme 2. Poly(amic acid)s were obtained by reacting 3 with 4,4'-diaminodiphenyl ether (DDE), (4,4'-diaminodiphenyl)methane (DDM), 4,4'-diaminodiphenyl sulfone (DDS), 3,3'-diaminodiphenyl ketone (DDK), 1,3-bis(4-aminophenoxy)benzene (BAB), and 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) in *N*-methyl-2-pyrrolidone (NMP) in the presence of pyridine at room temperature for 2 days under a nitrogen atmosphere. The resultant viscous poly(amic acid) solutions were cast on glass plates and dried under vacuum, and then the poly(amid acid)s were transformed into the corresponding polyimides by curing at 220 °C for 2 h in a preheated oven. Polyimides were also obtained by a thermal solution imidization method where the NMP solutions of poly(amic acid)s were heated at 200 °C for 2 h. All the reactions proceeded homogeneously without gelation or precipitation of the resultant polymers.

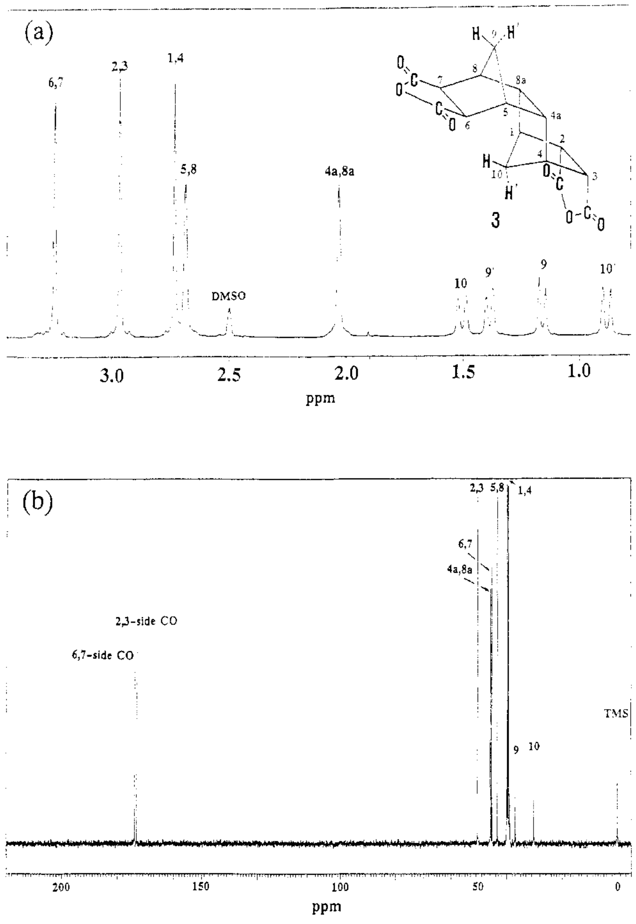


Figure 1. (a) 400-MHz ^{1}H NMR and (b) 100-MHz ^{13}C NMR spectra of 3 in DMSO-d_6 at ambient temperature. The atom labeling used here is the same as for 3 in Scheme 1. The assignments were made for H,H-COSY (Figure 2), NOESY (elimination of the *J* correlation) (Figure 3), and H,C-COSY (Figure 4) spectra.

Characterization and Properties of Polymers. The molecular weights and the molecular weight distributions of the polyimides measured using gel permeation chromatography (GPC) (0.05 M DMF solution of LiBr as an eluent) and the film qualities are summarized in Table 4. These polymers possessed molecular weights in the range from 1.1 × 10^4 to 5.8 × 10^4 as $\bar{M}_n$ and molecular weight distributions in the range from 1.46 to 3.46 and formed tough and flexible films except for the polyimide from DDS. All of the obtained films were transparent and almost colorless, although they turned pale yellow after curing over 400 °C. The solubility of the polyimides was studied qualitatively, and the results are shown in Table 5 compared with those from bialicyclic dianhydride 5. The polyimides from 3 and the various diamines exhibited similar solubility behaviors and were more soluble than those derived from 5. Thus, the incorporation of the tetraalicyclic unit into the polyimide main chain may be

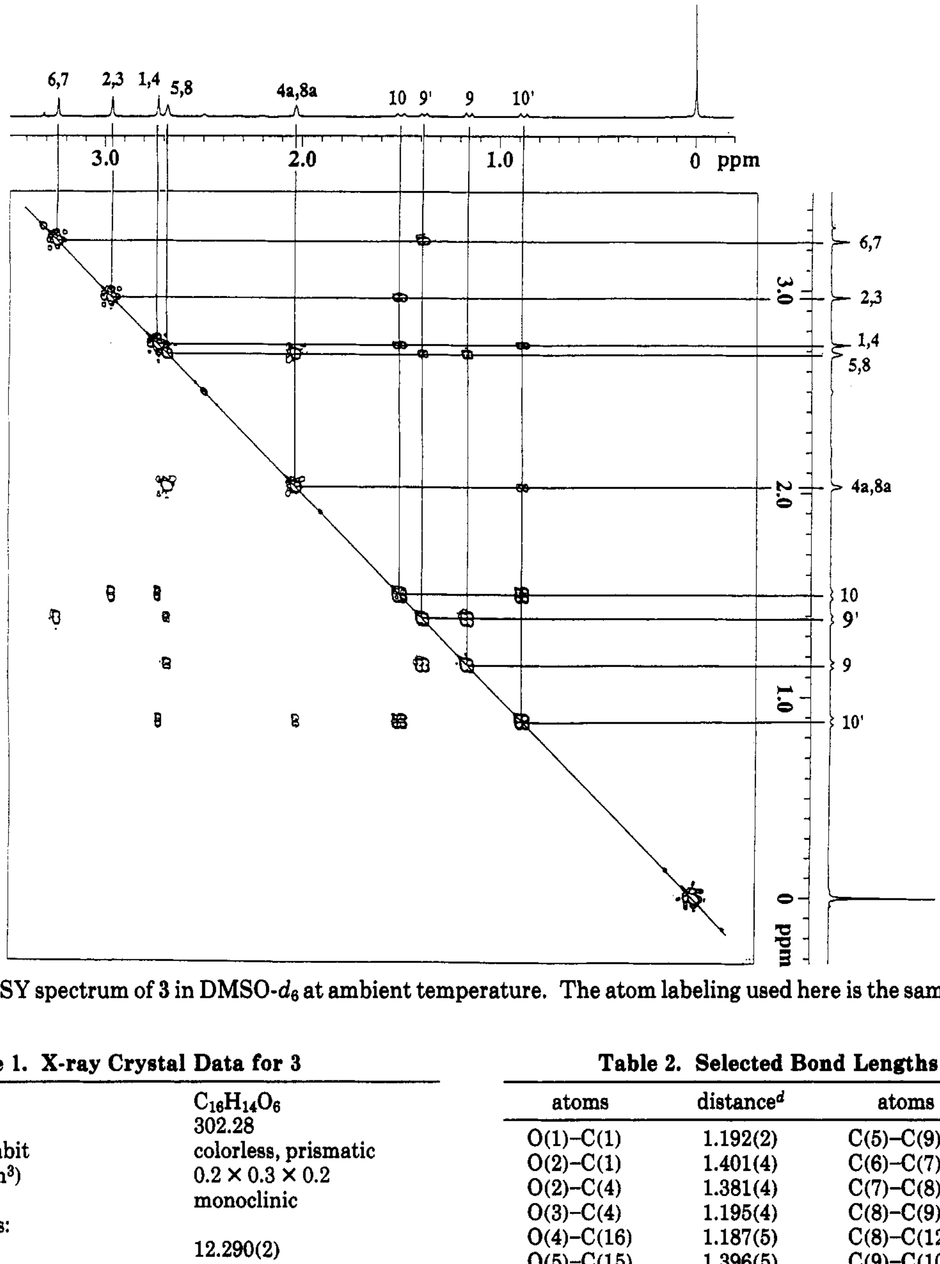


Figure 2. H,H-COSY spectrum of 3 in DMSO-d_6 at ambient temperature. The atom labeling used here is the same as for 3 in Scheme 1.

Table 1. X-ray Crystal Data for 3

formula	$C_{16}H_{14}O_6$
fw	302.28
cryst color, habit	colorless, prismatic
cryst size (mm^3)	0.2 × 0.3 × 0.2
cryst syst	monoclinic
lattice params:	
a (Å)	12.290(2)
b (Å)	10.699(2)
c (Å)	19.611(1)
β (deg)	90.249(9)
V (Å^3)	2578.7(6)
space group	$P2_1/c$ (No. 14)
Z	8
λ(Cu K_α) (Å)	1.542
μ (cm^{-1})	9.66
no. of measd reflns	4085
no. of obsd reflns	2637
R	0.049
R_w	0.060
temp (°C)	23

Table 2. Selected Bond Lengths (Å) for 3[a]

atoms	distance[d]	atoms	distance[b]
O(1)–C(1)	1.192(2)	C(5)–C(9)	1.541(5)
O(2)–C(1)	1.401(4)	C(6)–C(7)	1.535(6)
O(2)–C(4)	1.381(4)	C(7)–C(8)	1.546(5)
O(3)–C(4)	1.195(4)	C(8)–C(9)	1.571(5)
O(4)–C(16)	1.187(5)	C(8)–C(12)	1.537(5)
O(5)–C(15)	1.396(5)	C(9)–C(10)	1.539(5)
O(5)–C(16)	1.396(5)	C(10)–C(11)	1.532(5)
O(6)–C(15)	1.202(5)	C(10)–C(14)	1.540(5)
C(1)–C(2)	1.488(5)	C(11)–C(12)	1.535(5)
C(2)–C(3)	1.526(5)	C(12)–C(13)	1.551(5)
C(2)–C(5)	1.543(5)	C(13)–C(14)	1.546(5)
C(3)–C(4)	1.503(5)	C(13)–C(16)	1.499(5)
C(3)–C(7)	1.542(5)	C(14)–C(15)	1.495(5)
C(5)–C(6)	1.532(6)		

[a] The atom labeling used here is the same as in Figure 5. [b] Estimated standard deviations in the least significant figure are given in parentheses.

considered to offer these materials excellent solubility. By thermogravimetric analysis (TGA) of the poly(amic acid)s, the imidization was found to commence at around 110 °C and to be complete at 200 °C. This fact was also substantiated by IR spectroscopy, that is, strong absorptions at 1765–1775 and 1710–1720 cm^{-1} due to the imide carbonyl appeared after heating over 200 °C, while the absorptions at *ca.* 3300 and 1550–1650 cm^{-1} due to the carboxylic and amide–carbonyl groups of poly(amic acid) that were initially observed disappeared entirely. The thermal properties of the polyimide films were evaluated by the 5% weight loss and the decomposition temperatures (T_5 and T_{dec}) measured using TGA that was carried out with a heating rate of 5 °C/min in air or nitrogen and by the T_g measured using a thermomechanical analyzer (TMA) with a penetration probe of 1.0-mm diameter and using an applied constant load of 10 g at a heating rate of 10 °C/min in air. In the TGA profile, T_{dec} is noteted as the point where the TGA curve intersects the bisected line drawn through the intersection of the extrapolations of the two slopes in the TGA curve.[17] These results are listed in Table 6. All the polyimides have good thermal stability with no significant weight loss up to 420 °C. The T_5's in a nitrogen atmosphere are over 460 °C. Especially, those of the polyimides from DDE and DDM are over 500 °C and are comparable to those of the wholly aromatic polyimides. These T_5's are 70–160 and 20–60 °C higher than those from bicyclo[2.2.2]oct-7-ene-2-*exo*,3-*exo*,5-

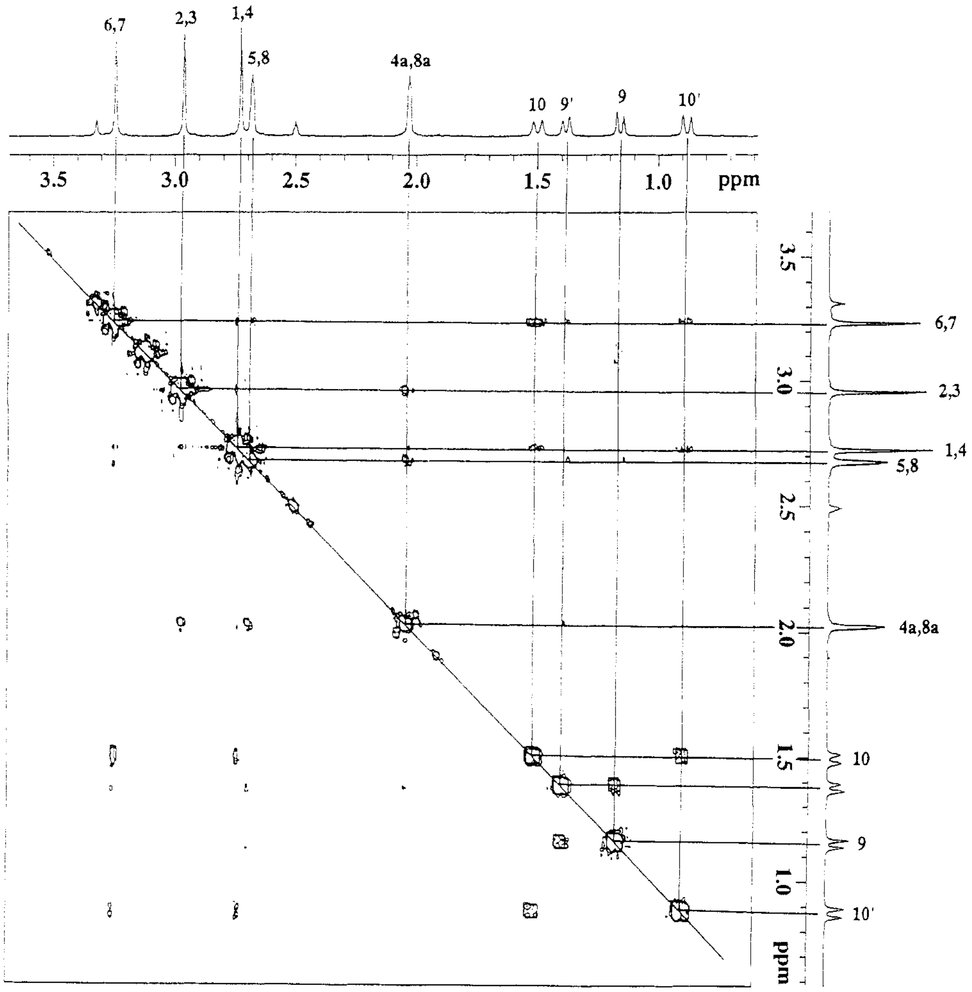


Figure 3. NOESY (elimination of the *J* correlation) spectrum of **3** in DMSO-d_6 at ambient temperature. The atom labeling used here is the same as for **3** in Scheme 1.

Table 3. Selected Bond Angles (deg) for 3[a]

atoms	angle[b]	atoms	angle[b]
O(1)–C(1)–O(2)	118.9(4)	C(5)–C(9)–C(8)	103.0(3)
O(1)–C(1)–C(2)	130.9(4)	C(5)–C(9)–C(10)	122.6(3)
O(2)–C(1)–C(2)	110.1(3)	C(6)–C(5)–C(9)	99.9(3)
O(2)–C(4)–O(3)	118.9(4)	C(6)–C(7)–C(8)	99.7(3)
O(2)–C(4)–C(3)	110.5(3)	C(7)–C(8)–C(9)	102.5(3)
O(3)–C(4)–C(3)	130.5(4)	C(7)–C(8)–C(12)	122.8(3)
O(4)–C(16)–O(5)	119.2(4)	C(8)–C(9)–C(10)	102.8(3)
O(4)–C(16)–C(13)	130.6(4)	C(8)–C(12)–C(11)	104.2(3)
O(5)–C(15)–O(6)	118.8(4)	C(8)–C(12)–C(13)	104.5(3)
O(5)–C(15)–C(14)	110.9(4)	C(9)–C(8)–C(12)	103.4(3)
O(5)–C(16)–C(13)	110.1(3)	C(9)–C(10)–C(11)	104.9(3)
O(6)–C(15)–C(14)	130.2(4)	C(9)–C(10)–C(14)	105.0(3)
C(1)–O(2)–C(4)	110.1(3)	C(10)–C(11)–C(12)	95.4(3)
C(1)–C(2)–C(3)	105.0(3)	C(10)–C(14)–C(13)	103.7(3)
C(1)–C(2)–C(5)	113.6(3)	C(10)–C(14)–C(15)	111.1(3)
C(2)–C(3)–C(4)	104.1(3)	C(11)–C(10)–C(14)	99.6(3)
C(2)–C(3)–C(7)	103.8(3)	C(11)–C(12)–C(13)	99.7(3)
C(2)–C(5)–C(6)	101.4(3)	C(12)–C(13)–C(14)	103.4(3)
C(2)–C(5)–C(9)	110.0(3)	C(12)–C(13)–C(16)	111.3(3)
C(3)–C(2)–C(5)	103.5(3)	C(13)–C(14)–C(15)	103.9(3)
C(3)–C(7)–C(6)	101.0(3)	C(14)–C(13)–C(16)	104.8(3)
C(3)–C(7)–C(8)	111.7(3)	C(15)–O(5)–C(16)	110.1(3)
C(4)–C(3)–C(7)	112.2(3)	H(7)–C(6)–H(8)	113(3)
C(5)–C(6)–C(7)	94.5(3)	H(11)–C(11)–H(12)	102(3)

[a] The atom labeling used here is the same as in Figure 5. [b] Estimated standard deviations in the least significant figure are given in parentheses.

exo,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (**4**) and from bicyclo[2.2.1]heptane-2-*exo*,3-*exo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (**5**), respectively, which have been prepared previously in our laboratory. The polyimides from **3** have T_g's over 250 °C except for the polyimide using DDS as an aromatic diamine. The lower T_g of the polymer from DDS may be due to the lower molecular weight. The mechanical properties of the polyimide films were examined at room temperature in air using a thermomechanical analyzer with a constant drawing rate of 10 mm/min (sample size: 10-mm length, 3-mm width, about 20-μm thick). The results are summarized in Table 7 along with those of the polyimides from **5** reported previously.[17] These polyimide films from **3** have a tensile modulus range of 1.71–2.30 GPa, a tensile strength range of 91–112 MPa, and an elongation range at break of 19–35%, whereas the corresponding values of polyimide films from **5** have ranged from 1.05 to 1.67 GPa, from 91 to 145 MPa, and from 9 to 15%, respectively. The mechanical properties of the polyimides from **3** at room temperature are superior to those of the polyimides from **5**, and especially the improvement in an elongation at break is notable.

We could successfully produce the soluble, thermally stable and almost colorless polyimides with excellent mechanical properties using a novel tetraalicyclic dianhydride, (4a*rH*,8a*cH*)-decahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene-2*t*,3*t*,6*c*,7*c*-tetracarboxylic 2,3:6,7-dianhydride (**3**) and conventional aromatic diamines.

Experimental Section

Materials. 2,5-Norbornadiene was purified by distillation from activated alumina. Acetic anhydride was distilled fractionally through a 50-cm column packed with glass helices. Methanol was refluxed with $CaSO_4$ and distilled fractionally. Dicyclopentadiene, 5% Pd/C, $CuCl_2$, carbon monoxide, *p*-toluenesulfonic acid, and formic acid were of commercial grade and

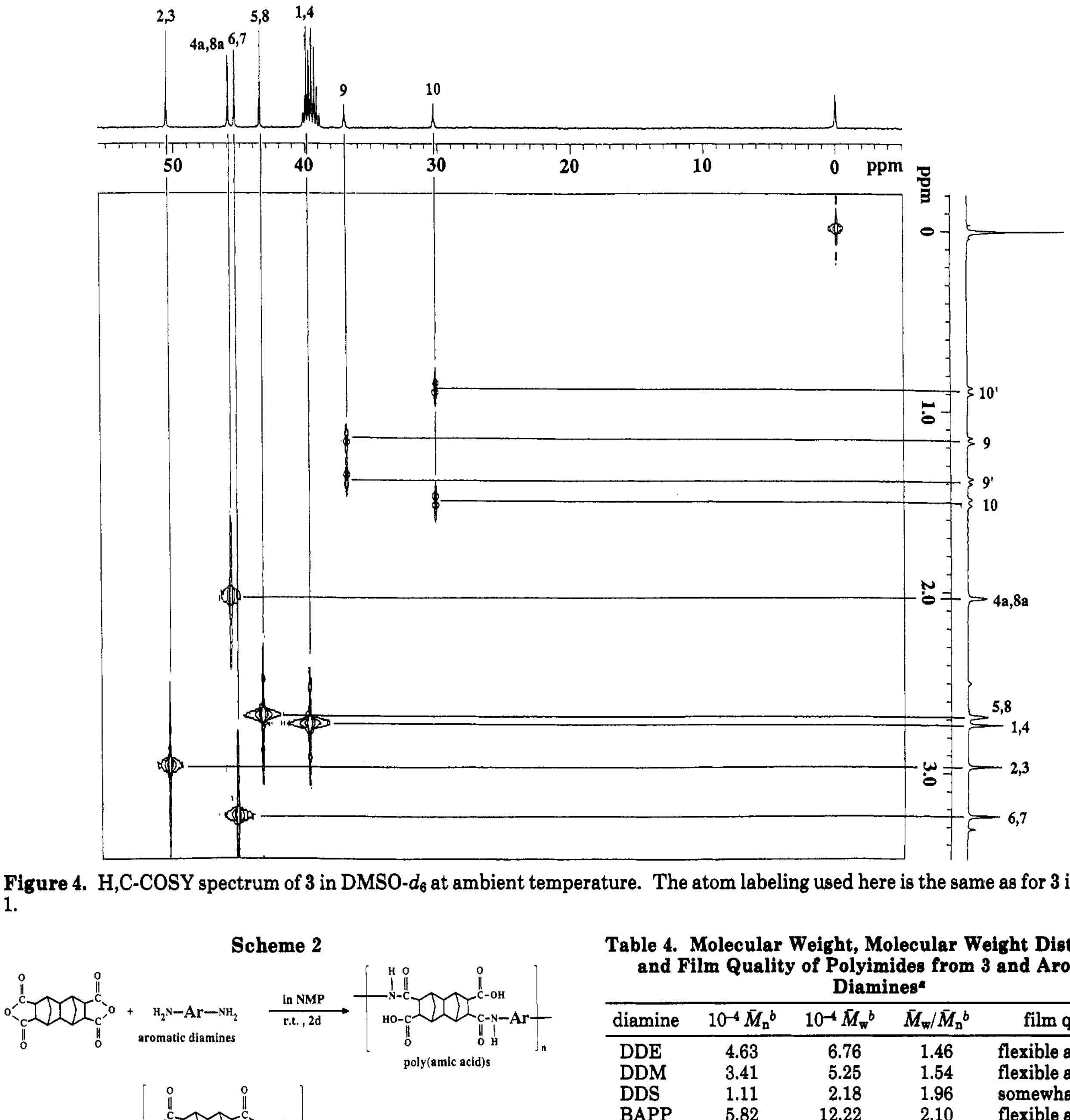


Figure 4. H,C-COSY spectrum of 3 in DMSO-d_6 at ambient temperature. The atom labeling used here is the same as for 3 in Scheme 1.

Scheme 2

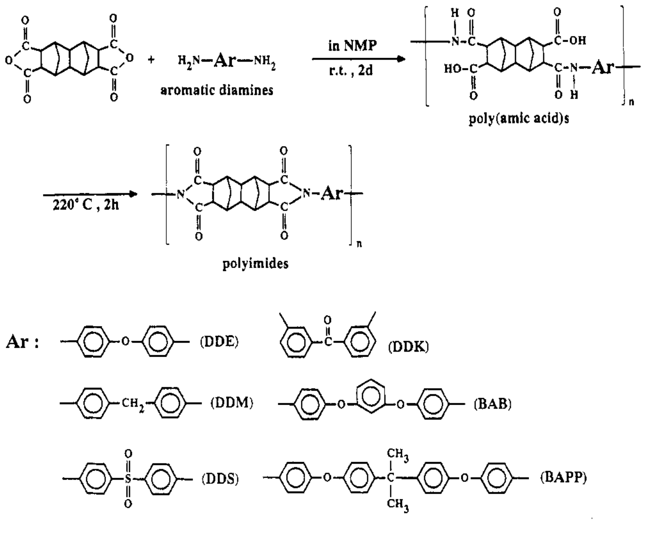


Table 4. Molecular Weight, Molecular Weight Distribution, and Film Quality of Polyimides from 3 and Aromatic Diamines[a]

diamine	$10^{-4}\bar{M}_n$[b]	$10^{-4}\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$[b]	film quality
DDE	4.63	6.76	1.46	flexible and tough
DDM	3.41	5.25	1.54	flexible and tough
DDS	1.11	2.18	1.96	somewhat brittle
BAPP	5.82	12.22	2.10	flexible and tough
BAB	2.13	7.37	3.46	flexible and tough
DDK	1.54	4.99	3.24	flexible and tough

[a] Polymerization: dianhydride, 2.1 mmol; diamine, 2.1 mmol; pyridine, 1.0 mL; solvent (NMP), 8 mL; room temperature; 2 days. Imidization: 220 °C; 1 h. [b] GPC (0.05 M DMF solution of LiBr), polystyrene standards.

were used as received. *N*-Methyl-2-pyrrolidone was dried by removing water as benzene azeotrope and distilled fractionally. Pyridine was refluxed with CaH_2 and fractionally distilled. DDE, DDS, and BAB were purified by recrystallization from methanol. BAPP, DDK, and DDM were recrystallized from ethanol, ethyl acetate, and benzene–hexane (1:1 vol/vol), respectively.

Measurements. ^1H and ^{13}C NMR spectra were recorded using a JEOL JNM-EX400WB spectrometer operating at 400 and 100 MHz, respectively. Proton and carbon signals in ^1H and ^{13}C NMR spectra were assigned in H,H-COSY and H,C-COSY and NOESY (with elimination of the *J* correlation) spectra. Signals are singlets where no multiplicity is shown. Deuteriochloroform was used as the solvent except as otherwise indicated. The internal standard was tetramethylsilane. *J* values are given in hertz. IR spectra were measured using a JASCO A-102 spectrophotometer. Elemental analyses were performed using a Perkin-Elmer CHN 2400 elemental analyzer. Melting points were obtained using a Shimadzu DT-30 thermal analyzer. Molecular weights and molecular weight distributions were determined using a JASCO 800 gel permeation chromatograph equipped with an RI detector and a Shodex KD-80M column in 0.05 M DMF solution at 50 °C; molecular weight calculations were made on the basis of polystyrene standards. Thermogravimetric analyses were performed using a Shimadzu DT-30 thermal analyzer at a heating rate 5 °C/min in an air or a N_2 atmosphere. Thermomechanical analyses were made using a Seiko Instruments TMA/SS equipped with a penetration probe of 1.0 mm diameter and using an applied constant load of 10 g (stress, 0.125 MPa) at a heating rate of 10 °C/min in air. The mechanical properties were examined at room temperature in air using a Seiko Instruments TMA/SS at a drawing rate of 10 mm/min; the sample

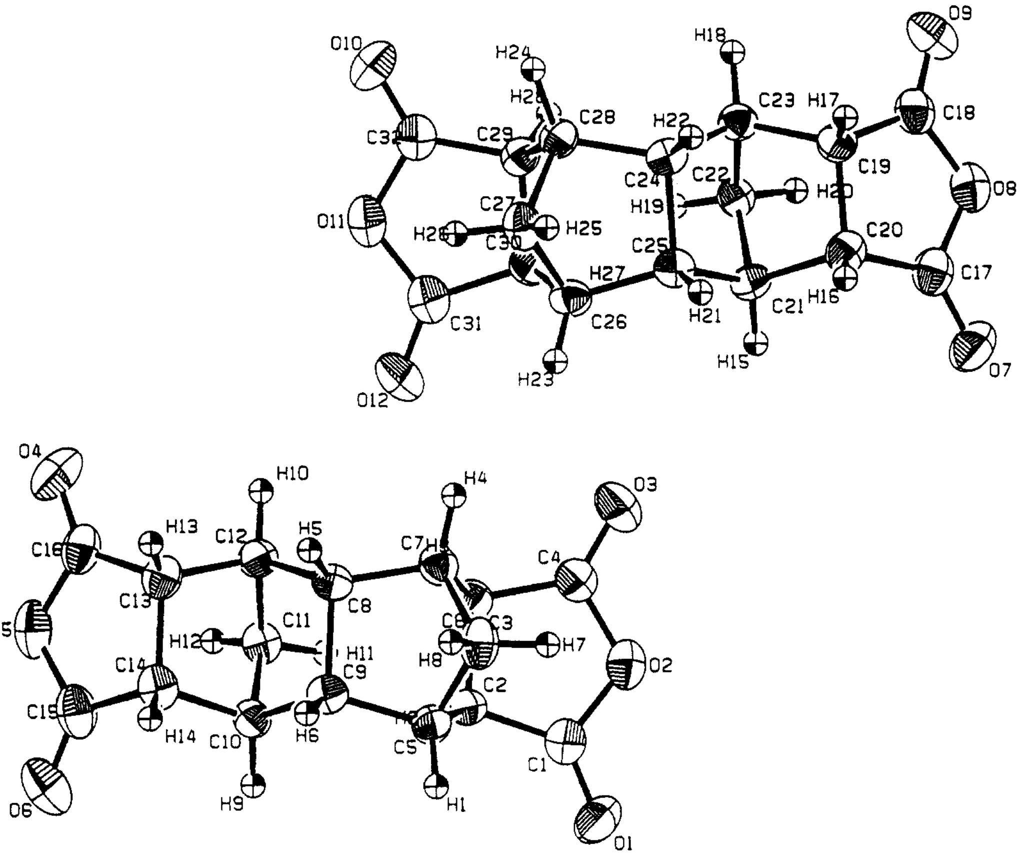


Figure 5. Perspective view of **3**. Thermal ellipsoids are drawn at the 50% probability level. The atom labeling used here is the same as in Tables 2 and 3.

Table 5. Solubility of Polyimides[a]

solvents	solubility[b] 3 + DDE	 5 + DDE
N-methyl-2-pyrrolidone	++	++
N,*N*-dimethylformamide	++	++
N,*N*-dimethylacetamide	++	++
conc H_2SO_4	++	++
pyridine	++	+
chloroform	++	–
m-cresol	++	+
1,3-dimethyl-2-imidazolinone	+	+
dioxane	+	–
dimethyl sulfoxide	+	+
acetonitrile	–	–
ethanol	–	–
ethyl acetate	–	–
tetrachloromethane	–	–
benzene	–	–
hexane	–	–
acetone	–	–

[a] Sample form: film. [b] ++, soluble at room temperature; +, soluble on heating; –, insoluble even on heating.

Table 6. Thermal Properties of Polyimides from 3 and Aromatic Diamines[a]

diamine	T_5 (°C)[b] in air	 in N_2	T_{dec} (°C)[c] in air	 in N_2	T_g (°C)[d] in air
DDE	470	521	488	543	404
DDM	466	501	488	529	301
DDS	442	462	456	486	201
BAPP	441	473	468	495	295
BAB	452	484	473	493	256
DDK	439	476	464	491	261

[a] Sample form: film. [b] 5% weight loss temperature measured by TGA with a heating rate of 5 °C/min. [c] Decomposition temperature measured by TGA with a heating rate 5 °C/min. [d] Glass transition temperature measured by TMA with a penetration probe of 1.0-mm diameter and using an applied constant load of 10 g (stress, 0.125 MPa) with a heating rate of 10 °C/min.

Table 7. Mechanical Properties of Polyimide Films from 3, 5, and Aromatic Diamines[a]

dianhydride	diamine	tensile modulus (GPa)	tensile strength (MPa)	elongation at break (%)
3	DDE	2.30	112	30
3	DDM	1.71	91	19
3	BAPP	1.77	99	35
5[b]	DDE	1.25	145	15
5[b]	DDM	1.67	91	12
5[b]	BAPP	1.05	96	9

[a] Measured by TMA at room temperature with a drawing rate of 10 mm/min (sample size: 10-mm length, 3-mm width, about 20-μm thickness). [b] In ref 17.

size (film) was 10-mm length, 3-mm width, and about 20-μm thick.

Monomer Synthesis. (4a*rH*,8a*cH*)-1,4,4a,5,8,8a-Hexahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene (1). 2,5-Norbornadiene (40 g, 0.43 mol) was allowed to react with cyclopentadiene (28.8 g, 0.44 mol) in a 200-mL autoclave at 195 °C for 6 h. Upon fractional distillation of the reaction mixture a colorless fraction was collected (31%): bp 60 °C (2 mmHg); ^{1}H NMR δ 0.960 (1H, d, $J_{10',10}$ = 8.8, H'-10), 1.49 (1H, d, $J_{9',9}$ = 7.8, H'-9), 1.62 (1H, dd, $J_{9,9'}$ = 7.8, $J_{9,5}$ = $J_{9,8}$ = 2.0, H-9), 2.19 (2H, d, $J_{4a,5}$ = $J_{8a,8}$ = 2.0, H-4a,8a), 2.46 (2H, d, $J_{1,2}$ = $J_{4,3}$ = 2.0, H-1,4), 2.55 (1H, d, $J_{10,10'}$ = 8.8, H-10), 2.66 (2H, ddd, $J_{5,6}$ = $J_{8,7}$ = 1.5, $J_{5,4a}$ = $J_{8,8a}$ = 2.0, $J_{5,9}$ = $J_{8,9}$ = 2.0, H-5,8), 6.02 (2H, d, $J_{6,5}$ = $J_{7,8}$ = 1.5, H-6,7), 6.19 (2H, d, $J_{2,1}$ = $J_{3,4}$ = 2.0, H-2,3); ^{13}C NMR δ 40.40 (C-10), 42.63 (C-1,4), 44.39 (C-5,8), 48.10 (C-4a,8a), 55.63 (C-9), 136.04 (C-6,7), 141.17 (C-2,3); IR (neat) 3050, 2950, 1650, 1570, 1450, 1350, 1335, 1315, 1295, 1245, 1215, 1130, 1095, 1020, 955, 890, 800, 755, 735, 710, 680 cm^{-1}.

Tetramethyl (4a*rH*,4a*cH*)-Decahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene-2*t*,3*t*,6*t*,7*t*-tetracarboxylate (2). In a 500-mL three-necked flask were placed 1 (16.2 g, 0.10 mol), $CuCl_2$ (110.4 g, 0.82 mol), 5% Pd/C (3.1 g, 0.29 mmol as Pd atom), and absolute methanol (300 mL). After replacement of the air in the flask with carbon monoxide, the reaction was allowed to proceed at room temperature with magnetic stirring, carbon monoxide being sometimes introduced through a balloon in which carbon monoxide was stored at normal pressure until no more consumption of carbon monoxide was observed (~3 h). The reaction mixture was filtrated through Celite and then evaporated to dryness. A mixture of chloroform (100 mL) and water (100 mL) was added to the residue, and the organic layer was separated. The organic solution was washed throughly with an aqueous $NaHCO_3$ solution and then water. After removal of the solvent under reduced pressure, the resulting solid was recrystallized from ethanol to give **2** as a white crystallite (23.8 g, 63%): mp 169–170 °C; ^{1}H NMR δ 1.34 (1H, d, $J_{9',9}$ = 10.3, H′-9), 1.55 (1H, d, $J_{10,10'}$ = 12.2, H-10), 1.86 (2H, H-4a,8a), 1.95 (1H, d, $J_{10',10}$ = 12.2, H-10′), 2.12 (1H, d, $J_{9,9'}$ = 10.3, H-9), 2.55 (2H, H-1,4), 2.60 (4H, H-2,3, H-5,8), 3.07 (2H, H-6,7), 3.60 (8H, 2,3-side CH_3), 3.61 (8H, 6,7-side CH_3); ^{13}C NMR δ 32.61 (C-10), 39.52 (C-9), 40.12 (C-1,4), 44.06 (C-5,8), 45.21 (C-6,7), 48.88 (C-4a,8a), 51.68 (CH_3), 52.14 (C-2,3), 173.21 (6,7-side CO), 173.59 (2,3-side CO); IR (KBr) 3000, 2950, 1730, 1430, 1370, 1315, 1245, 1200, 1160, 1120, 1095, 1030, 915, 820 cm^{-1}. Anal. Calcd for $C_{20}H_{26}O_8$: C, 60.91; H, 6.60. Found: C, 61.08; H, 6.70.

(4a*rH*,8a*cH*)-Decahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene-2*t*,3*t*,6*c*,7*c*-tetracarboxylic 2,3:6,7-Dianhydride (3). In a 500-mL three-necked flask were placed **2** (10 g, 0.025 mol), formic acid (120 mL), and catalytic amounts of *p*-toluenesulfonic acid, and the mixture was stirred magnetically at 90 °C for 5 h. Benzene (*ca.* 100 mL) was added to the reaction mixture and the generated methyl formate and formic acid (as the benzene azeotrope) were removed. To the residue was added formic acid (120 mL) and then the temperature was elevated to 90 °C. While the temperature was maintained, acetic anhydride (150 mL) was added dropwise to the solution (about 6 h), and then the mixture was allowed to react for 2 h. The reaction mixture was evaporated to dryness under reduced pressure. The resulting solid was washed with ether and recrystallized from acetic anhydride to give **3** as a colorless crystallite (6.6 g, 86%): mp 312 °C; ^{1}H NMR δ (DMSO-d_6) 0.88 (1H, d, $J_{10',10}$ = 13.4, H′-10), 1.16 (1H, d, $J_{9,9'}$ = 11.2, H-9), 1.38 (1H, dd, $J_{9',9}$ = 11.2, $J_{9',6}$ = $J_{9',7}$ = 1.0 (W-coupling), H′-9), 1.50 (2H, dd, $J_{10,10'}$ = 13.4, $J_{10,2}$ = $J_{10,3}$ = 1.0 (W-coupling), H-10), 2.03 (2H, H-4a,8a), 2.68 (2H, H-5,8), 2.73 (2H, H-1,4), 2.96 (2H, d, $J_{2,10}$ = $J_{3,10}$ = 1.0 (W-coupling), H-2,3), 3.24 (2H, d, $J_{6,9'}$ = $J_{7,9'}$ = 1.0 (W-coupling)); ^{13}C NMR δ (DMSO-d_6) 30.29 (C-10), 36.96 (C-9), 39.85 (C-1,4), 43.42 (C-5,8), 45.39 (C-6,7), 45.87 (C-4a,8a), 50.47 (C-2,3), 173.19 (2,3-side CO), 173.96 (6,7-side CO); IR (KBr) 3000, 1860, 1780, 1215, 1085, 930, 925 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_6$: C, 63.58; H, 4.64. Found: C, 63.60; H, 4.77.

X-ray Crystallographic Analysis of 3. A colorless prismatic crystal recrystallized from acetic anhydride was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Cu Kα radiation and a 12-kW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $69.29 < 2\theta < 79.44°$ corresponding to a monoclinic cell. The data were collected using the ω–2θ scan technique to a maximum 2θ value of 120.2°. Scans of $(1.37 + 0.30 \tan \theta)°$ were made at a speed of 32.0°/min (in ω). The diameter of the incident beam collimator was 0.5 mm, and the crystal to detector distance was 258 mm. An empirical absorption correction, using a program DIFABS,[19] was applied which resulted in the transmission factors ranging from 0.84 to 1.19. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (MITHRIL and DIRDIF).[20] All calculations were performed using a TEXSAN crystallographic software package from the Molecular Structure Corp.

General Polymerization Procedure. In a 30-mL three-necked flask containing NMP (8 mL) were placed the diamine (2.1 mmol) and pyridine (1 mL) while a slow stream of nitrogen was maintained. The mixture was stirred mechanically until the diamine was entirely dissolved. The tetracarboxylic dianhydride (2.1 mmol) was then added into the clear solution by one-fifth portions over a 5-h period. After being stirred at room temperature for 2 days in a nitrogen stream, the reaction mixture was poured into methanol (300 mL). The precipitated poly(amic acid) was filtered off and dried at room temperature for 1 day under vacuum and at 240 °C for 5 h to effect cyclization to the polyimide. Alternatively, the polyimide was also prepared by means of a thermal solution imidization technique, that is, by heating the poly(amic acid) solution at 200 °C for 1 h, followed by precipitation from methanol.

Polyimide Film. The poly(amic acid) solutions were cast onto glass plates using a doctor blade set at 30 mils. Polyimide films were prepared by drying under vacuum at room temperature for 1 day and then heating at 240 °C for 1 h. The polyimide films were also obtained from polyimide solutions by drying the glass plates on which the polyimide solutions prepared as described above were cast under vacuum at room temperature for 1 day and then at 100 °C for several hours.

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