Macromolecules **1999,** *32,* 4933−4939

Nonaromatic Polyimides Derived from Cycloaliphatic Monomers[1]

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Received March 16, 1999; Revised Manuscript Received May 24, 1999

ABSTRACT: A novel tetracarboxylic dianhydride bearing a cycloaliphatic structure, (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 (DNDA), was synthesized, and its structure was determined using X-ray crystallographic analysis. Polycondensation of DNDA or bicyclo[2.2.1]heptane-2-*endo*,3-*endo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (BHDA) with a cycloaliphatic diamine, bis(aminomethyl)bicyclo[2.2.1]heptane (BBH) was carried out in HMPA. A viscous poly(amic acid) solution was obtained only when BBH was slowly added to the HMPA solution of the dianhydride, whereas the reverse adding order of the monomers resulted in precipitation due to salt formation. The poly(amic acid) solutions afforded nonaromatic polyimides as flexible and free-standing films after being cast and cured. The polyimide films were soluble in organic solvents such as DMAc and were colorless with a cutoff at wavelength shorter than 235 nm. The average refractive index of the BHDA−BBH polyimide film was 1.522, and the optical anisotropy, the difference between in-plane and out-of-plane indices, was nearly zero. The dielectric constant that was estimated from the refractive index according to the modified Maxwell equation was 2.55. The polyimides have good thermal stability with the 5% weight-loss temperatures around 450 °C. The polyimide films exhibit higher T_g's over 290 °C. The high-temperature stability may be caused by the introduction of polyalicyclic structures, which results in an increase in the polymer main chain rigidity and less probability of main-chain scission.

Introduction

The earliest of the thermally stable polymers, and now one of the most common commercial materials, is an aromatic polyimide that was initially synthesized by DuPont and marketed under the name H-Film and later Kapton as a yellow film.[2] Because most of the aromatic polyimides including Kapton were insoluble in organic solvents and strongly absorbed in the visible region, great endeavor has been concentrated on the solubility enhancement and the achievement of colorlessness. Although a number of soluble polyimides have been prepared in recent years, most of them bear pendant alkyl and phenyl groups in the polymer backbone.[3,4] Colorless polyimides have been also reported where fluorinated monomers[5−12] or 1,1-bis(4-aminocyclohexyl)-methane and its analogue[13,14] were employed. Recently, we have synthesized soluble and colorless polyimides using dianhydrides with polyalicyclic (cycloaliphatic) structures and aromatic diamines, so-called “semiaromatic polyimides”.[15−20] The introduction of a cycloaliphatic unit into the polyimide backbone would facilitate less polymer−polymer interaction and enhance the solubility in organic solvents. The lack of color is generally associated with the absence or inhibition of intra- and/or intermolecular charge-transfer interactions. These polyimides showed excellent thermal stability with no significant weight loss up to approximately 400 °C, and the 5% weight-loss temperatures in N_2 were over 450 °C; some of them had glass transition temperatures over 380 °C. The high-temperature stability can also be explained by the introduction of a cycloaliphatic structure, which would foster less probability of main-chain scission because of the presence of multibonds and would increase main-chain rigidity. Of course, the use of aliphatic polymer constituents implies that the ultimate end use of such materials is targeted for applications with less stringent thermal requirements than those of aromatic polyimides, although there are some limited examples that may nearly compare with aromatic polyimides in thermal stability as described above. Aliphatic polyimides, however, have attracted much attention in recent years because of their potential applications including use as liquid crystal orientation layers, NLO buffer layers, or low dielectric materials.[21,22]

Aliphatic polyimides are classified into three distinct categories according to their chemical structures. Category 1 would be comprised of polyimides derived from aromatic dianhydrides and aliphatic diamines, which is one group of semiaromatic polyimides. The polyimides were first synthesized by Edwards from pyromellitic dianhydride and aliphatic diamines with a single chain like 1,9-diaminononane in 1955.[23] Recently, Imai prepared this type of polyimide with a high inherent viscosity from 3,3′,4,4′-benzophenonetetracarboxylic acid and aliphatic diamines using a high-pressure method via nylon-type monomers.[24] Category 2 comprises polyimides derived from aliphatic dianhydrides and aromatic diamines, which is another example of semiaromatic polyimides. Earlier, Tabushi reported the polyimides from tricyclo[4.2.2.0^{2,5}]dec-10-ene-3,4,7,8-tetracarboxylic 3:4,7:8-dianhydride or cyclobutane-1,2,3,4-tetracarboxylic dianhydride (CBDA) and aromatic diamines.[25] The CBDA-based polyimides were also synthesized and characterized by Nakanishi.[26] Moore reported that polyimides derived from CBDA were intrinsically photosensitive and formed a positive photoimage after light irradiation.[27,28] Some other examples have been synthesized using cycloaliphatic dianhydrides.[29,30] Category 3 would consist of fully aliphatic polyimides, “nonaromatic polyimides”, derived from aliphatic dianhydrides, and aliphatic diamines, although only a few papers have reported work on these polyimides. Pioneer research on the polyimides was carried out in 1962 by Wu using bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic 2:3,5:6-dianhyderide derivatives and aliphatic diamine with a single chain.[31] Recently, Volksen reported the synthesis of a fully cycloaliphatic polyimide from CBDA

10.1021/ma9903862 CCC: $18.00

and 1,1-bis(4-aminocyclohexyl)methane and investigated the optical properties such as the light transmittance and the refractive index, although the film was not tough but brittle.[22] Yokota prepared the same polyimide as a tough film and discussed the absorption, fluorescence, and thermal properties.[32]

In the present article, the synthesis and the properties of novel nonaromatic polyimides derived from bis(aminomethyl)bicyclo[2.2.1]heptane and bicyclo[2.2.1]heptane-2-*endo*,3-*endo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride or (4a*r**H*,8a*c**H*)-decahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene-2*c*,3*c*,6*c*,7*c*-tetracarboxylic 2,3:6,7-dianhydride will be described.

Experimental Section

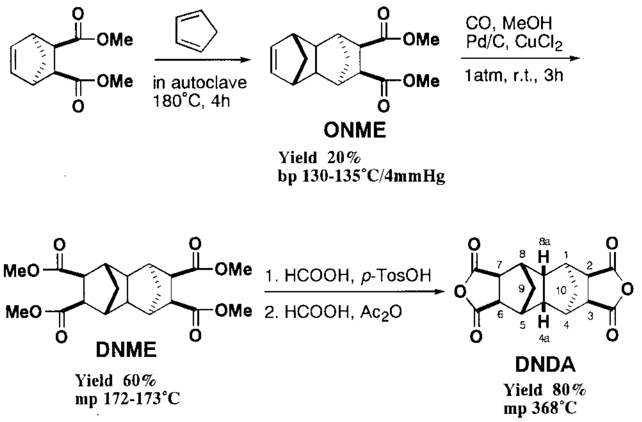
Materials. Bis(aminomethyl)bicyclo[2.2.1]heptane (BBH) was donated from Mitsui Chemicals, Co. Ltd., and used as received. BBH consists of four isomers, 2-*exo*,5-*exo*-bis(aminomethyl)bicyclo[2.2.1]heptane (30 wt %) and 2-*endo*,5-*exo*- (35 wt %), 2-*exo*,6-*exo*- (20 wt %), and 2-*endo*,6-*exo*- (15 wt %) isomers. Cyclopentadiene was prepared by thermal decomposition (retro-Diels–Alder reaction) of dicyclopentadiene at 180 °C which was obtained from Maruzen Petrochemical Co., Ltd. Hexamethylphosphoramide (HMPA) and *N*,*N*-dimethylacetamide (DMAc) were fractionally distilled over CaH$_2$ under reduced pressure and stored over molecular sieve 4A.

Measurements. The ^{1}H and ^{13}C NMR spectra were obtained using a JEOL JNM-EX 400WB and a JEOL JNM-LA500 spectrometer. The proton signals in the ^{1}H NMR spectrum were assigned in the H,H, C,H-COSY, and NOESY (elimination of *J* correlation) spectra. Infrared spectra were recorded using a JASCO VALOR III Fourier transform spectrometer. UV–vis spectra of the polyimide films were recorded on a Jasco V-570 UV/vis/NIR spectrophotometer. Film thickness and refractive index were measured by a Metricon model PC-2010 prism coupler (thin film thickness/refractive index measurement system) at room temperature in open air. The measurements were made at a wavelength of 632.8 nm (He–Ne laser). A prism 6561 designated 200-P-4 with a refractive index of 2.1677 at the He–Ne wavelength was used for the experiments. Using parallel (TE) and perpendicularly (TM) polarized laser light, the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of the sample films were determined. Thermal analyses were carried out using a Seiko SSC 5200-TG/DTA 220 instrument at a heating rate of 10 °C/min in a nitrogen atmosphere or in air for the thermogravimetric analysis (TGA). Thermomechanical analyses (TMA) were done using a Seiko Instruments TMA/SS 100 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. Melting points were determined using a Seiko SSC 5200-TG/DTA 220 instrument at a heating rate of 5 °C/min in air. Inherent viscosities were measured with an Ostwald viscometer in a 0.5 g/dL HMPA solution of poly(amic acid) at 30 °C.

Monomer Synthesis. *Bicyclo[2.2.1]heptane-2-endo,3-endo,5-exo,6-exo-tetracarboxylic 2,3:5,6-Dianhydride (BHDA).* BHDA was synthesized from bicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarboxylic anhydride according to the previous paper.[18,33]

(4arH,8acH)-1,2,3,4,4a,5,8,8a-Octahydro-1t,4t:5c,8c-dimethanonaphthalene-2c,3c-dicarboxylate (ONME). In a 200 mL autoclave were placed dimethyl bicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarboxylate (126 g, 0.6 mol) and cyclopentadiene (26.4 g, 0.4 mol), and the apparatus was heated at 180 °C for 6 h. By fractional distillation of the reaction mixture, ONME was obtained as a colorless fraction (22.1 g, 20% based on cyclopentadiene): bp 130–135 °C/4 mmHg. ^{1}H NMR δ (CDCl$_3$): 0.667 (1H, d, $J_{10',10} = 9$, H′-10(2,3-side)), 1.20 (1H, d, $J_{9,9'} = 8$, H-9), 1.27 (1H, d, $J_{9',9} = 8$, H′-9(6,7-side)), 2.43 (1H, d, $J_{10,10'} = 9$, H-10), 2.46 (2H, s, H-1,4), 2.55 (2H, s, H-4a,8a), 2.86 (2H, s, H-2,3), 2.91 (2H, s, H-5,8), 3.65 (6H, s, CH$_3$), 6.01 (2H, s, H-6,7). ^{13}C NMR δ (CDCl$_3$): 35.1 (C-10), 42.2 (C-4a,8a), 42.5 (C-1,4), 46.9 (C-5,8), 48.7 (C-2,3), 51.3 (CH$_3$), 53.2 (C-9), 136.6 (C-6,7), 172.8 (C=O). IR (KBr): 3050, 2950, 1733, 1430, 1342, 1200, 1170, 1093, 1059, 935, 910, 850, 815, 790, 770, 750 cm^{-1}. The atom labeling in the NMR spectra is same as in Scheme 1.

Scheme 1. Synthetic Route to DNDA



(4arH,8acH)-Decahydro-1t,4t:5c,8c-dimethanonaphthalene-2c,3c,6c,7c-tetracarboxylate (DNME). In a 500 mL three-necked flask were placed ONME (13.8 g, 0.05 mol), CuCl$_2$ (13.5 g, 0.10 mol), 5% Pd/C (1.6 g, 0.15 mmol as Pd), and absolute methanol (300 mL). After replacement of the air with carbon monoxide, the reaction was allowed to proceed at room temperature with magnetic stirring, carbon monoxide being sometimes introduced at normal pressure, until no further consumption of carbon monoxide was observed (about 3 h). The reaction mixture was filtered 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 and washed thoroughly with aqueous NaHCO$_3$ solution and then with water. After removal of the solvent under reduced pressure, the resulting solid was recrystallized from ethanol to give DNME as a white crystalline material (11.8 g, 60%): mp 172–173 °C. ^{1}H NMR δ (CDCl$_3$): 1.20 (1H, d, $J_{10',10} = 12$, H′-10(2,3-side)), 1.36 (1H, d, $J_{9',9} = 10$, H′-9(6,7-side)), 1.73 (1H, d, $J_{10,10'} = 10$, H-10), 2.08 (1H, d, $J_{9,9'} = 10$, H-9), 2.38 (2H, s, H-4a,8a), 2 57 (2H, s, H-1,4), 2.62 (2H, s, H-5,8), 2.99 (2H, s, H-2,3), 3.03 (2H, s, H-6,7), 3.61 (6H, s, 6,7-side CH$_3$), 3.63 (6H, s, 2,3-side CH$_3$). ^{13}C NMR δ (CDCl$_3$): 36.2 (C-10), 39.2 (C-9), 40.7 (C-1,4), 42.4 (C-4a,8a), 44.3 (C-5,8), 45.5 (C-6,7), 48.0 (C-2,3), 51.4 (2,3-side CH$_3$), 51.7 (6,7-side CH$_3$), 172.4 (2,3-side C=O), 173.7 (6,7-side C=O). IR (KBr): 2930, 1720, 1429, 1359, 1341, 1270, 1237, 1190, 1173, 1050, 1028, 925, 902 cm^{-1}. Anal. Calcd for C$_{20}$H$_{26}$O$_8$: C, 60.91; H, 6.60. Found: C, 60.98; H, 6.79.

(4arH,8acH)-Decahydro-1t,4t:5c,8c-dimethanonaphthalene-2c,3c,6c,7c-tetracarboxylic 2,3:6,7-Dianhydride (DNDA). In a 500 mL three-necked flask were placed DNME (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 were removed as the benzene azeotrope. 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 DNDA as a colorless crystalline solid (6.1 g, 80%): mp 368 °C. ^{1}H NMR δ (DMSO-d_6): 1.10 (1H, $J_{9',9} = 11$, H′-9(6,7-side)), 1.34 (1H, d, $J_{10',10} = 12$, H′-10(2,3-side), 1.45 (1H, d, $J_{9,9'} = 11$, H-9), 1.63 (1H, d, $J_{10,10'} = 12$, H-10), 1.85 (2H, s, H-4a,8a), 2.67 (2H, s, H-5,8), 2.80 (2H, d, $J_{1,2} = J_{4,3} = 1$, H-1,4), 3.25 (2H, s, H-6,7), 3.51 (2H, d, $J_{2,1} = J_{3,4} = 1$, H-2,3). ^{13}C NMR δ (DMSO-d_6): 36.7 (C-9), 37.1 (C-10), 39.2 (C-1,4), 43.3 (C-4a,8a), 43.9 (C-5,8), 45.5 (C-6,7), 50.6 (C-2,3), 172.4 (2,3 side C=O), 173.9 (6,7 side C=O). IR (KBr): 3045, 2960, 2900, 1840, 1770, 1480, 1300, 1232,

1140, 1085, 920 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_6$: C, 63.58; H, 4.64. Found: C, 63.55; H, 4.80.

X-ray Crystallographic Analysis of DNDA. A colorless prismatic crystal of DNDA recrystallized from acetic anhydride was mounted on a glass fiber. All measurements were done on a MAC Science MXC18 automated four-circle diffractometer with graphite-monochromated Cu Kα radiation and a 12 kW rotating anode generator. The 2479 reflections were collected, and 2177 of them were unique. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic was carried out. The function minimized was $\sum[w(|F_0|^2 - |F_c|^2)^2]$, in which $w = 1/[\sigma^2(F_0) + 0.0001|F_0|^2]$. Final R and R_w values were 0.043 and 0.056, respectively. The calculations were performed on a SUN SPARC station 2 using the program system CRYSTAN (Crystal Structure Analysis, MAC Science Structure Determination Package, MAC Science Co., Ltd., Tokyo, Japan). Atomic scattering factors were taken from ref 34.

General Polymerization Procedure and Film Preparation of Polyimide. In a 30 mL three-necked flask equipped with a mechanical stirrer were placed the dianhydride (2.0 mmol) and 3 mL of HMPA. As a slow stream of nitrogen gas was maintained, the mixture was stirred until the dianhydride was entirely dissolved. BBH (2.0 mmol) and an additional 2 mL of HMPA were then added into the clear solution. The flask was heated at 60 °C, and the solution was stirred for 2 days. An aliquot of the polycondensation solution containing poly(amic acid) was cast on a glass plate using a doctor blade. The remainder was poured into 300 mL of acetone in order to obtain the polymer as a solid which was subjected to the viscosity measurement. The polyimide film was prepared by heating the glass plate at 80 °C for 3 h, at 200 °C for 1 h, and then at 250 °C for 1 h under vacuum. After curing, the glass plate was immersed in boiling water to facilitate removal of the free-standing polyimide film.

Results and Discussion

Synthesis of DNDA. The synthetic route of (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 (DNDA) is illustrated in Scheme 1. The tetramethyl ester DNME was synthesized by the Pd-catalyzed bis-methoxycarbonylation of ONME, which was afforded by the Diels–Alder reaction of dimethyl bicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarboxylate with cyclopentadiene.

The assignment of the stereochemistry of DNME made by the NMR spectra is coincident with Stille's description that, in the palladium(II)-catalyzed bis-methoxycarbonylation of norbornene, the two methoxycarbonyl groups are introduced with the *exo*-configuration.[35] That is, two pairs of the two carbonyl groups have *endo*- and *exo*-configurations toward the two methylene bridge heads, respectively. The former is due to the starting material (ONME), and the latter is introduced by the bis-methoxycarbonylation. After the ester-exchange reaction of DNME catalyzed by *p*-toluenesulfonic acid in formic acid, the resulting tetracarboxylic acid was dehydrated in acetic anhydride to the dianhydride DNDA. The X-ray crystal data for DNDA were acquired from a colorless crystal (Table 1). Selected bond distances and bond angles are listed in Tables 2 and 3, respectively. The ORTEP drawing of DNDA is shown in Figure 1. The dianhydride is crystallized in the space group $P2_1/a$ (No. 14) and has four formula units in the unit cell.

Table 1. X-ray Crystal Data for DNDA

formula	$C_{16}H_{14}O_6$
fw	302.30
cryst color, habit	colorless, plates
cryst size (mm^3)	0.40 × 0.30 × 0.20
cryst syst	monoclinic
lattice parameters	
a (Å)	14.825(2)
b (Å)	11.083(2)
c (Å)	8.124(1)
β (deg)	99.89(1)
V (Å^3)	1314.9(3)
space group	$P2_1/a$ (No. 14)
Z	4
λ(Cu Kα) (Å)	1.542
μ (cm^{-1})	8.88
no. of measd reflns	2479
no. of obsd reflns	2090
R	0.043
R_w	0.056
temp (°C)	23

Table 2. Bond Lengths (Å) for DNDA[a]

atoms	distance[b]	atoms	distance[b]
O1–C7	1.389(3)	C13–H13	0.97(2)
O1–C8	1.397(2)	C13–C14	1.545(2)
O2–C7	1.191(3)	C13–H14	0.99(2)
O3–C8	1.191(3)	C14–C18	1.546(2)
O4–C22	1.381(3)	C14–C15	1.565(3)
O4–C21	1.394(3)	C15–H15	1.00(2)
O5–C22	1.192(3)	C15–C16	1.549(2)
O6–C21	1.181(3)	C16–H16	0.97(3)
C7–C10	1.496(3)	C16–C17	1.534(3)
C8–C9	1.498(3)	C16–C20	1.547(3)
C9–H9	0.96(3)	C17–H17B	0.99(3)
C9–C10	1.537(3)	C17–H17A	1.03(2)
C9–C13	1.558(3)	C17–C18	1.536(3)
C10–H10	0.98(2)	C18–H18	0.96(2)
C10–C11	1.561(2)	C18–C19	1.539(3)
C11–H11	0.96(2)	C19–H19	0.96(3)
C11–C12	1.538(3)	C19–C22	1.506(2)
C11–C15	1.541(2)	C19–C20	1.530(3)
C12–H12B	0.98(2)	C20–H20	0.99(2)
C12–H12A	1.02(2)	C20–C21	1.510(2)
C12–C13	1.536(2)		

[a] The atom labeling used here is same as in Figure 1. [b] Estimated standard deviations in the least significant figure are given in parentheses.

Polymer Synthesis. A viscous poly(amic acid) solution was obtained only when BBH was slowly added to the HMPA solution of the dianhydride, BHDA, or DNDA. Although in the initial stage of the polymerization a solid appeared, the solid was gradually dissolved and the mixture yielded a clear solution. However, a precipitate developed when adding the dianhydride to the HMPA solution containing BBH in the reverse adding order of monomers, which is used as a conventional method in poly(amic acid) preparations. The precipitate once formed was practically insoluble even after standing for 2 days at 60 °C with stirring. As illustrated in Figure 2, the nature can be explained by salt formation. That is, in the latter case, the carboxyl group of poly(amic acid) that was produced by the reaction between the diamine and the dianhydride is easily reacted with an excess of the free diamine to form the salt. In polycondensations of an aromatic diamine with aromatic or aliphatic dianhydrides, the addition order of the monomers does not strongly affect the polymerization behavior, although higher molecular weights are obtained for many poly(amic acid)s when the dianhydride is added to the diamine rather than the reverse addition. However, in the reaction using an aliphatic diamine the order becomes significantly important. The basicity of primary aliphatic amines (pK_b = 3.4) such as cyclohexylamine is about a million times higher than that of aromatic amines (pK_b = 9.4) such as aniline, and the difference influences the polymerization behavior as Volksen pointed out.[22] The insoluble

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

atoms	angle[b]	atoms	angle[b]
C7−O1−C8	110.9(2)	H15−C15−C16	105(1)
C22−O4−C21	110.5(1)	H15−C15−C14	110(1)
O2−C7−O1	120.0(2)	C11−C15−C16	123.2(2)
O2−C7−C10	129.8(2)	C11−C15−C14	103.6(1)
O1−C7−C10	110.2(2)	C16−C15−C14	102.6(1)
O3−C8−O1	120.2(2)	H16−C16−C17	117(2)
O3−C8−C9	130.4(2)	H16−C16−C20	112(1)
O1−C8−C9	109.4(2)	H16−C16−C15	113(1)
H9−C9−C8	109(1)	C17−C16−C20	100.2(1)
H9−C9−C10	112(1)	C17−C16−C15	99.4(1)
H9−C9−C13	111(1)	C20−C16−C15	112.6(2)
C8−C9−C10	105.0(2)	H17B−C17−H17A	109(2)
C8−C9−C13	115.1(1)	H17B−C17−C16	113(1)
C10−C9−C13	103.8(1)	H17B−C17−C18	114(1)
H10−C10−C7	108(1)	H17A−C17−C16	112(1)
H10−C10−C9	115(1)	H17A−C17−C18	113(1)
H10−C10−C11	110(1)	C16−C17−C18	94.6(1)
C7−C10−C9	104.3(2)	H18−C18−C17	115(2)
C7−C10−C11	115.9(2)	H18−C18−C19	115(1)
C9−C10−C11	103.7(1)	H18−C18−C14	112(1)
H11−C11−C12	118(1)	C17−C18−C19	101.8(1)
H11−C11−C15	115(1)	C17−C18−C14	99.8(1)
H11−C11−C10	113(1)	C19−C18−C14	111.1(1)
C12−C11−C15	104.0(1)	H19−C19−C22	107(1)
C12−C11−C10	97.5(1)	H19−C19−C20	116(1)
C15−C11−C10	107.9(1)	H19−C19−C18	114(1)
H12B−C12−H12A	107(2)	C22−C19−C20	104.8(2)
H12B−C12−C13	113(1)	C22−C19−C18	111.9(2)
H12B−C12−C11	111(1)	C20−C19−C18	103.2(1)
H12A−C12−C13	114(1)	H20−C20−C21	107(1)
H12A−C12−C11	116(1)	H20−C20−C19	116(1)
C13−C12−C11	95.6(1)	H20−C20−C16	115(1)
H13−C13−C12	117(1)	C21−C20−C19	104.0(1)
H13−C13−C14	117(1)	C21−C20−C16	110.3(2)
H13−C13−C9	112(1)	C19−C20−C16	104.1(1)
C12−C13−C14	104.6(1)	O6−C21−O4	120.3(2)
C12−C13−C9	98.1(1)	O6−C21−C20	129.4(2)
C14−C13−C9	106.4(1)	O4−C21−C20	110.2(2)
H14−C14−C13	110(1)	O5−C22−O4	120.0(2)
H14−C14−C18	104(1)	O5−C22−C19	129.7(2)
H14−C14−C15	113(1)	O4−C22−C19	110.3(2)
C13−C14−C18	122.9(2)	C12−H12A−H12B	36(1)
C13−C14−C15	103.0(1)	C12−H12B−H12A	38(1)
C18−C14−C15	103.2(1)	C17−H17A−H17B	35(1)
H15−C15−C11	111(1)	C17−H17B−H17A	36(1)

[a] The atom labeling used here is same as in Figure 1. [b] Estimated standard deviations in the least significant figure are given in parentheses.

salt formation was also observed using *N*,*N*-dimethylacetamide (DMAc) as a polymerization medium instead of HMPA. The structures and the abbreviations of the polyimides are illustrated in Figure 3 together with semiaromatic and aromatic polyimides that were synthesized in this study. Inherent viscosities (η_{inh}) measured using a 0.5 g/dL HMPA solution of poly(amic acid) at 30 °C were 1.50 dL/g for the BHDA−BBH polymer and 1.57 dL/g for the DNDA−BBH polymer. The flexible, free-standing, and colorless polyimide films were prepared by doctor blading the polymerization solutions onto glass slides and curing under vacuum.

Properties of Polyimides. The nonaromatic polyimide films were free-standing and soluble in polar solvents such as HMPA, DMAc, 1-methyl-2-pyrrolidinone, etc. In the IR spectrum of the PI(DNDA−BBH) film, strong absorptions at 1768 and 1695 cm^{-1} assigned to the imide carbonyl group appear, and they are 10−20 cm^{-1} lower than those of an aromatic polyimide (1775 and 1717 cm^{-1}). Nonconjugation of the imide carbonyl group due to the absence of an aromatic ring causes the absorption shifts.

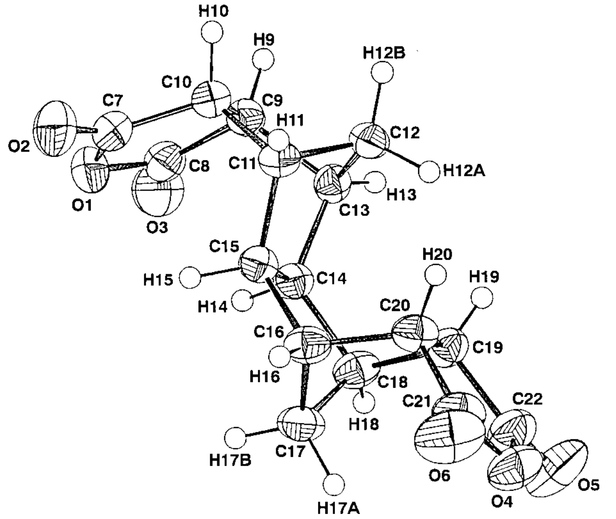


Figure 1. Perspective view of DNDA. Thermal ellipsoids are drawn at the 50% probability level. The atom labeling is the same as in Tables 2 and 3.

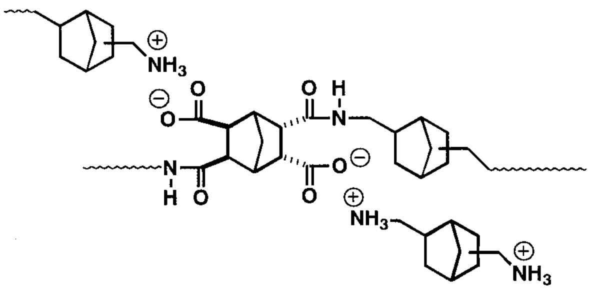


Figure 2. Salt formation between an excess of the free diamine and a carboxyl group of poly(amic acid). An example for the polycondensation of BHDA with BBH.

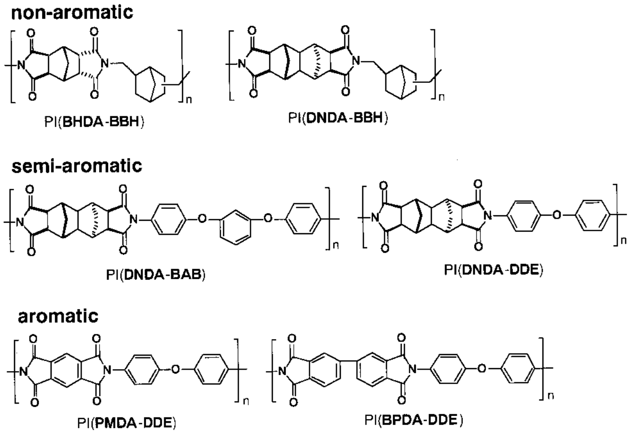


Figure 3. Structures and abbreviations of nonaromatic, semiaromatic, and aromatic polyimides synthesized in this study.

The transmission UV−vis spectrum of the PI(DNDA−BBH) film is shown in Figure 5 together with those of a semiaromatic polyimide PI(DNDA−BAB) and aromatic polyimides, PI(PMDA−DDE) and PI(BPDA−DDE). The nonaromatic polyimide PI(DNDA−BBH) film exhibits a cutoff at 234 nm and is entirely colorless, although a small absorption around 280 nm due to the carbonyl n−π^* can be observed. A cutoff wavelength is defined here as the point where the transmittance becomes below 1% in the spectrum. In the case of the semiaromatic polyimide, a strong absorption assigned to the benzenoid B-band appears at 280 nm, even

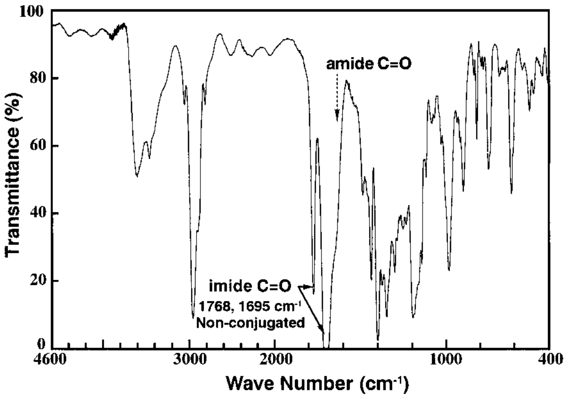


Figure 4. FT-IR spectrum of free-standing PI(DNDA–BBH) film.

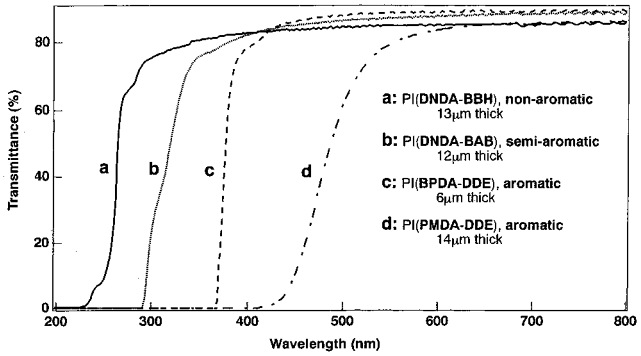


Figure 5. UV–vis spectra for free-standing films of nonaromatic, semiaromatic, and aromatic polyimides.

though the film is colorless. Aromatic polyimides absorb visible light due to the charge transfer. The cutoff wavelengths of PI(PMDA–DDE) and PI(BPDA–DDE) films are 426 and 377 nm, respectively, and the former is colored reddish yellow and the latter is light yellow.

Film refractive index and thickness were determined by a prism coupler method.[36–38] The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of the sample films can be determined using polarized laser light. An average refractive index (n_{AV}) was calculated using the equation $n_{\mathrm{AV}} = (2n_{\mathrm{TE}} + n_{\mathrm{TM}})/3$, and its optical anisotropy (Δn) is given as the difference between n_{TE} and n_{TM}. The results are listed in Table 4 along with those of a semiaromatic and aromatic polyimides for comparative purposes. The n_{AV} of the PI(BHDA–BBH) film is as low as 1.522 and is comparable to poly(ethylene) (density 0.94–0.945 g/cm^3). The decreasing aromatic character of the polyimide diminishes the refractive index as exemplified by the comparison of PI(DNDA–BAB) and PI(PMDA–DDE), in agreement with one generalization that aromatic polymers possess high refractive indices.[39] The Δn of the PI(BHDA–BBH) film is nearly zero. Optical anisotropy is related to the degree of orientation of the refracting units; therefore, it provides additional information regarding the orientational effects of the polyimide. It has been reported that aromatic polyimides may exhibit a large anisotropy which indicates the preference of the polymer chains to orient in the plane of the film.[40] The negligibly small anisotropy in PI(BHDA–BBH) implies that the polymer chains are randomly oriented in the film, and it may be caused by the nature of the "copolyimide" stereochemistry because the cycloaliphatic diamine BBH used here is not a single compound but a mixture of four isomers as described in the Experimental Section. The dielectric constant ϵ of the material at optical frequencies can be estimated roughly from the refractive index n according to Maxwell's equation, $\epsilon \cong n^2$. The ϵ around 1 MHz is evaluated to be $\epsilon \cong 1.10n^2$, including an additional contribution of approximately 10% from the infrared absorption.[41] Volksen stated that the experimental ϵ value measured electrically was quite consistent with that estimated from the refractive index data.[22] The refractive index of 1.522 determined for PI(BHDA–BBH) translates into a dielectric constant of 2.55, whereas the dielectric constants are 2.82 and 3.14 for PI(DNDA–BAB) and PI(PMDA–DDE), respectively.

The thermogravimetric analyses (TGA) of polymer films were done at a heating rate of 10 °C/min. The profile of the PI(DNDA–BBH) film measured in nitrogen is shown in Figure 6 along with those of a semiaromatic polyimide PI(DNDA–DDE) and poly(ethylene) as a representative nonaromatic polymer. PI(DNDA–BBH) has good thermal stability with no significant weight loss up to approximately 350 °C, and the 5% weight-loss temperature (T_5) is 459 °C, although that of PI(DNDA–DDE) is as high as 514 °C. In the differential TG (DTG) curve for PI(DNDA–BBH), the temperature with a maximum rate of the decomposition in N_2 appears clearly at 500 °C. On the other hand, the weight loss of poly(ethylene) starts around 250 °C and the T_5 is 367 °C. The glass transition temperature (T_g) of the polyimide films was measured using a thermomechanical analyzer (TMA) equipped with a penetration probe. The nonaromatic polyimides have T_g's over 290 °C, and this may be caused by the introduction of polyalicyclic structures which results in an increase in the polymer main-chain rigidity. The T_5's were also measured in air, and the results are summarized in Table 5. The stability of these nonaromatic polyimides toward thermal decomposition would be explained by their chemical structure. The degradation of polymers in an inert atmosphere is caused by homolytic C–C bond scission. If the polymer backbone consists of a single chain like that of poly(ethylene), the scission results in direct decreasing of the molecular weight. In most cases, volatile compounds are produced and released as a decomposed gas. On the other hand, in the case of stepladder type polymers bearing double strands such as the cycloaliphatic polyimides, even if the C–C bond scission occurs, it does not lead to a significant decrease in the molecular weight or to the production of volatile compounds. In other words, the introduction of the multibonds facilitates less probability of main-chain scission.

Conclusions

(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 (DNDA) was synthesized using dimethyl bicyclo[2.2.1]-hept-5-ene-2-*endo*,3-*endo*-dicarboxylate as a starting material via several steps. DNDA and bicyclo[2.2.1]-heptane-2-*endo*,3-*endo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (BHDA) were condensed with a cycloaliphatic diamine, bis(aminomethyl)bicyclo[2.2.1]heptane (BBH), in HMPA to form the corresponding poly(amic acid)s. A viscous poly(amic acid) solution was obtained only when BBH was slowly added to the HMPA solution of the dianhydride. A precipitate developed when adding the dianhydride to the HMPA solution containing BBH in the reverse adding order of monomers, and the nature can be explained by insoluble

Table 4. Refractive Indices and Dielectric Constants of Polyimide Films

polyimides	category	d (μm)[a]	n_{TE}[b]	n_{TM}[c]	n_{AV}[d]	Δn[e]	ϵ[f]
PI(BHDA−BBH)	nonaromatic	14.8	1.522	1.522	1.522	0.000	2.55
PI(DNDA−BAB)	semiaromatic	12.3	1.607	1.594	1.603	0.013	2.83
PI(PMDA−DDE)	aromatic	6.2[g]	1.715[g]	1.636[g]	1.689	0.079	3.14

[a] Film thickness. [b] The in-plane refractive indices. [c] The out-of-plane refractive indices. [d] Average refractive index; $n_{AV} = (2n_{TE} + n_{TM})/3$. [e] Optical anisotropy; $\Delta n = n_{TE} - n_{TM}$. [f] Optically estimated dielectric constant; $\epsilon = 1.10n_{AV}^2$. [g] By Noe et al. in ref 37.

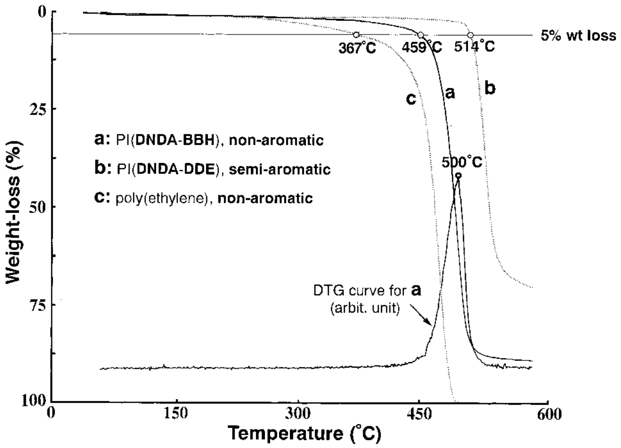


Figure 6. TGA profiles of polyimide films along with poly(ethylene) and the differential TG curve (DTG) for PI(DNDA−BBH) film: measured at a heating rate of 10 °C/min in N_2 (flow rate: 200 mL/min).

Table 5. Thermal Properties of Polymers

polymer	category	T_5 (°C)[a] in N_2	T_5 (°C)[a] in air	T_g (°C)[b]
PI(PMDA−DDE)	aromatic	515	480	429
PI(DNDA−DDE)	semiaromatic	514	470	404
PI(PMDA−BBH)	semiaromatic	448	406	282
PI(BHDA−BBH)	nonaromatic	455	411	297
PI(DNDA−BBH)	nonaromatic	459	416	340
poly(ethylene)	nonaromatic	367	352	135

[a] 5% weight-loss temperature measured by TGA at a heating rate of 10 °C/min in N_2 or air. Gas flow rate: 200 mL/min. [b] 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) at a heating rate of 10 °C/min in air.

salt formation. The poly(amic acid) solutions gave the nonaromatic polyimides as flexible and free-standing films. The films were soluble in organic solvents such as DMAc. In the IR spectrum of the polyimide, the absorptions due to the imide carbonyl group appear at a 10−20 cm^{-1} lower region than those of an aromatic polyimide. The nonaromatic polyimide film exhibits a cutoff at a wavelength shorter than 235 nm and is entirely colorless. The average refractive index of PI(BHDA−BBH) film was 1.522, and the optical anisotropy was nearly zero. When the dielectric constant ϵ is estimated roughly from the refractive index according to the modified Maxwell equation, $\epsilon \cong 1.10n^2$, the refractive index of 1.522 translates into a dielectric constant of 2.55. The polyimides have good thermal stability with no significant weight loss up to approximately 350 °C, and the T_5 is around 450 °C. The polyimide films possess T_g's over 290 °C, which may be caused by the introduction of cycloaliphatic structures which results in an increase in the polymer main-chain rigidity.

The nonaromatic polyimides may be of interest for microelectronics or optoelectronics applications.

Acknowledgment. The author is indebted to Messrs. Y. Takahashi and S. Okuda of the Tokyo Institute of Polytechnics for their technical assistance. He acknowledges Dr. C. Feger at T. J. Watson Research Center, IBM, for measuring the refractive index and thanks Dr. W. Volksen at Almaden Research Center, IBM, for helpful discussion. This work was partly supported by a research grant from the Tokyo Ohka Foundation for the Promotion of Science and Technology and by a Grant-in-Aid for Scientific Research (No. 09651004) from the Ministry of Education, Science, Sports and Culture, Japan.

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MA9903862