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Soluble and Colorless Polyimides from Bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic 2,3:5,6-Dianhydrides[1]

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ABSTRACT: Two tetracarboxylic dianhydrides with a polyalicyclic structure, bicyclo[2.2.2]octane-2-*endo*,3-*endo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (**5a**) and bicyclo[2.2.2]octane-2-*exo*,3-*exo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (**5b**), were synthesized, and polycondensations of the dianhydrides with aromatic diamines were carried out in well-purified *N*,*N*-dimethylacetamide (DMAc) at 85−105 °C under N_2. The resulting poly(amic acid)s as precipitated possessed inherent viscosities in the range 0.5−0.1 dL/g. Some of the poly(amic acid)s formed flexible and tough films after curing. Polyimides were also obtained by a thermal solution imidization method where the DMAc solutions of poly(amic acid)s were heated at reflux temperature for 6 h. All of the examined polyimides were soluble at room temperature in aprotic and protic polar solvents such as DMAc and *m*-cresol. All of the 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. The polyimides had glass transition temperatures over 380 °C except for the polyimides using 1,3-bis(4-aminophenoxy)benzene as an aromatic diamine. The flexible polyimide films possessed a tensile modulus range of 1.5−2.6 GPa, a tensile strength range of 52−96 MPa, an elongation at break of 3−11%, and a dielectric constant range of 3.2−3.7. These films exhibited cutoffs at wavelengths shorter than 320 nm and were entirely colorless. Normalized transparencies in the visible region (400−780 nm) were over 86% and, notably, the film prepared from **5a** and 4,4′-diaminodiphenyl ether had an excellent transparency of 94%. Colorlessness and transparency of the film at room temperature were maintained up to 200 °C when the film was heated in air and to 400 °C in N_2. The polyimide of which the end group (the aromatic amino group) was capped using acetic anhydride was almost colorless even when heated at 300 °C in air.

Introduction

Polyimides synthesized from only aromatic monomers, wholly aromatic polyimides, exhibit excellent electrical and high-temperature mechanical properties, and their use for microelectronic applications has dramatically increased over the past several years. Unless carefully designed, however, polyimides are often insoluble and intractable in their fully imidized form, thus presenting serious processing difficulties. Therefore, the soluble precursor polymers, poly(amic acid)s, are deposited onto the substrates and thermally cyclodehydrated at elevated temperature to yield the insoluble polyimide coatings or films. One of the major drawbacks of these precursors is that they have a limited pot life and must generally be kept refrigerated during storage. Additionally, water is given off during the cyclization process, which may lead to voids, shrinkage, and stress formation in the final coating. Much effort has been spent on synthesizing tractable, processable polyimides that reasonably maintain the desired properties. One of the more successful attempts to accomplish this goal is to incorporate pendant alkyl and phenyl groups or fluorine, chlorine, phosphorus, and flexible bridging units into the polyimide backbone.[2−7] Another approach to enhance solubility is to utilize alicyclic dianhydrides, though the high-temperature stability is significantly sacrificed.[8−10]

On the other hand, the wholly aromatic polyimides strongly absorb in the visible region of their UV−vis spectra and are pale yellow or deep reddish yellow because of their highly conjugated aromatic structures and/or the intermolecular charge-transfer (CT) complex formation.[11−13] Consequently, they cannot be used in areas where colorlessness and transparency are important requirements. The first example of colorless polyimides prepared from hexafluoroisopropylidene-bridged diamine and dianhydride was reported as a patent by Rogers about 30 years ago.[14] St. Clair et al. focused much attention on colorless polyimides from the viewpoint of the potential applications on space components such as multilayer insulation blankets, solar cells, and thermal control coating systems.[15−17] They demonstrated that polyimides containing the hexafluoroisopropylidene group and/or sulfone linkage exhibited high transparency in the visible region. Their approach was to separate the chromophoric groups and reduce the electronic interaction between the color-causing centers in the polymer molecular structure by employing the steric hindrance and electronic effects of the groups. In another approach, they performed polymerizations with highly purified monomers. Many other examples have since been reported where dianhydrides with a biphenyl structure and fluorinated or aliphatic monomers were employed.[18−23]

We have already achieved the synthesis of soluble and almost colorless polyimides using dianhydrides with polyalicyclic structures.[24−26] Moreover, we reported soluble and entirely colorless polyimides prepared from a dianhydride with a bicyclo[2.2.1]heptane structure and aromatic diamines, although it was essential that a mixture of triphenyl phosphite and pyridine (TPP/Py) was added during the course of the polymerization process.[27] The obtained polyimide film showed a cutoff at around 280 nm and was entirely transparent and colorless, whereas those prepared without TPP/Py when polymerized were slightly reddish yellow. Their nature is considered to contribute to the inhibition of intra- and/or intermolecular CT complex formation by incorporation of a polyalicyclic unit in the polymer chain. Fur-

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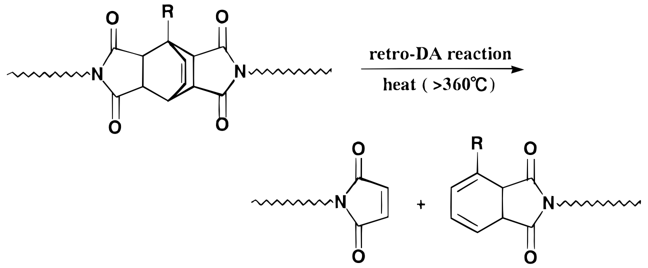
Scheme 1

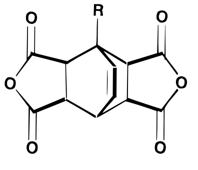


thermore, because it has been reported that tervalent phosphorus compounds such as TPP served as an antioxidizing agent or as a reductant for *N*-oxides and peroxides, TPP/Py is thought to inhibit trace amounts of readily oxidizable compounds, which are contained in the reactants and the solvent, from being oxidized to colored substances during the polymerization or heat imidization. The addition of TPP/Py during polymerization endowed the polyimides with not only colorlessness but also enhancement in film formability.

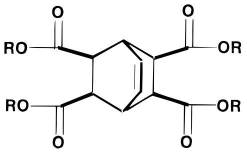
Recently, we briefly reported the preparation and characterization of soluble and colorless polyimide films without TPP/Py from bicyclo[2.2.2]octane-2-*endo*,3-*endo*,5-*exo*,6-*exo*-2,3:5,6-dianhydride or the all-*exo* isomer and aromatic diamines.[28] The present article describes in further detail the synthesis and structural eludication of the dianhydrides and a wide variety of the interesting properties of these polyimides.

Results and Discussion

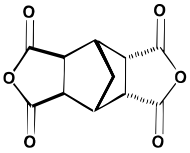
Monomer Synthesis. In our first study, bicyclo[2.2.2]oct-7-ene-2-*exo*,3-*exo*,5-*exo*,6-*exo*-2,3:5,6-dianhydride and its homolog (**6a** and **6b**) were synthesized and used for polycondensation with aromatic diamines in order to obtain the polyimides.[24] The polymers underwent thermal decomposition around 360 °C in N_2, which was a consequence of the retro-Diels–Alder (DA) reaction of the retrodegradative bicyclo[2.2.2]oct-7-ene structure from the GC–MS analysis of the pyrolyzed products of the prototype of the polyimides, as illustrated in Scheme 1. This fact let us attempt the synthesis of a saturated dianhydride, bicyclo[2.2.2]octane-2-*exo*,3-*exo*,5-*exo*,6-*exo*-2,3:5,6-dianhydride (**5b**), which was postulated to give more thermally stable polyimides because the retro-Diels–Alder reaction did not appear to occur at the polyalicyclic unit. At first, compound **5b** was thought to be obtained easily by hydrogenation of the carbon–carbon double bond of **6a**. Although a wide variety of procedures were employed for the reduction of **6a** or the esters (**7a** and **7b**) derived from **6a** (Table 1), these attempts were unsuccessful and the raw materials were recovered in all cases. This is probably due to a steric hindrance toward catalytic hydrogenation. Generally, catalytic hydrogenation proceeds heterogeneously and the reaction is known to occur on the surface of the solid catalyst. All *exo* configurations of the four carbonyl groups of the dianhydride or the esters may make it impossible for the π electron cloud of the carbon–carbon double bond to come close to the catalyst surface as shown in Figure 1a. Adoption of a quite novel method has recently enabled us to prepare the dianhydride, and the synthetic route is illustrated in Scheme 2. The phthalic acid was reduced electrochemically in acidic media to give (±)-*trans*-1,2-dihydrophthalic acid (**1**) in good yield. Although **1** was a racemic mixture of two isomers with different configurations (1*S*,2*S* and 1*R*,2*R*), it is illustrated in Scheme 2 as the 1*S*,2*S*



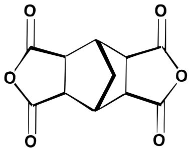
R: H (6a) CH3 (6b)



R: CH3 (7a) C2H5 (7b)



8a



8b

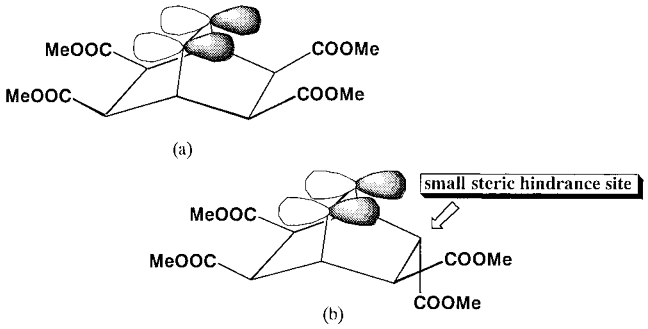
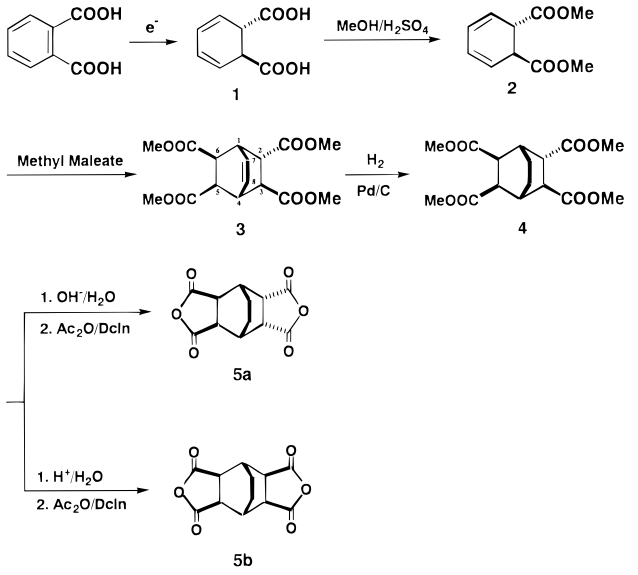


Figure 1. Steric hindrance toward catalytic hydrogenation of tetramethyl bicyclo[2.2.2]hept-7-ene-2,3,5,6-tetracarboxylates (a) with all-*exo* (**7a**) and (b) with three-*exo* and one-*endo* (**3**) configurations.

Table 1. Catalytic Hydrogenation of 6a, 7a, and 7b

substrate	cat.	solvent	H_2 press. (kg/cm^2)	reacn temp (°C)	reacn time (h)
6a	Pt/C	dioxane	1	reflux	6
6a	Pd/C	*N*,*N*-dimethyl-acetamide	1	r.t.	8
6a	Pd/C	dioxane	1	reflux	6
6a	Raney Ni-W2	dioxane	1	reflux	8
6a	Pt/C	dioxane	50	160	12
6a	Pd/C	dioxane	50	160	14
6a	Raney Ni-W2	dioxane	50	160	12
7a	Pd/C	EtOH	20	r.t.	20
7b	Raney Ni-W2	EtOH	90	80	8

Scheme 2



product. The acid was esterified with methanol in the presence of a catalytic amount of concentrated sulfuric acid. The resultant dimethyl ester (**2**) was allowed to react with dimethyl maleate at 190 °C for 9 h in a nitrogen atmosphere to give the tetramethyl ester (**3**) as a Diels–Alder adduct. According to the Woodward–Hoffmann rule, ester **3** was considered to have one *endo* and three *exo* configurations, which was supported by the NMR spectrum of **3**. Judging from the NMR spectrum and the optical rotation value (0°), it was found that **3** was a racemic mixture of two compounds with 2-*endo*,3-*exo*,5-*exo*,6-*exo* and 2-*exo*,3-*endo*,5-*exo*,6-*exo* configurations. The NMR signals were assigned as the 2-*endo*,3-*exo*,5-*exo*,6-*exo* product, illustrated in Scheme 2 as **3**. Ester **3** was hydrogenated in an autoclave using Pd/C as a catalyst to give ester **4** with a saturated polyalicyclic structure, bicyclo[2.2.2]octane. The NMR signals of **4** were also assigned as the 2-*endo*,3-*exo*,5-*exo*,6-*exo* tetramethyl ester, although **4** was, of course, a racemic mixture. Ester **3** has one *endo*-configurated carbonyl group and it may make the steric hindrance become lower compared with the all-*exo* configurated ester shown in Figure 1b. Therefore, **3** would come close to the catalyst surface and undergo a hydrogenation reaction. Ester **4** was hydrolyzed in two ways, a base-catalyzed hydrolysis and an acid-catalyzed hydrolysis, to give the tetracarboxylic acids. The tetracarboxylic acids were, without being isolated, converted into dianhydrides by heating in a mixture of acetic anhydride and decahydronaphthalene (decalin). Interestingly, two kinds of dianhydrides with different configurations were obtained using different hydrolysis conditions. Base-catalyzed hydrolysis followed by dehydration gave bicyclo[2.2.2]octane-2-*endo*,3-*endo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (**5a**), whereas the all-*exo* isomer (**5b**) was produced by the acid-catalyzed hydrolysis. Although at the present time we cannot exactly explain the reason why distinct dianhydrides were produced under the different hydrolysis conditions, different kinds of isomerization reactions may occur there along with the hydrolysis reactions.

Polymer Synthesis. St. Clair et al. stated that polymerizations must be performed with highly purified monomers in order to synthesize polyimide films with the objective of obtaining maximum optical transparency and that special care has to be exercised to prevent contamination of the polymerization media by impurities.[29] The polymerization solvent, *N*,*N*-dimethylacetamide (DMAc), was carefully purified and stored over 4A molecular sieves under N_2 in the dark, and monomers were recrystallized twice and then sublimed just prior to use. In general, polyimides were prepared via two steps: the first step includes the poly(amic acid) formation at room temperature, and as the second step, the viscous polymer solutions are deposited onto the substrates and thermally cyclodehydrated at elevated temperature to yield the corresponding polyimide. The dianhydrides **5a** and **5b** with a bicyclooctane structure were less reactive than those (**8a** and **8b**) with the bicycloheptane structure, which were previously reported,[25,27] due to the smaller strain of the bicyclo ring structure. That is, the bicyclooctane backbone is made up of three cyclohexane structures with a smaller ring strain, whereas the bicycloheptane backbone is made up to two cyclopentane and one cyclohexane structure with a larger strain. Therefore, even during the first polymerization step, a higher temperature was needed in order to obtain high molecular weight poly(amic acid)s which could be converted to the polyimides with film formability after the thermal cyclodehydration processing. As can be seen in Table 2, the polymerization of **5a** with 4,4′-diaminodiphenyl ether (DDE) at 90 °C gave a higher molecular weight poly(amic acid) ($\eta_{\mathrm{inh}} = 0.53$ dL/g), which formed a flexible and tough film after being cast on a glass plate and cured at 80 °C for 2 h under vacuum and then at 250 °C for 2 h. On the other hand, the polymerization at room temperature yielded a poly(amic acid) with a low molecular weight ($\eta_{\mathrm{inh}} = 0.14$ dL/g), which was only converted into a brittle and pulverized polyimide film. Several kinds of poly(amic acid)s other than that from **5a** and DDE gave flexible and tough films after curing. The aromatic diamines used here were DDE, 4,4′-diaminodiphenylmethane (DDM), 4,4′-diaminodiphenyl sulfone (DDS), and 1,3-bis(4-aminophenoxy)benzenne (BAB), whose structures are shown in Scheme 3 along with the polymer synthesis route. Poly(amic acid)s as precipitated possess inherent viscosities in the range 0.53–0.10 dL/g. The IR spectra of the precipitated polymers showed that the poly(amic acid)s partly contained the

Table 2. Polymerizations of 5a and 5b with Aromatic Diamines[a]

dianhydride	diamine	*T* (°C)[b]	(dL/g)[c]	film
5a	DDE	rt	0.14	brittle
5a	DDE	90	0.53	flexible
5a	DDM	90	0.16	flexible
5a	DDS	95	0.10	powdery
5a	BAB	95	0.18	flexible
5b	DDE	95	0.34	flexible
5b	DDM	85	0.18	brittle
5b	DDS	90	0.16	brittle
5b	BAB	90	0.20	flexible

[a] Dianhydride, 2.0 mmol; diamine, 2.0 mmol; solvent (DMAc), 4–5 mL; in N_2, 2 days. [b] Polymerization temperature. [c] Reprecipitated polymer (poly(amic acid) partly containing the polyimide moiety), measured in DMAc at concentration of 0.5 g/dL at 30 °C.

Scheme 3

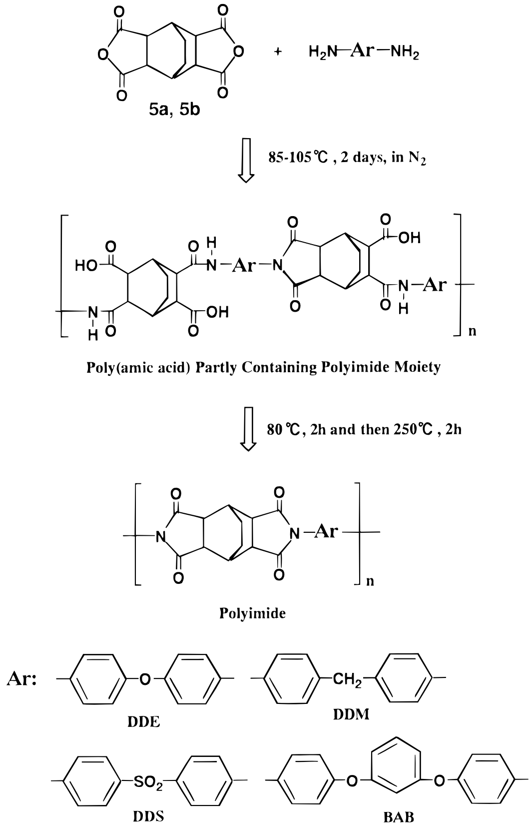


Table 3. Solubilities of Polyimides[a]

	5a			5b	
solvent	DDE	DDM	BAB	DDE	BAB
N-methyl-2-pyrrolidone	++	++	++	++	++
N,*N*-dimethylformamide	++	++	++	++	++
N,*N*-dimethylacetamide	++	++	++	++	++
1,3-dimethyl-2-imidazolinone	++	++	++	++	++
dimethyl sulfoxide	++	++	++	++	++
pyridine	++	++	++	++	++
conc H_2SO_2	++	++	++	++	++
chloroform	−	−	++	−	−
dioxane	−	−	+	−	−
acetonitrile	−	−	−	−	−
ethanol	−	−	−	−	−
ethyl acetate	−	−	−	−	−
tetrachloromethane	−	−	−	−	−
benzene	−	−	−	−	−
hexane	−	−	−	−	−
acetone	−	−	−	−	−

[a] Samples: powdery polyimides obtained by heating reprecipitated poly(amic acid)s at 250 °C for 2 h in vacuum. ++, soluble at room temperature; +, soluble on heating −, insoluble even on heating.

Table 4. Thermal Properties of Polyimides

dianhydride	diamine	T_5 (°C)[a]	T_{10} (°C)[b]	T_{dec} (°C)[c]	T_g (°C)[d]
5a	DDE	464	482	484	383
5a	DDM	474	487	495	385
5a	BAB	451	464	469	211
5b	DDE	447	459	462	385
5b	BAB	491	503	509	225

[a] 5% weight loss, [b] 10% weight loss, [c] decomposition temperatures measured by TGA at a heating rate of 10 °C/min in N_2. [d] Glass transition temperatures measured by TMA at a heating rate of 10 °C/min in air.

Table 5. Mechanical Properties of Polyimide Films

dianhydride	diamine	TM (GPa)[a]	TS (MPa)[b]	EB (%)[c]
5a	DDE	1.6	64	8.6
5a	BAB	2.6	57	2.9
5b	DDE	2.0	96	11.0
5b	BAB	1.5	52	4.0

[a] Tensile modulus, [b] tensile strength, [c] elongation at break measured by TMA at room temperature with a drawing rate of 1 mm/min. (Sample size: 3 mm long, 2 mm wide, about 20 μm thick).

Table 6. Dielectric Constants and Transparencies of Polyimide Films

dianhydride	diamine	film thickness (μm)	dielec const[a]	transparency (%)[b]	normalized transparency (%)[c]
5a	DDE	30	−	85	94
5a	DDM	11	3.4	89	88
5a	BAB	16	3.7	89	92
5b	DDE	11	3.4	87	86
5b	BAB	12	3.2	90	90
Kapton[d]		12	3.5	69	69

[a] 1.0 MHz; room temperature; about 50% relative humidity. [b] Average transmittance in the visible region (400−780 nm). [c] By supposing films to have the same thickness (12 μm). [d] Prepared in our laboratory.

imide moiety; that is, the absorptions at 1765−1775 and 1710−1720 cm^{-1} due to the imide carbonyl weakly appeared in addition to those of the carboxylic and amide-carbonyl groups of the poly(amic acid)s at ca. 3300 and 1550−1650 cm^{-1}. The partial imidization of the poly(amic acid)s probably occurs at high temperature (85−105 °C) during polymerization.

Polyimides could be obtained as a solid from the precipitated poly(amic acid)s by heating at 250 °C for 2 h under reduced pressure. The inherent viscosity of the polyimide from **5a** and DDE, which was measured in DMAc, was 0.51 dL/g. Furthermore, polyimides were also prepared using a one-step method, solution polyimidization, where DMAc solutions containing the dianhydrides and aromatic diamines were heated at reflux temperature for 12 h in N_2. The polyimide films could be obtained from the DMAc solutions by heating at 80 °C for 2 h under vacuum after being cast on glass plates. The solution polyimidization of **5a** with DDE afforded a higher molecular weight polyimide ($\eta_{inh} = 0.66$ dL/g) than the poly(amic acid) method ($\eta_{inh} = 0.51$ dL/g). In the poly(amic acid) method, high T_g polymers such as these often do not imidize well quantitatively because of a lack of chain mobility and an unfavorable equilibrium constant for amic acid formation. As a result, a significant amount of unreacted functional moieties may remain in the final polymer and the molecular weight may become lower than that of the polyimide prepared by the solution polyimidization.

Solubility of Polyimides. The solubility of the polyimides was qualitatively studied and the results are listed in Table 3. All the polyimides examined here were soluble at room temperature in DMAc, *N*,*N*-dimethylformamide, *N*-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolinone, dimethyl sulfoxide, pyridine, *m*-cresol, and concentrated H_2SO_4. Particularly, the polyimide obtained from **5a** and BAB was even soluble in chloroform at room temperature and in dioxane upon heating.

Thermal Properties. The thermal behaviors of the polyimide films under a nitrogen stream were evaluated by the 5% weight loss, the 10% weight loss, and the decomposition temperatures (T_5, T_{10}, and T_{dec}) measured using TGA with a heating rate of 10 °C/min and by the T_g measured using a thermomechanical analyzer (TMA) with a penetration probe of 1.0-mm diameter applying a constant load of 10 g at a heating rate of 10 °C/min in air. T_{dec} is noted in the TGA profiles 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.[25] These results are summarized in Table 4. All of the polyimides possess excellent thermal stability with no significant weight loss up to approximately 400 °C and the T_5's are over 450 °C. The polyimides have T_g's over 380 °C except for the polyimides using BAB as the aromatic diamine.

Mechanical Properties. The mechanical properties of the polyimides were estimated at room temperature in air using a thermomechanical analyzer with a constant drawing rate of 1 mm/min (sample size: 3-mm length, 2-mm width, about 20-μm thickness). The results are listed in Table 5. These polyimide films possess a tensile modulus range of 1.5−2.6 GPa, a tensile strength of 52−96 MPa, and an elongation at break of 3−11%.

Electrical Properties. Applied to interlayer dielectrics, low dielectric constant polyimides are vital for high signal propagation speeds. The dielectric constants of the polyimide films (11−30 μm) on which gold electrodes (5-mm diameter) were vacuum deposited were measured by the parallel-plate capacitor method at a frequency of 1 MHz in air (about 50% relative humidity). The results are shown in Table 6. As can be seen from Table 6, the polyimide films have a dielectric constant range of 3.2−3.7. Contrary to our expectation, the values are not very low and are almost comparable to that of Kapton prepared in our laboratory.

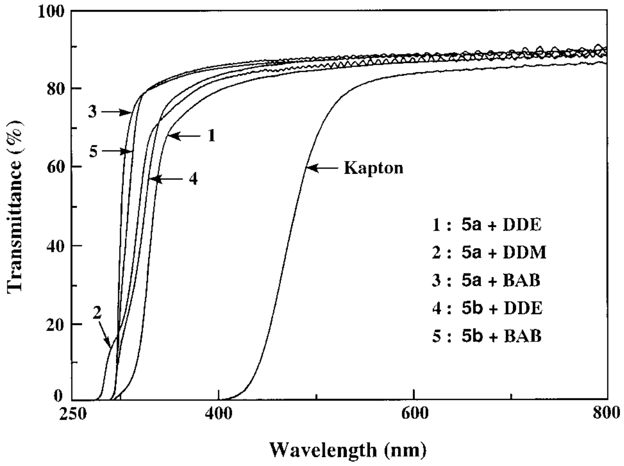


Figure 2. Transmission UV−vis spectra of 11−30 μm thick polyimide films prepared from aromatic diamines and **5a** or **5b**.

Optical Properties. The transmission UV−vis spectra of 11−30 μm thick polyimide films are shown in Figure 2. The polyimide films exhibit cutoffs at wavelengths shorter than 320 nm and are entirely transparent and colorless. Transparency in the visible region was evaluated by averaging the transmittances in the range from 400 to 780 nm in the UV−vis spectrum. Normalized transparency was also calculated from the transparency by assuming the films to have the same thickness (12 μm). The results are listed in Table 6 together with that of Kapton. Normalized transparency of each polyimide film is over 86% and, particularly, the film prepared from **5a** and DDE has an excellent transparency of 94%. Dependencies of curing temperature and atmosphere in the postcure process on colorlessness and transparency were investigated by a heat-cycle method using a film obtained from **5a** and DDE. The film was heated at the prescribed temperature for 30 min in air, and then the UV−vis spectrum was measured after the film was cooled to room temperature. The curing temperature was increased stepwise by 50 °C increments in the range of 200−400 °C using the same specimen. Figure 3a shows the UV−vis spectra of the film at room temperture after being cured at each temperature in air. The colorlessness (cutoff wavelength) and the transparency (average transmittance) at room temperature are maintained up to 200 °C when the film is heated in air. When the film is cured at temperatures higher than 200 °C, a cutoff wavelength in the UV−vis spectrum became longer (red shift) and the transmittances were decreased with an increase in curing temperature. However, as shown in Figure 3b, when the film was cured in a N_2 atmosphere, the colorlessness and/or the transparency both before and after curing at 400 °C were almost the same. The colorlessness of the film at high temperature is strongly influenced by its curing atmosphere.

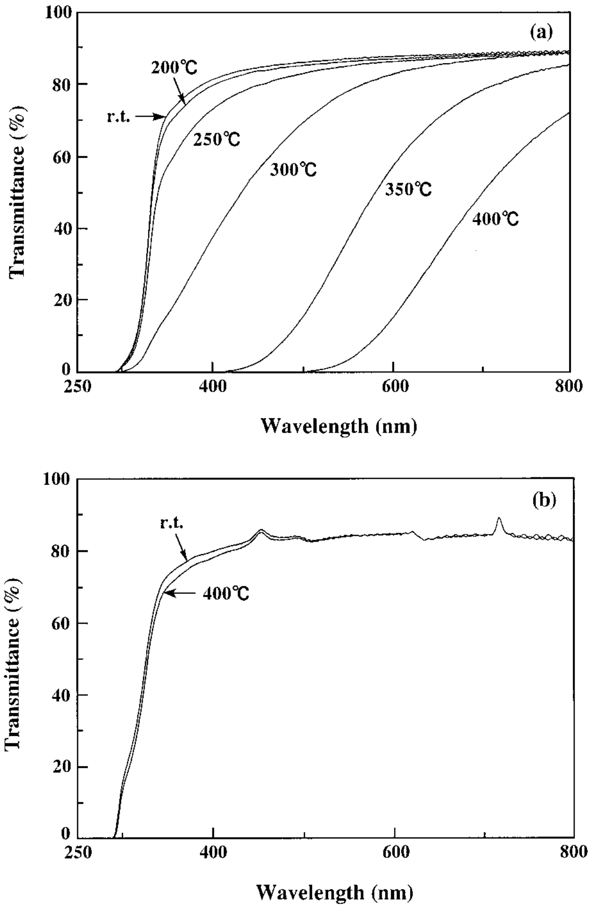


Figure 3. Dependencies of curing temperature and atmosphere in postcure process on the transmittances using the polyimide film obtained from **5a** and DDE (without being end-capped): (a) Postcure in air by heating-cycle method; (b) postcure in N_2.

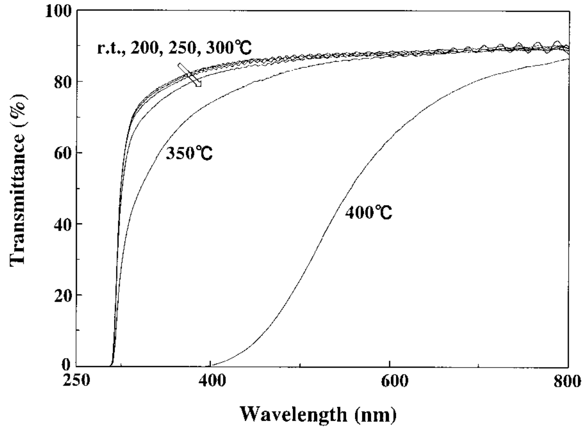


Figure 4. Effect of curing temperature in postcure process on the transmittances using the end-capped polyimide film obtained from **5a** and DDE. Postcure: in air by heating-cycle method.

When a sensitive property like color is involved, the presence of the end groups cannot be neglected, particularly the aromatic amino groups which readily undergo air oxidation to form colored byproducts. The end-capped polyimide was also synthesized by adding acetic anhydride as a monofunctional capping reagent to the one-step polymerization solution and then heating at 60 °C for 6 h in a nitrogen atmosphere. Figure 4 shows the UV−vis spectra of the end-capped polyimide film (**5a** and DDE) at room temperature after being cured at each temperature in air. Figure 5 illustrates the effect of curing temperature on the transparencies in the visible region of the polyimide films with and without being end-capped. There is a striking conclusion from the inspection of Figure 5. The end-capped polyimide is scarcely colored up to around 300 °C whereas the transparency of the polyimide without being end-capped begins to reduce at about 200 °C. This result let us know that this polymer takes its color from trace amounts of readily oxidizable compounds which are contained in the polymer such as an unreacted and/or terminated diamine moiety.

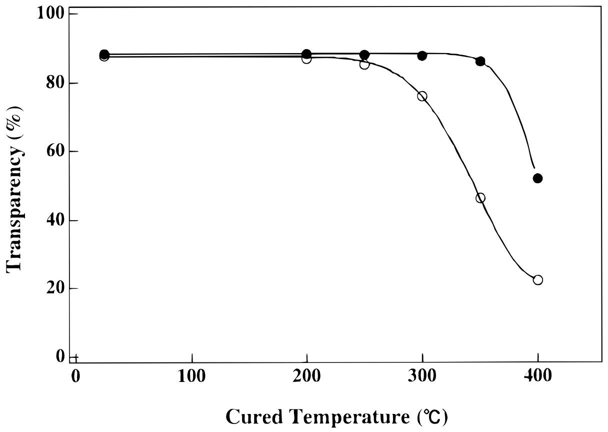


Figure 5. Dependencies of curing temperature in postcure process on the transparency using polyimide films prepared from **5a** and DDE. Postcure: in air by heating-cycle method. Open circles denote the transparencies of the polyimide without being end-capped, and full circles denote the transparency of the end-capped polyimide film.

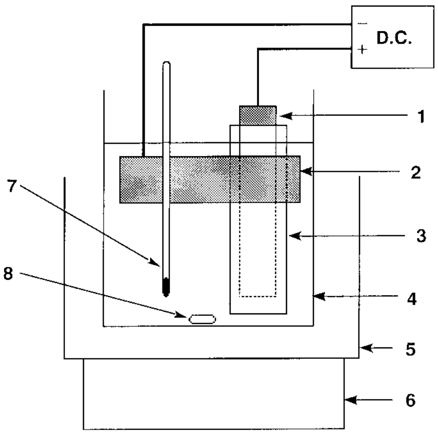


Figure 6. Schematic diagram of electrolytic reduction cell: (1) anode (Pb; 40-mm width, 125-mm length, 1-mm thickness); (2) cathode (Pb; 70-mm width, 130-mm length, 1-mm thickness); (3) unglazed diaphragm (45-mm i.d., 50-mm o.d., 150-mm height; anolyte: 5% H_2SO_4 (300 mL)); (4) 1-L beaker (catholyte: 5% H_2SO_4 (200 mL), 1,4-dioxane (300 mL), phthalic acid (40 g)); (5) ice−salt bath; (6) magnetic stirrer; (7) thermometer; (8) stirring bar.

Experimental Section

Materials. DMAc, a polymerization solvent, was shaken with P_2O_5 overnight at room temperature in order to remove dimethylamine contained in the solvent as a contaminant and then decanted. The DMAc was refluxed with BaO for 1 h, then fractionally distilled under reduced pressure, and stored over Linde type 4A molecular sieves in the dark under N_2. 1,4-Dioxane and methanol were refluxed with CaH_2 and $CaSO_4$, respectively, and then fractionally distilled. DDE, DDS, and BAB were recrystallized twice from methanol and then sublimed under reduced pressure. DDM was also purified by two recrystallizations from benzene−hexane (1:1) and then by sublimation. Phthalic acid, dimethyl maleate, *p*-toluenesulfonic acid, and hydrogen were of commercial grade and used as received.

Measurements. ^1H and ^{13}C NMR spectra were recorded using a JEOL JNM-EX 400WB spectrometer operating at 400 and 100 MHz, respectively. The internal standard was tetramethylsilane. *J* values are given in hertz. IR spectra were obtained on a Jasco VALOR-III Fourier-transform infrared spectrometer. Melting points were taken on a Seiko Instruments TG/DTA 220 thermal analyzer. Inherent viscosities were measured in 0.5 g/dL DMAc solutions of poly(amic acid)s at 30 °C using an Ostwald viscometer. Elemental analyses were made using a Perkin-Elmer CHN 2400 elemental analyzer. Thermogravimetric analyses were performed using a Seiko TG/DTA 220 thermal analyzer at a heating rate of 10 °C in a N_2 atmosphere. Thermomechanical analyses were made 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 in air. The mechanical properties were examined at room temperature in air using a Seiko Instruments TMA/SS 100 at a drawing rate of 1 mm/min; the sample size (film) was 3 mm long, 2 mm wide, and about 20 μm thick. The dielectric constants were measured by the parallel-plate capacitor method with a HP 4284A LCR meter at a frequency of 1 MHz (1.0 V) and a temperature of 20 °C in air (about 50% relative humidity). Gold electrodes (5-mm diameter) were vacuum deposited on both surfaces of the polyimide films (11−30 μm). UV−vis spectra of the polyimide films were recorded on a Jasco Ubest-50 spectrophotometer at room temperature in air. The effect of curing temperature on film colorlessness was examined using a polyimide film prepared from **5a** and DDE. After the temperature of the film was elevated to 200 °C and held for 30 min in air, the film was cooled to room temperature, and then the UV−vis spectrum was measured in air. The curing temperature was increased stepwise by 50 °C increments in the range of 200−400 °C. The same specimen was used during these heat-cycle experiments. Another specimen obtained from **5a** and DDE was heated in a N_2 atmosphere at 400 °C for 30 min, and then the UV−vis spectrum was measured at room temperature.

Monomer Synthesis. (±)-*trans*-1,2-Dihydrophthalic Acid (1). Phthalic acid was electrolytically reduced as follows: ***(A) Apparatus.*** The reduction was carried out in a 1-L beaker which was surrounded by a vessel suitable as an ice−salt cooling bath. The cathode and the anode were lead sheets (cathode, 70 mm long, 130 mm wide, and 1 mm thick; anode, 125 mm long, 40 mm wide, and 1 mm thick). The anode was separated from the catholyte by suspending it in a porous tube (50-mm outer diameter, 45-mm inner diameter, 150-mm height) which was immersed in the beaker. The two electrodes were set parallel to each other at a distance of about 50 mm. An efficient magnetic stirrer was provided in the catholyte. The current used for this experiment was drawn from a Takasago GPO 60-10R regulated dc power supply in the constant-current mode. ***(B) Reduction of Phthalic Acid.*** After the apparatus was assembled, a mixture of 5% sulfuric acid (300 mL) and 1,4-dioxane (300 mL) was placed in the beaker and the porous tube was filled to the same level with 5% sulfuric acid. The stirrer was started, and 40.0 g (0.241 mol) of phthalic acid was suspended in the catholyte. The current was turned on and the power supply was regulated until a steady current of 8 A was flowing. A thermometer was placed in the catholyte, and the beaker was efficiently cooled so as to keep the temperature below 70 °C. A schematic diagram of the reduction cell used here is shown in Figure 6, and the reduction required 3 h. After the catholyte was concentrated by evaporation, the resulting precipitate was filtered and recrystallized from water to give (±)-*trans*-1,2-dihydrophthalic acid as a white crystallite (39.0 g, 96%): mp 212−213 °C (lit.[30] mp 210 °C); ^1H NMR δ (DMSO-d_6) 3.57 (2H, s, H-1,2), 5.83 (2H, d, $J_{3,4} = J_{6,5} = 9$, H-3,6), 6.01 (2H, d, $J_{4,3} = J_{5,6} = 9$, H-4,5), 12.66 (2H, br s, COOH); ^{13}C NMR δ (DMSO-d_6) 41.2 (C-1,2), 123.5 (C-4,5), 123.7 (C-3,6), 173.7 (COOH); IR (KBr) 3100−3000 (br), 1700, 1650 cm^{-1}.

Dimethyl (±)-*trans*-1,2-Dihydrophthalate (2). In a 1-L three-necked flask equipped with a reflux condenser were placed 50.0 g (0.297 mol) of (±)-*trans*-1,2-dihydrophthalic acid, 400 mL of methanol, and 8 mL of concentrated sulfuric acid. The mixture was magnetically stirred at the reflux temperature for 18 h. After the reaction mixture was evaporated, the remaining liquid was neutralized with a saturated $NaHCO_3$ aqueous solution and then the products were extracted three times with 300 mL of diethyl ether. The extract was dried over $MgSO_4$, the solvent was removed on a rotary evaporator, and the products were distilled under reduced pressure through a Vigreux column to yield a center-cut fraction of 45.0 g (77%): bp 87−88 °C/1.5 mmHg (lit.[31] bp 82−85 °C/1.0 mmHg); ^1H NMR δ ($CDCl_3$) 3.71 (6H, s, CH_3), 3.79 (2H, s, H-1,2), 5.82 (d, $J_{3,4} = J_{6,5} = 9$, H-3,6), 5.97 (2H, d, $J_{4,3} = J_{5,6} = 9$, H-4,5); ^{13}C NMR δ ($CDCl_3$) 41.3 (C-1,2), 52.0 (CH_3), 122.8 (C-4,5), 123.7 (C-3,6), 172.9 (C=O); IR (KBr) 2980, 1730, 1200 cm^{-1}.

Tetramethyl Bicyclo[2.2.2]oct-7-ene-2-*endo*,3-*exo*,5-*exo*,6-*exo*-tetracarboxylate (3). In a 200-mL three-necked flask equipped with an Allihn condenser and a nitrogen inlet were placed 113.6 g (0.579 mol) of **2** and 79.4 g (0.579 mol) of dimethyl maleate. The mixture was magnetically stirred, nitrogen being slowly introduced, and heated at 190 °C for 9 h. Upon fractional distillation of the reaction mixture, a colorless and viscous fraction was collected (70%): bp 159−160 °C (0.5 mmHg); ^{1}H NMR δ ($CDCl_3$) 2.95 (1H, dd, $J_{2,1} = 4$, H-2), 3.06 (1H, d, $J_{6,5} = 11$, H-6), 3.18 (1H, d, $J_{3,2} = 2$, H-3), 3.19 (1H, d, $J_{5,6} = 11$, H-5), 3.29 (1H, dd, $J_{1,2} = 4$, $J_{1,7} = 7$, H-1), 3.43 (1H, d, $J_{4,8} = 7$, H-4), 3.57 (3H, s, CH_3 (C-6 side)), 3.59 (3H, s, CH_3 (C-5 side)), 3.66 (3H, s, CH_3 (C-3 side)), 3.75 (3H, s, CH_3 (C-2 side)), 6.24 (1H, dd, $J_{8,4} = J_{8,7} = 7$, H-8), 6.42 (1H, dd, $J_{7,1} = J_{7,8} = 7$, H-7); ^{13}C NMR δ ($CDCl_3$) 35.3 (C-4), 35.5 (C-1), 42.6 (C-6), 44.8 (C-3), 44.9 (C-2), 46.3 (C-5), 51.7 (CH_3 (C-5,6 side)), 52.3 (CH_3 (C-3 side)), 52.5 (CH_3 (C-2 side)), 130.9 (C-8), 133.1 (C-7), 172.3 (C=O (C-5 side)), 172.5 (C=O (C-6 side)), 173.1 (C=O (C-3 side)), 173.5 (C=O (C-2 side)). $[\alpha]_D^{23} = 0$ ($c = 1.0$ in acetone).

Tetramethyl Bicyclo[2.2.2]octane-2-*endo*,3-*exo*,5-*exo*,6-*exo*-tetracarboxylate (4). A solution of 24.4 g (71.8 mmol) of **3** in absolute ethanol (50 mL) containing 5% Pd/C (0.244 g, 0.115 mmol as Pd atom) was hydrogenated at 50 kg/cm^2 hydrogen pressure for 12 h at room temperature using a 200-mL autoclave with mechanical stirring. The reaction mixture was filtered through Celite in order to remove the catalyst, and the solution was concentrated under reduced pressure to give an oily substance. Upon fractional distillation of the resultant liquid, a colorless fraction was collected (99%): bp 162−163 °C (1.5 mmHg); ^{1}H NMR δ ($CDCl_3$) 1.35 (1H, m, H-8 (2,3 side)), 1.52 (1H, ddd, $J_{7',1} = 2$, $J_{7',7} = 12$, $J_{7',8} = 2$, H′-7 (5,6 side)), 1.63 (1H, ddd, $J_{8',4} = 3$, $J_{8',7} = 12$, $J_{8',8} = 12$, H′-8 (5,6 side)), 1.93 (1H, m, H-7 (2,3 side)), 2.53 (1H, dd, $J_{1,6} = 2$, $J_{1,7'} = 2$, H-1), 2.57 (1H, dd, $J_{4,3} = 3$, $J_{4,8'} = 3$, H-4), 2.85 (1H, d, $J_{2,3} = 11$, H-2), 3.09 (1H, dd, $J_{3,2} = 11$, $J_{3,4} = 3$, H-3), 3.12 (1H, d, $J_{5,6} = 7$, H-5), 3.18 (1H, dd, $J_{6,1} = 2$, $J_{6,5} = 7$, H-6), 3.64 (3H, s, CH_3), 3.67 (3H, s, CH_3), 3.73 (6H, s, CH_3); ^{13}C NMR δ ($CDCl_3$) 17.3 (C-7), 21.0 (C-8), 29.9 (C-1), 30.4 (C-4), 39.4 (C-2), 43.6 (C-6), 43.7 (C-3), 44.2 (C-5), 51.6 (CH_3), 51.8 (CH_3), 52.3 (CH_3), 52.4 (CH_3), 172.9 (C=O), 173.1 (C=O), 173.7 (C=O), 174.5 (C=O).

Bicyclo[2.2.2]octane-2-*endo*,3-*endo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-Dianhydride (5a). In a 1-L three-necked flask equipped with an Allihn condenser were placed 43.7 g (0.128 mol) of **4**, 30.6 g (0.75 mol) of NaOH, 220 mL of distilled water, and 440 mL of ethanol. The mixture was magnetically stirred at the reflux temperature for 6 h. After the reaction mixture was concentrated by evaporation under reduced pressure, the unreacted compounds were removed by extraction with ethyl acetate. The aqueous layer was acidified with hydrochloric acid and then the products were extracted three times with ethyl acetate. The extract was dried over $MgSO_4$, and the solvent was removed on a rotary evaporator to give a white powder. A 1-L three-necked flask equipped with an Allihn condenser and a nitrogen inlet tube was charged with the resulting powder, which was used without further purification, 300 mL of distilled acetic anhydride, and 200 mL of decahydronaphthalene. A slow stream of nitrogen gas was maintained. After the mixture was heated at reflux temperature for 16 h, the solution was concentrated under reduced pressure to dryness. The resulting solid was recrystallized from acetic anhydride, and **5a** was obtained as a white crystalline solid (16.8 g, 53% from **4**): mp 231 °C; ^{1}H NMR δ (DMSO-d_6) 1.45 (2H, d, $J_{7,7'} = J_{8,8'} = 9$, H-7,8 (5,6-side)), 1.67 (2H, d, $J_{7',7} = J_{8',8} = 9$, H′-7,8 (2,3-side)), 2.57 (2H, s, H-1,4), 3.09 (2H, s, H-2,3), 3.51 (2H, s, H-5,6); ^{13}C NMR δ (DMSO-d_6) 19.2 (C-7,8), 27.5 (C-1,4), 40.8 (C-2,3), 42.4 (C-5,6), 172.7 (C-2,3 side CO), 173.2 (C-5,6 side CO); IR (KBr) 2959, 2891, 1863, 1782, 1220, 1091, 984, 950, 921, 748 cm^{-1}. Anal. Calcd for $C_{12}H_{10}O_6$: C, 57.6; H, 4.0. Found: C, 57.3; H, 4.1.

Bicyclo[2.2.2]octane-2-*exo*,3-*exo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-Dianhydride (5b). To a mixture of concentrated HCl (20 mL) and water (100 mL) was added 24.5 g (0.0716 mol) of **4**. The turbid solution was magnetically stirred at the reflux temperature, concentrated HCl (10 mL) being added three times at 1-h intervals. The solution became clear after 9 h. The reaction mixture was concentrated under reduced pressure to give a white solid. As described above for **5a**, **5b** was prepared from the resulting solid by a dehydration reaction with a mixture of acetic anhydride and decahydronaphthalene (3.4 g, 19% from **4**): mp 389 °C (dec); ^{1}H NMR δ (DMSO-d_6) 1.38 (4H, s, H-7,8), 2.48 (2H, s, H-1,4), 3.52 (4H, s, H-2,3,5,6); ^{13}C NMR δ (DMSO-d_6) 17.2 (C-7,8), 27.5 (C-1,4), 42.8 (C-2,3,5,6), 173.2 (CO); IR (KBr) 2958, 2891, 1863, 1779, 1219, 1092, 984, 951, 921, 748 cm^{-1}. Anal. Calcd for $C_{12}H_{10}O_6$: C, 57.6; H, 4.0. Found: C, 57.7; H, 3.9.

Polymer Synthesis and Film Preparation. The dianhydrides and aromatic diamines were purified by two recrystallizations and a sublimation just before being used for the polymerization. In a 30-mL three-necked flask equipped with an Allihn condenser, a mechanical stirrer, and a nitrogen inlet were placed 2 mmol of an aromatic diamine and 5 mL of well-purified *N*,*N*-dimethylacetamide (DMAc). A slow stream of nitrogen gas was maintained, and the mixture was stirred at room temperature until the diamine was entirely dissolved. Equimolecular quantities of the dianhydride were then added to the colorless and clear solution over a 5-h period. After the addition of the dianhydride was finished, the temperature was elevated to 85−105 °C and the mixture was stirred for 2 days. An aliquot of the reaction mixture was cast on a glass plate using a doctor blade and the remainder was poured into 300 mL of acetone. The precipitated polymer was filtered off and dried at room temperature for 1 day under reduced pressure. The polyimide film was prepared by heating the glass plate at 80 °C for 2 h and then at 250 °C for 2 h under vacuum. Polyimides were also prepared using a one-step method, solution polyimidation, where DMAc solutions containing the dianhydrides and aromatic diamines were heated at reflux temperature for 12 h. The polyimide films could be obtained from the DMAc solutions by heating at 80 °C for 2 h under vacuum after being cast on glass plates. The end-capped polyimide was synthesized by adding 0.5 mL of acetic anhydride to the one-step polymerization solution, which had been prepared as described above, and then heating 60 °C for 6 h under a nitrogen atmosphere.

Conclusions

Two kinds of tetracarboxylic dianhydrides with a polyalicyclic structure, bicyclo[2.2.2]octane-2-*endo*,3-*endo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride and the all-*exo* isomer, were successfully synthesized from phthalic acid via several steps. The polymerizations of the dianhydrides with well-purified aromatic dianhydrides were carried out in carefully purified DMAc at 85−105 °C under N_2. Poly(amic acid)s as reprecipitated possessed inherent viscosities in the range 0.5−0.1 dL/g. The IR spectra of the reprecipitated polymers showed that the poly(amic acid)s partly contained the imide moiety. The partial imidization of the poly(amic acid)s probably occurred at high temperature (85−105 °C) during polymerization. The poly(amic acid)s which were cast on glass plates gave flexible polyimide films after being cured at 80 °C for 2 h and then at 250 °C for 2 h under vacuum. All the polyimides were soluble at room temperature in DMAc, *N*,*N*-dimethylformamide, *N*-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolinone, dimethyl sulfoxide, pyridine, *m*-cresol, and concentrated H_2SO_4. Particularly, the polyimide obtained from **5a** and BAB was even soluble in chloroform at room temperature and in dioxane upon heating. The polyimides possessed excellent thermal stability with no significant weight loss up to approximately 400 °C and the T_5's are over 450 °C. The polyimides had T_g's over 380 °C except for the polyimides using BAB as the aromatic diamine. These polyimide films showed a tensile modulus range of 1.5−2.6 GPa, a tensile strength of 52−96 MPa, an elongation at break of 3−11%, and a dielectric constant range of 3.2−3.7. The polyimide films exhibited cutoffs at wavelengths shorter than 320 nm and were entirely transparent and colorless. The colorlessness (cutoff wavelength) and the transparency (average transmittance) at room temperature were maintained up to 200 °C when the films were heated in air. On the other hand, when the films were cured in a N_2 atmosphere, the colorlessness and the transparency both before and after curing at 400 °C were almost the same. In the case of the polyimide which was end-capped with acetic anhydride, the film was almost colorless even when heated at 300 °C in air.

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References and Notes

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