

# Semi- and Non-aromatic Polyimides Derived from Polyalicyclic Monomers

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## ABSTRACT

Tetracarboxylic dianhydrides bearing a polyalicyclic structure, bicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylic 2,3:5,6-dianhydride (**BHDA**), bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic 2,3:5,6-dianhydride (**BODA**), (4*arH*,8*acH*)-decahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene-2,3,6,7-tetracarboxylic 2,3:6,7-dianhydride (**DNDA**), and bicyclo[2.2.1]heptane-2-*exo*,3-*exo*,5-*exo*-tricarboxyl-5-*endo*-acetic 2,3:5,5-dianhydride (**BSDA**) were synthesized and polycondensated with aromatic diamines or cycloaliphatic diamines including bis(aminomethyl)bicyclo[2.2.1]heptane (**BBH**) in DMAc, DMI or HMPA at room temperature or at 140°C under N<sub>2</sub>. The polymerization solutions gave the flexible and free-standing films after being cast on glass plates and then cured. The films were soluble in aprotic polar solvents such as DMAc and *N*-methyl-2-pyrrolidone at room temperature. Some among them dissolved in CHCl<sub>3</sub> or dioxane. The polyimides showed good thermal stability and the 5% weight loss temperatures in N<sub>2</sub> were over 450°C. The polyimide films exhibited *T<sub>g</sub>*'s in the range of 250-400°C. The cutoffs at wavelengths of the non-aromatic polyimides such as PI(**DNDA-BBH**) and PI(**BHDA-BBH**) were shorter than 235 nm, and around 290-330 nm for the semi-aromatic polyimides. The transparencies in the visible region (400-780 nm) were over 85%. The flexible polyimide possessed an average refractive index of 1.522-1.617, and the optical anisotropy, the difference between in-plane and out-of-plane refractive indices, was 0.000-0.017. The dielectric constant  $\epsilon'$ 's that were estimated from the refractive indices according to the modified Maxwell's equation were 2.55-2.87.

## 1. INTRODUCTION

Polyimides synthesized from only aromatic monomers, aromatic polyimides, are often insoluble in their fully imidized form. Additionally, most of the aromatic polyimides intensely absorb visible light. Consequently, they cannot be used in areas where colorlessness is important requirements. It is well known that the origin of the coloration in aromatic polyimides is caused by the charge-transfer. From the molecular orbital calculations, we confirmed the origin of the coloration is attributable to an *intra*-molecular charge-transfer from the diamine moiety to the dianhydride one. We have synthesized the soluble and colorless semi-aromatic polyimides. 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. Aliphatic polyimides, however, have attracted much attention in recent years because of their potential applications including use as liquid crystal orientation layers, light-guide, or high-temperature low dielectric materials.[1,2] Aliphatic polyimides, we will present here, are classified into three distinct categories according to their chemical structures

Figure 1). The first category would be comprised of polyimides derived from alicyclic dianhydrides and aromatic diamines, which is called here *alipharomatic* type semi-aromatic polyimides. The second category is polyimides obtained from aromatic dianhydrides and alicyclic diamines, *aromaliphatic* type semi-aromatic polyimides. The third category would consist of non-aromatic polyimides based on alicyclic dianhydrides and diamines. In this presentation, the aliphatic polyimide syntheses and their properties will be discussed.

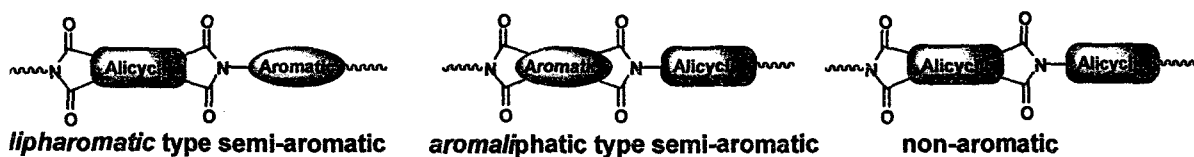


Figure 1. Three categories of aliphatic polyimides classified according to the chemical structure.

## 2. EXPERIMENTAL

**2.1. Materials** Bis(aminomethyl)bicyclo[2.2.1]heptane (**BH**) was donated from Mitsui Chemicals, Co. Ltd. and used as received. **BH** consists of four isomers, 2-*exo*,5-*exo*-is(aminomethyl)bicyclo[2.2.1]heptane (30 wt-%), 2-*endo*,5-*exo*- (35 wt-%), 2-*exo*,6-*exo*- (20 wt-%), and 2-*endo*,6-*exo*- (15 wt-%) isomers. Hexamethylphosphoramide (HMPA), *N,N*-dimethylacetamide (DMAc), 1,3-dimethyl-2-imidazolinone (DMI) were fractionally distilled over CaH<sub>2</sub> under reduced pressure and stored over molecular sieve 4 Å.

**2.2. Measurements** UV-Vis spectra of the polyimide films were recorded on a Jasco V-570 UV/VIS/IR spectrophotometer. Film thickness and refractive index were measured by a Metricon Model C-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). 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 K/min in a nitrogen atmosphere or in air for the thermogravimetric analysis (TGA). The melting points and the glass transition temperatures were measured using a TA Instruments DSC 2920 Modulated DSC instrument and a Seiko Instruments SSC/5200 DSC instrument at a heating rate of 10 K/min. 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 K/min in air. Inherent viscosities were measured with an Ostwald viscometer in a 0.5 g/dL solution of poly(amic acid) or polyimide at 30°C.

**2.3. Monomer Synthesis** The tetracarboxylic dianhydrides, **BHDA**, **BODA**, **DNDA**, and **BSDA** were synthesized according to the previous papers.[3-7]

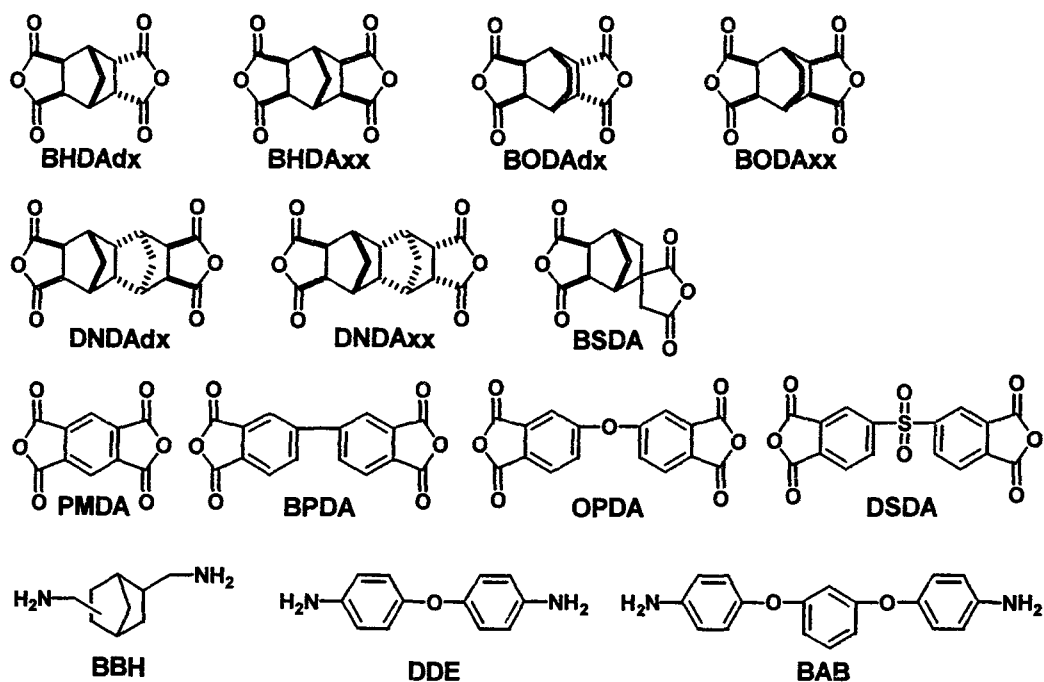
### 2.4. Polyimide Synthesis and Film Preparation

**Two-step poly(amic acid) method for semi-aromatic polyimides** In a 30-mL three-necked flask equipped with an Allihn condenser and a nitrogen inlet were placed 2 mmol of an aromatic diamine

and 5 mL of well-purified DMAc or DMI. A slow stream of nitrogen gas was maintained, and the mixture was magnetically stirred at room temperature until the diamine was entirely dissolved. Equimolar quantities of the dianhydride were then added to the solution over a 3-h period. After the addition of the dianhydride was completed, the temperature was raised to 85-105°C and the mixture was stirred for 2 days. An aliquot of the resulting polymerization solution was cast on a glass plate using a doctor blade set at 5 mils, and the plate was heated in a vacuum oven at 80°C for 2 h then at 250°C for 2 h. The remainder of the solution was poured into 300 mL of acetone, and precipitated polymer was filtered off and dried at room temperature for 1 day under vacuum. Removal of the polyimide films from the glass plates was aided by immersion in hot water. The peeled film was dried in a vacuum oven at room temperature for 1 day.

**Two-step poly(amic acid) method for non-aromatic polyimides** 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. The polyimide film was prepared according to the same manner as described above.

**One-step solution imidization method for semi-aromatic polyimides** In a 30-mL three-necked flask equipped with an Allihn condenser and a nitrogen inlet were placed 2 mmol of an aromatic diamine, the dianhydride, and 5 mL of well-purified DMAc. A slow stream of nitrogen gas was maintained, and the mixture was heated at 140°C for 12 h with magnetic stirring. The polyimide film was prepared according to the similar manner as described above.



**Figure 2.** The structures and abbreviations of monomers for polyimide synthesis

☆ 容易に水化物の、ジアミンを少しずつ加えると、塩形成が阻害される。

☆

### 3. RESULTS AND DISCUSSION

#### 3.1 Polymer Synthesis

The structures of monomers used in this study are illustrated in **Figure 2**. In order to synthesize polyimide films with the objective of obtaining maximum optical transparency, polymerizations must be performed with highly purified monomers and special care has to be exercised to prevent the polymerization media from contamination by impurities. The polymerization media were carefully purified and stored over 4A Molecular Sieves under N<sub>2</sub> in the dark, and the monomers were recrystallized and then sublimed just prior to use. *Alipharomatic* type semi-aromatic polyimides were prepared using a conventional two-step method. Of course, they can be synthesized by a one-step solution imidization method, because these polyimides are soluble in polymerization medium. The inherent viscosities ( $\eta_{inh}$ 's) of the poly(amic acid)s were in the range from 0.8 to 0.53 dL/g (at 30°C, 0.5g/dL). The poly(amic acid)s gave flexible polyimide films after cast then cured. For the polycondensation of an alicyclic diamine with aromatic dianhydrides, a viscous poly(amic acid) solution was obtained only when the diamine was slowly added to the dianhydride solution. When aromatic diamines are used for the polycondensation, the addition order of the monomers is not so important. In the reaction using a polyalicyclic diamine, however, the order becomes significant. In a conventional addition order, a precipitate is produced. This phenomenon can be explained by salt formation where the carboxyl group of poly(amic acid) easily reacts with an excess of the free diamine to form the insoluble salt. The difference in the basicity between an aliphatic and an aromatic amines influences the polymerization behavior. *Aromaaliphatic* type semi-aromatic polyimides were prepared by adding **BBH** into DMI solutions of aromatic dianhydrides in DMI using a two-step method. The  $\eta_{inh}$ 's of the polyimides measured in *m*-cresol were in the range from 1.0 to 0.62 dL/g. The poly(amic acid)s gave flexible polyimide films after cast then cured. Non-aromatic polyimides were synthesized from an alicyclic diamine **BBH** and three types of alicyclic dianhydrides(**BHDAdx**, **DNDAdx**, **BSDA**) in HMPA using a two-step poly(amic acid) method. In these polycondensations, the monomer addition order also plays a significant role. Although the  $\eta_{inh}$ 's of the resulting non-aromatic poly(amic acid)s were somewhat low (0.36-0.21 dL/g), they formed flexible and tough films. It is interesting that polyimide films of high quality can be obtained despite the lower inherent viscosities. The

**Table 1. Thermal properties of polyimides**

polyimide	category	$T_5$ (°C) <sup>a</sup>		$T_g$ (°C) <sup>b</sup>
		in N <sub>2</sub>	in air	
PI(PMDA-DDE)	<i>aromatic</i>	515	480	429
PI(DNDAdx-DDE)	<i>alipharomatic</i>	514	470	404
PI(PMDA-BBH)	<i>aromaliphatic</i>	448	406	282
PI(BHDA-BBH)	<i>non-aromatic</i>	455	411	297
PI(DNDAdx-BBH)	<i>non-aromatic</i>	459	416	340

<sup>a</sup>5% weight loss temperature measured by TGA at a heating rate of 10K/min. <sup>b</sup>measured by TMA.

alicyclic diamine **BBH** used here is not a single compound but a mixture of four isomers. In the sense, the polymers are practically “co-polyimides” in stereochemistry. The disorder of the polymer chain may enhance its film-formability.

### 3.2 The properties of Polyimides

**Solubility** All the polyimides examined here are soluble in DMAc and NMP. Particularly, the semi-aromatic polyimides were soluble even in chloroform. Thus, the incorporation of alicyclic structure into the polyimide backbone may facilitate less polymer-polymer interaction and offer these materials excellent solubility.

**Thermal Property** The thermal behavior of the polyimides was evaluated by the 5% weight loss temperature, denoted as  $T_5$ , and by the  $T_g$  measured using a TMA. These results are summarized in **Table 1**. All of the polyimides possess excellent thermal stability with no significant weight loss up to approximately 350°C and the  $T_5$ 's in N are over 450°C. The *alipharomatic* type polyimide, PI(**DNDA-DDE**) shows a  $T_5$  around 510°C<sup>2</sup> and is comparable to that of aromatic polyimides. The polyimides have a  $T_g$  range from 250 to 400°C. The introduction of a polyalicyclic structure would facilitate less probability of main chain scission because of the presence of multibonds, and would increase main chain rigidity.

**Table 2. Mechanical properties of polyimides**

polyimide	category	TM(GPa) <sup>a</sup>	TS(MPa) <sup>b</sup>	EB(%) <sup>c</sup>
PI( <b>PMDA-DDE</b> )	<i>aromatic</i>	3.5	160	40
PI( <b>BHDAxx-DDE</b> )	<i>alipharomatic</i>	1.3	145	15
PI( <b>BODAXx-DDE</b> )	<i>alipharomatic</i>	2.0	96	11
PI( <b>DNDAxx-DDE</b> )	<i>alipharomatic</i>	2.3	112	30
PI( <b>PMDA-BBH</b> )	<i>aromaliphatic</i>	3.0	115	5
PI( <b>OPDA-BBH</b> )	<i>aromaliphatic</i>	1.6	84	6

<sup>a</sup>tesile modulus, <sup>b</sup>tensile strength, and <sup>c</sup>elongation at break by TMA at room temperature.

**Mechanical Properties** The mechanical properties of the semi-aromatic polyimide films were investigated using a TMA, and the results are listed in **Table 2**. These polyimide films possess a tensile modulus range from 1.6 to 3.0 GPa, a tensile strength range from 84 to 145 MPa, and an elongation at break range from 5 to 30 %.

**Optical Properties** The transmission UV-visible spectra of the polyimide films are shown in **Figure 3** together with that of an aromatic polyimide, PI(**PMDA-DDE**). The alicyclic polyimide films exhibit cutoff wavelengths shorter than 330 nm and are completely colorless. The cutoff's of the non-aromatic polyimides are 235 nm, while that of PI (**PMDA-DDE**) is 426 nm. The chemical structure depends on the cut-off wavelength, and the polyimides are clearly classified into four groups. The order from the longer side is *aromatic*, *aromaliphatic*, *alipharomatic*, and *non-aromatic*. Film thick-

2,3 ; 芳香族の芳香族+脂肪族ジアミン  
 4,5,6 ; 芳香族ジアミン+脂肪族酸誘引物

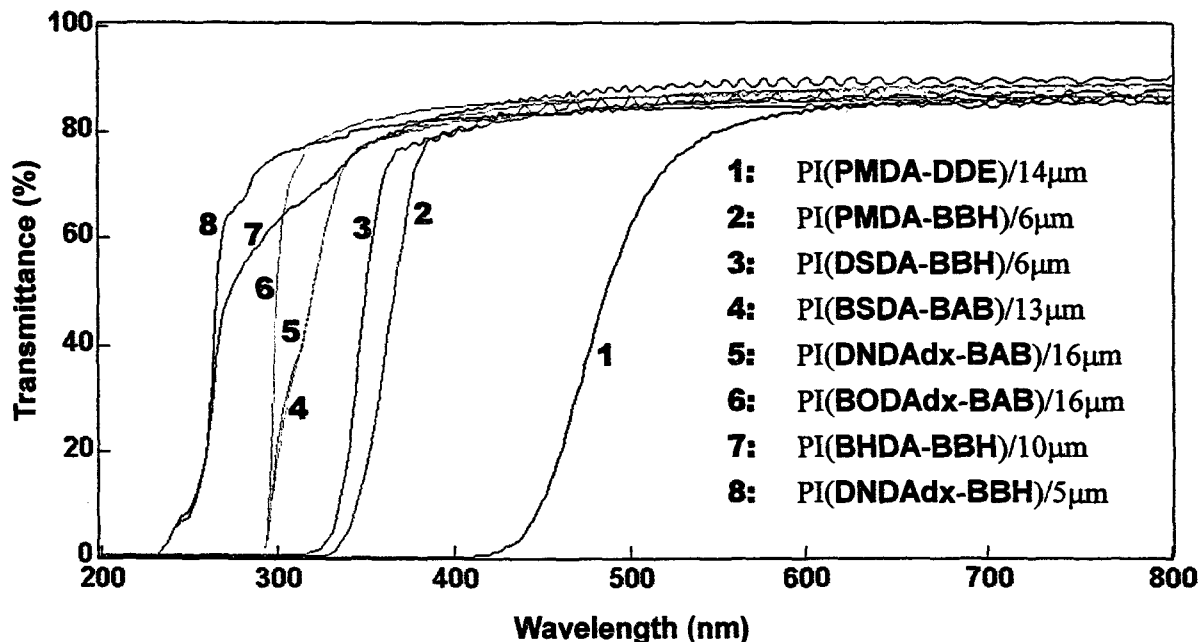


Figure 3. UV-Vis spectra of polyimide films /film thickness

1: aromatic type 2,3: aromaliphatic type 4-6: alipharomatic type 7,8: non-aromatic type

ness and refractive index were determined using a prism coupling (*m*-line) method. An average refractive index is calculated using the equation,  $n_{AV} = (2n_{TE} + n_{TM})/3$ , where  $n_{TE}$  and  $n_{TM}$  are the in-plane and the out-of-plane refractive indices, respectively. Its birefringency is given as the difference between  $n_{TE}$  and  $n_{TM}$ . Birefringency is related to the degree of orientation of the refracting units; therefore, it provides additional information regarding the orientational effects of the polyimide. The dielectric constant  $\epsilon$  of the material at optical frequencies can be estimated roughly from the refractive index according to Maxwell equation,  $\epsilon \cong n^2$ . The  $\epsilon$  around 1 MHz is evaluated to be  $\epsilon \cong 1.10n^2$

Table 3. Refractive indices, birefringency, and dielectric constants

polyimide	category	$d^a$	$n_{TE}^b$	$n_{TM}^c$	$n_{AV}^d$	$\Delta n^e$	$\epsilon(\text{opt})^f$
PI(PMDA-DDE)	aromatic	6.2	1.715	1.636	1.689	0.079	3.14
PI(BODAdx-DDE)	alipharomatic	4.6	1.605	1.588	1.599	0.017	2.81
PI(BODAdx-BAB)	alipharomatic	14.7	1.615	1.615	1.615	0.000	2.87
PI(BODAx-DDE)	alipharomatic	13.1	1.605	1.588	1.600	0.017	2.81
PI(BODAx-BAB)	alipharomatic	11.3	1.617	1.617	1.617	0.000	2.88
PI(DNDAdx-BAB)	alipharomatic	12.3	1.607	1.594	1.603	0.013	2.83
PI(DNDAdx-BAB)	alipharomatic	12.3	1.607	1.594	1.603	0.013	2.83
PI(BHDAdx-BBH)	nonaromatic	14.8	1.552	1.552	1.552	0.000	2.55

<sup>a</sup> Film thickness. <sup>b</sup> The in-plane refractive indices. <sup>c</sup> The out-of-plane refractive indices. <sup>d</sup> Averaged refractive indices,  $n_{AV} = (2n_{TE} + n_{TM})/3$ . <sup>e</sup> Birefringency (optical anisotropy),  $\Delta n = n_{TE} - n_{TM}$ . <sup>f</sup> Optically estimated dielectric constant,  $\epsilon = 1.10 n_{AV}^2$ .

including an additional contribution of about 10% from the infrared absorption[8,9]. The results are listed in Table 3 together with that of an aromatic polyimide, PI(PMDA-DDE), for comparative purposes. The  $n_{AV}$  of the non-aromatic polyimide film is as low as 1.52. The decreasing aromatic character of the polyimide diminishes the refractive index as exemplified by the comparison of *alipharomatic* type and aromatic polyimide in agreement with one generalization that aromatic polymers possess high refractive indices. 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. The negligibly small anisotropy in semi- and non-aromatic polyimides implies that the polymer chains are randomly oriented in the film due to a weak polymer-polymer interaction. If applied to interlayer dielectrics, low dielectric constant polyimides are vital for high signal propagation speed. As stated above, the dielectric constant of a polyimide film can be evaluated semi-empirically from the refractive index. The refractive index of 1.52 determined for the non-aromatic polyimide translates into a dielectric constant of 2.55. On the other hand the dielectric constants are around 2.8 and 3.14 for *alipharomatic* type semi-aromatic polyimide and aromatic polyimide, respectively.

#### 4. CONCLUSION

As a conclusion, semi-aromatic and non-aromatic polyimides were prepared from alicyclic monomers. When an alicyclic diamine, **BBH** is used, the monomer addition order plays a significant role. The resulting poly(amic acid) solutions gave flexible and free-standing polyimide films by curing after cast. These polyimides were soluble in organic solvents such as DMAc and NMP. The polyimides exhibited good thermal stability, and the  $T_g$ 's were over 420°C, in particular, the  $T_g$  of an *alipharomatic* type polyimide is comparable to those of aromatic polyimides. The polyimide films had a cut-off in UV region and were completely colorless. The refractive indices were around 1.6, particularly that of the non-aromatic polyimide is as low as 1.52, birefringence is nearly zero. The optically estimated dielectric constants are around 2.8 for *alipharomatic* type polyimides and 2.55 for the non-aromatic polyimide. These polyimides are expected to be useful and suitable for electronics and opto-electronic materials.

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