

## Colorless Polyimides Derived from Cyclopentanone Bis-spiro-norbornane Tetracarboxylic Dianhydride

Eriko Ishiguro, Kazuhiko Taneda, Yusuke Iguchi, Ryosuke Kimura, Toshihiko Matsumoto\*  
Department of Life Science & Sustainable Chemistry, Tokyo Polytechnic University  
1583 Iiyama, Atsugi, Kanagawa 243-0297, Japan E-mail: [matumoto@chem.t-kougei.ac.jp](mailto:matumoto@chem.t-kougei.ac.jp)

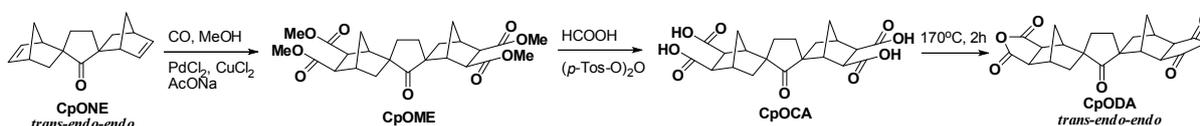
### Introduction

Most of aromatic polyimides intensely absorb visible light and are colored reddish yellow or pale yellow, so they can be hardly used in areas where absence of coloration is important requirement. Recently, soluble and colorless polyimides using monomers with alicyclic structures, so-called "alicyclic polyimides" have been reported. The introduction of an alicyclic 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 CT interactions. These polyimides show excellent thermal stability and the high-temperature stability can also be explained by an alicyclic structure, which would foster less probability of main chain scission because of the presence of multibonds and would increase main chain rigidity. Alicyclic polyimides have attracted much attention in recent years because of their potential applications including use as liquid crystal orientation layers, flexible solar cell substrates, organic EL substrates, light guide and low dielectric materials. This article deals with the alicyclic polyimides consisting of aromatic diamines and alicyclic dianhydrides having cyclopentanone bis-spiro-norbornane structure.

### Results and Discussion

#### 1. Monomer Synthesis

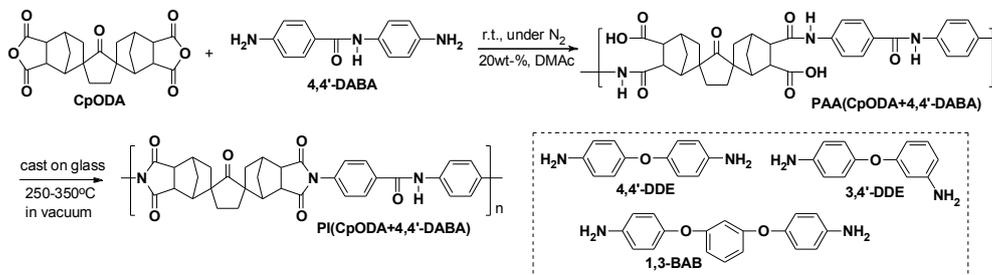
The synthetic route of cyclopentanone bis-spiro-norbornane dianhydride CpODA (norbornane-2-spiro- $\alpha$ -cyclopentanone- $\alpha'$ -spiro-2''-norbornane-5,5'',6,6''-tetracarboxylic dianhydride) is illustrated in **Scheme 1**. The Pd-catalyzed tetramethoxycarbonylation of 5-norbornene-2-spiro- $\alpha$ -cyclopentanone- $\alpha'$ -spiro-2''-5''-norbornene (CpONE), which consists of six stereo-isomers, with carbon monoxide in methanol in the presence sodium acetate and CuCl<sub>2</sub> afforded the tetramethyl ester (CpOME). After the ester-exchange of CpOME in formic acid using *p*-toluene sulfonic anhydride as a catalyst, the resulting tetracarboxylic acid was dehydrated thermally to the dianhydride CpODA. Judging from the <sup>13</sup>C-NMR spectra, the dianhydride is a mixture of *trans-endo-endo* (major) and *cis-endo-endo* (minor) isomers.



**Scheme 1.** The synthetic route of cyclopentanone bis-spiro-norbornane dianhydride (CpODA).

#### 2. Polymer Synthesis

Polymerization must be performed with highly purified monomers in order to prepare polyimide film with the objective of obtaining maximum optical transparency. All the monomers were purified by vacuum sublimation just prior to use. Polyimides were synthesized by a two-step method: 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 glass plates and thermally cyclodehydrated at elevated temperature to yield the corresponding polyimide film. The synthetic route, the chemical structures of monomers, and their abbreviations are shown in **Scheme 2**.



**Scheme 2.** Synthesis alicyclic polyimides and the chemical structures of monomers.

Poly(amic acid)s possessed inherent viscosities ( $\eta_{inh}$ ) in the range of 1.1-0.6 dL/g and gave flexible and colorless films after cured at 250-350 °C under vacuum. The viscosity of poly(amic acid) derived from CpODA and 1,3-BAB was increased with an increase of the reaction time and equilibrium ( $\eta_{inh} = 0.68$  dL/g)

was closely approached after 4 hours. All the polyimides cured at 250 °C were soluble in aprotic polar solvents such as DMAc.

**Table 1.** Inherent viscosity of poly(amic acid) and the properties of CpODA-based polyimide films

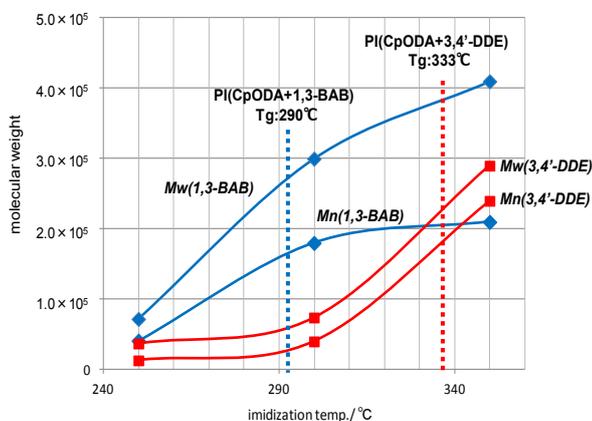
polyimide	$\eta_{inh}^a$ (dL/g)	$T5^b$ (°C)	$Td^c$ (°C)	$Tg^d$ (°C)	$t^e$ (%)	$\lambda_{cut-off}^f$ (nm)	Film Quality	CTE <sup>g</sup> (ppm/K)
PI(CpODA+1,3-BAB)	0.71	487	496	290	89	290	flexible	56
PI(CpODA+4,4'-DDE)	1.07	468	488	354	85	283	flexible	49
PI(CpODA+3,4'-DDE)	0.61	484	496	333	85	265	flexible	57
PI(CpODA+4,4'-DABA)	0.75	488	501	369	85	328	flexible	15

<sup>a</sup> poly(amic acid), 0.5g/dL in DMAc at 30 °C. <sup>b</sup> 5 % weight-loss and <sup>c</sup> decomposition temperatures in N<sub>2</sub>. <sup>d</sup> measured by TMA. <sup>e</sup> an averaged transmittance in visible region (400-800nm). <sup>f</sup> 1 % transmittance in UV-vis spectrum. <sup>g</sup> coefficient of thermal expansion estimated within 100-200 °C.

### 3. Properties of Polyimides

All the polyimides prepared in this work had excellent thermal stability with no significant weight loss up to 400 °C and the 5% weight-loss temperatures ( $T5$ 's) in N<sub>2</sub> are over 470 °C (**Table 1**). The polyimides have  $Tg$ 's over 330 °C except for the 1,3-BAB-based one. The high  $Tg$  is due to a dipole-dipole interaction between the keto groups of the polymer chains as well as to a development of rigid polycyclic units. Most of the CpODA-based polyimide films show CTE values common to flexible polyimide systems, ranging 50-60 ppm/K. It is noteworthy that PI(CpODA+4,4'-DABA) film possesses a much lower CTE value (15 ppm/K). 4,4'-DABA contains an amide-linkage having a planar structure and may give a rod-like nature to the polyimide backbone.[5] The polyimide films were transparent and colorless. They exhibited cutoffs, where the light transmittance becomes below 1%, at wavelengths shorter than 330 nm. Transparency in the visible region ( $t$ ) was evaluated by averaging the transmittance in the range from 400 to 800 nm in the UV-vis spectrum, and the value of each polyimide film is over 85%. Exclusion of benzene ring from the dianhydride and/or the diamine, that is alicyclic polyimide, depresses CT and result in the lack of color. Imidization temperature influenced strongly film quality and molecule weight of the polyimide. When poly(amic acid) PAA(CpODA+1,3-BAB) cast on the glass plate was cured at 250 °C, the resulting polyimide film PI(CpODA+1,3-BAB) was brittle and the number-averaged molecular weight  $M_n$  was  $4.1 \times 10^4$  (by SEC). However, on curing the poly(amic acid) at 300 °C and 350 °C over the  $Tg$ , the flexible polyimide films were obtained and the  $M_n$ 's were  $18.0 \times 10^4$  and  $21.0 \times 10^4$ , respectively. In the cases of PAA(CpODA+3,4'-DDE) and PAA(CpODA+4,4'-DDE), flexible films were given only when imidized at 350 °C over the  $Tg$ 's. From **Figure 1**, it is found that the molecular weights  $M_n$  and  $M_w$  increase 5-8 times by curing around or over the  $Tg$ , which means that the post-polymerization takes place at the temperature. The  $M_n$  enhancement was confirmed by not only SEC but end-group analysis using <sup>1</sup>H-NMR.

These CpODA-based polyimides developed in the present study are a promising candidate of colorless and high-temperature plastic substrate for flexible opto-electronic devices.



**Table 1.** Relation between imidization temperature and the molecular weight.

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