

# Full-Aliphatic Polyimides

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## 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, so they cannot be used in areas where colorlessness is important requirement. 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 are classified into three distinct categories according to their chemical structures. The first category would be comprised of polyimides derived from alicyclic dianhydrides and aromatic diamines. The second category is those obtained from aromatic dianhydrides and alicyclic diamines. These two types of polyimides belong to semi-aromatic polyimides. The last category would consist of full-aliphatic polyimides based on alicyclic dianhydrides and diamines. In this article, the full-aliphatic polyimide syntheses and the properties will be discussed.

## 2. Experimental

**2.1. Materials** Bicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylic 2:3,5:6-dianhydride was synthesized according to the previous paper. [3] 1,2,3,4-Butanetetracarboxylic dianhydride (BuDA) and *cis,cis,cis,cis*-1,2,3,4-cyclopentanetetracarboxylic dianhydride (CPDA) were prepared from the corresponding tetracarboxylic acids, which were obtained from Aldrich Chemical Co. Inc., by thermal dehydration and purified by sublimation. 4-(2,5-Dioxotetrahydrofuran-3-yl)-tetralin-1,2-dicarboxylic anhydride (tetralin-DA) was purchased from Tokyo Kasei Kogyo Co. Ltd., and heated at 130°C for 1 h in *vacuo* just prior to use in order to complete the dehydration. 4,4'-Methylenebis(2-methylcyclohexylamine) (MCHM, Aldrich), 1,3-cyclohexanebis(methylamine) (CHMA, Aldrich), 4,4'-methylenebis(cyclohexylamine) (MCHA, Tokyo Kasei), hexamethylphosphoric triamide (HMPA, Tokyo Kasei), and 1,1,3,3,-tetramethylurea (TMU, Aldrich) were used as received.

**2.2. Measurements** The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were obtained using a JEOL JNM-LA500 spectrometer.

The proton signals in the  $^1\text{H-NMR}$  spectrum were assigned in the H,H- and C,H-COSY spectra. Infrared spectra were recorded using a JASCO 460 plus Fourier transform spectrometer. UV-Vis spectra of the polyimide films were recorded on a JASCO V-570 UV/VIS/NIR spectrophotometer. 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 Seiko Instruments SSC/5200 DSC instrument at a heating rate of 10 K/min. Inherent viscosities were measured with an Ostwald viscometer in a 0.5 g/dL solution of poly(amic acid) at 30°C.

### 2.3. Polymerization Procedure

**Ordinary two step method:** In a 30 mL glass bottle with a polyethylene cap containing a magnetic stirring bar were placed the diamine (5.0 mmol) and 8 ml of HMPA or TMU. An equimolar amount of the dianhydride was added into the clear diamine solution. The mixture was stirred at room temperature for the prescribed period.

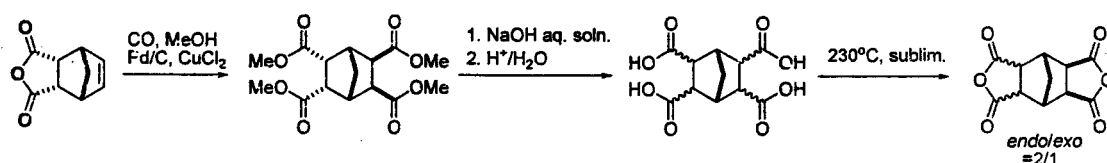
**Half-ester method:** In a 30-mL three-necked flask equipped with a nitrogen inlet and a reflux condenser were charged with the dianhydride (3.4 mmol) and methanol (8mL), and the solution was heated to reflux for 1 day. The methanol was removed by evaporation and 8 mL of TMU and the diamine were added to the residue. The mixture was heated at reflux temperature (170-180°C) for 5 h with a slow stream of nitrogen.

**Film preparation:** An aliquot of the polycondensation solution was cast on a glass plate using a doctor blade, and the remainder was poured into 300 mL of methanol. The polyimide film was prepared by heating the glass plate from room temperature to 250°C with a heating rate of 2K/min and keeping the temperature for 1 h under vacuum.

## 3. Results and Discussion

### 3.1. Monomer Synthesis

The synthetic route to bicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylic 2:3,5:6-dianhydride (BHDA) is illustrated in Scheme 1. Bicyclo[2.2.1]hept-5-ene-2-endo,3-endo-dicarboxylic anhydride was allowed to react with methanol and carbon monoxide in the presence of Pd-C and  $\text{CuCl}_2$ , and converted into the tetramethyl ester, tetramethyl bicyclo[2.2.1]heptane-2-endo,3-endo,5-exo,6-exo-tetracarboxylate. The tetramethyl ester was hydrolysed in aqueous sodium hydroxide, and the resulting solution was acidified with hydrochloric acid, then evaporated to dryness. The white solid containing sodium chloride was heated in a vacuum oven and the dianhydride (BHDA) was collected by sublimation. Judging from the  $^1\text{H-NMR}$  spectrum, it was revealed that the molar ratio of *endo-exo* / *exo-exo* was 2:1 from the integral areas of the proton signals.

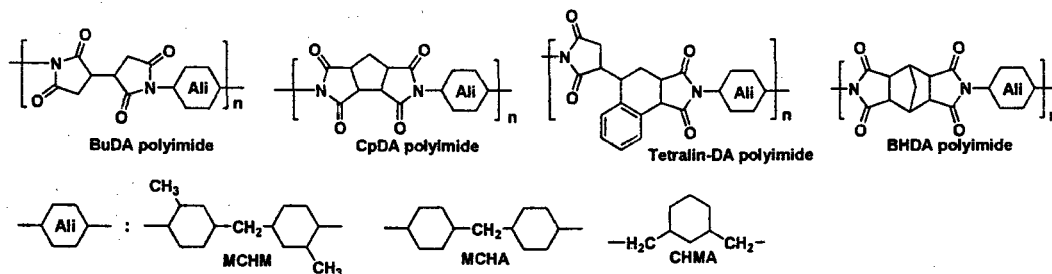


Scheme 1. Synthetic route to bicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylic 2:3,5:6-dianhydride (BHDA).

### 3.2. Polymer Synthesis

In general, polyimides are prepared via two steps, that is, the first step includes the poly(amic acid)s 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. In the present study, the half-ester method was adopted as another synthetic way to polyimide. The dianhydride was heated in excess amount of methanol to convert into the half-ester. The solvent was removed by evaporation to dryness and TMU was added to the residue. The mixture was heated at reflux temperature in a slow stream of nitrogen. The structures and abbreviations of polyimides used in this study are illustrated in **Figure 1**.



**Figure 1.** The structures and abbreviations of polyimides.

The polymerization condition, the film-formability, and color of the polyimide film are listed in **Table 1**. The polycondensations used HMPA as the solvent gave a flexible film. The half-ester technique improved the film-formability. Full-aliphatic polyimides are essentially colorless, however, in some cases yellow or light yellow film were obtained. The discoloration may be caused from contamination by impurities in the monomers and the polymerization medium.

**Table 1.** Polyimide synthesis and the film property.

dianhydride-diamine	solvent	method	film	color
BuDA-MCHM	TMU	2step	○	colorless
BuDA-CHMA	TMU	2step	○	light yellow
BuDA-MCHA	TMU	2step	×	—
BuDA-MCHA	HMPA	2step	○	yellow
BuDA-MCHA	TMU	half-ester	△	yellow
tetralin-DA-MCHM	TMU	2step	△	yellow
tetralin-DA-MCHM	HMPA	2step	○	yellow
tetralin-DA-MCHM	H <sub>2</sub> O	2step	×	—
tetralin-DA-MCHM	TMU	half-ester	○	colorless
CpDA-MCHM	TMU	half-ester	△	yellow
BHDA-MCHM	HMPA	2step	○	colorless

dianhydride: 1.000g, diamine: equimolar of dianhydride, solvent: 8 mL

film ○: flexible △: brittle ×: powdery

### 3.3. Properties of Full-aliphatic Polyimides

#### 3.3.1. Thermal Property

The thermogravimetric analyses of polymer films were done at a heating rate of 10K/min. The polyimide has a good thermal stability with no significant weight loss up to approximately 300°C and the 5% weight-loss temperature ( $T_5$ ) is 350°C. The glass transition temperature was obtained from the second run of DSC operated

at heating and cooling rate of 10 K/min in N<sub>2</sub>. The results along with the T<sub>5</sub>'s are summarized in Table 2. The full-aliphatic polyimides prepared in this study have the T<sub>g</sub>'s over 200°C, especially that of polyalicyclic polyimide PI(BHDA-MCHM) is as high as over 290°C. The higher T<sub>g</sub> is caused by the introduction of polyalicyclic structures which results in an increase in the polymer main chain rigidity.

Table 2. Thermal properties of the full-aliphatic polyimides.

dianhydride-diamine	solvent	method	T5(°C)	T10(°C)	Td(°C)	Tg(°C)
BuDA-MCHA	HMPA	2step	392	417	443	214
tetralin-DA-MCHM	HMPA	2step	416	430	440	207
tetralin-DA-MCHM	TMU	half-ester	375	398	442	269
BHDA-MCHM	HMPA	2step	379	398	431	290

T5,T10, Td: 5-%, 10-% weight loss, and decomposition temperatures measured by TGA

at a heating rate of 10 K/min in N<sub>2</sub>.

Tg: measured by DSC at a heating rate of 10K/min in N<sub>2</sub>.

### 3.3.2. Transparency

The transmission UV-vis spectra of the free-standing polyimide films are shown in Figure 2. The fully aliphatic polyimide films exhibit cutoff's at 235 nm except for BuDA-CHMA(HMPA), BuDA-CHMA, and tetralin-DA-MCHM(2step).

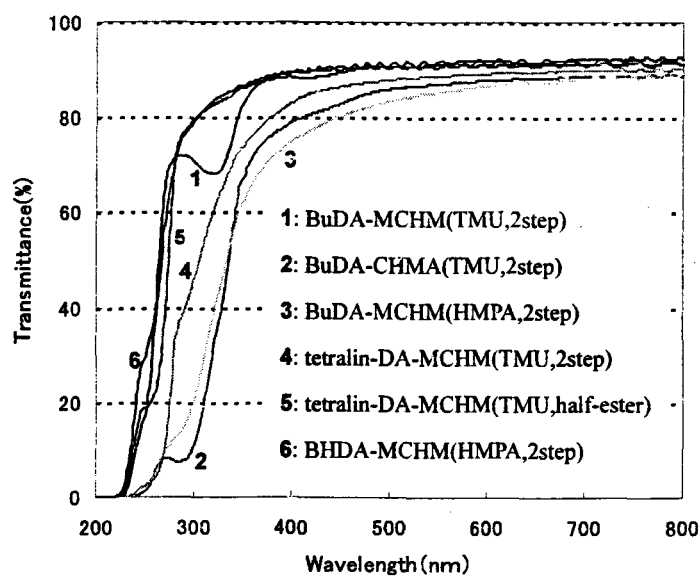


Figure 2. The transmission UV-vis spectra of the free-standing polyimide films of full-aliphatic polyimides.

### **Acknowledgments**

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