

Synthesis and Optical Performance of Polyimides with Alicyclic Tetracarboxylic Dianhydrides Derived from Cyclopentadiene

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Abstract: Transparent polyimides with two types of alicyclic dianhydrides, derived from cyclopentadiene; 1-carboxylmethy-1,2,3,5-cyclopentane tricarboxylic-2,6,3,5-dianhydride (TCA), with unsymmetrical structure, and *trans*-cyclopentane 1,2,3,4-tetracarboxylic dianhydride (*t*-CPDA), with a crank-shaft structure, were synthesized. The latter dianhydride was obtained by thermally driven isomerization of commercially available *cis*-isomer. The use of *trans*-isomer afforded PI of high molecular weight, which was a problem for *cis*-isomer. Higher water absorption of PI with TCA than that of *t*-CPDA was discussed from the standpoints of different imidization rate in PIs. Coloring of PI by formation of charge transfer complex was verified by a series of polyimides with TCA.

Keywords: Transparent, Cyclopentadiene, Alicyclic dianhydride, Isomerization, Imidization rate

1. Introduction

In recent years much attention is being denoted to develop thermally stable transparent polymers including polyimides (PIs). According to a series of studies by Matsumoto¹⁾ and several examples of press-released information by some chemical companies in Japan, alicyclic dianhydrides as monomers are advantageous for providing transparency with keeping high T_g. In this study we will report transparent PIs with two characteristic types of alicyclic dianhydrides; 1-carboxylmethy-1,2,3,5-cyclopentane tricarboxylic-2,6,3,5-dianhydride (TCA), with unsymmetrical structure, and *trans*-cyclopentane 1,2,3,4-tetracarboxylic dianhydride (*t*-CPDA), with a crank-shaft structure. They are derived from cyclopentadiene (CPD) contained in C₅ major fraction of petroleum.

2. Results and Discussion

1) Synthesis of alicyclic dianhydrides

Alicyclic dianhydrides, TCA and *t*-CPDA from CPD, were synthesized as outlined in Fig.1.

TCA was prepared *via* route A. CPD usually exists in its dimeric form (DCPD), as a Diels-Alder adduct with itself. Direct oxidation of DCPD resulted in lower product selectivity for corresponding tetracarboxylic acid. It is preferable to choose pathway *via* hydroxylated-DCPD (HO-DCPD) as an intermediate to tetracarboxylic acid and further to oxidize by nitric acid³⁾. Although TCA was patented in Germany and Great Britain in 1960, it was not developed for PI preparation that time. On the other hand, TCA-derived alicyclic PIs were developed as liquid crystal alignment coating since middle of 1980 by JSR Corporation⁴⁾.

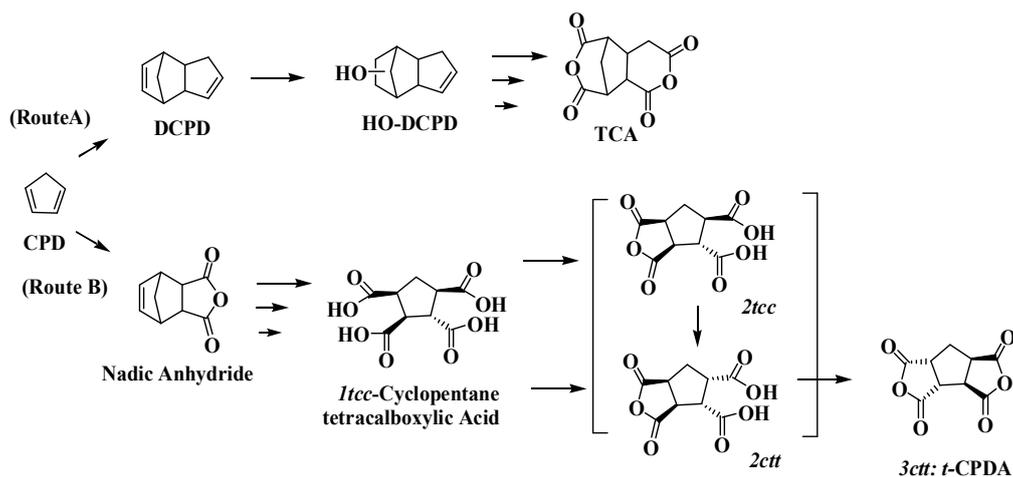


Fig.1. Synthesis Route for tetracarboxylic anhydride derived from cyclopentadiene

3ctt:*t*-CPDA was prepared *via* route B. Usually, oxidation of nadic anhydride (prepared from CPD and maleic anhydride by Diels-Alder reaction) leads to *3ccc*:*cis*-dianhydride (mp. 222 °C), which is not able to get high molecular weight of corresponding PI. This is a major issue in the synthesis of PI from C

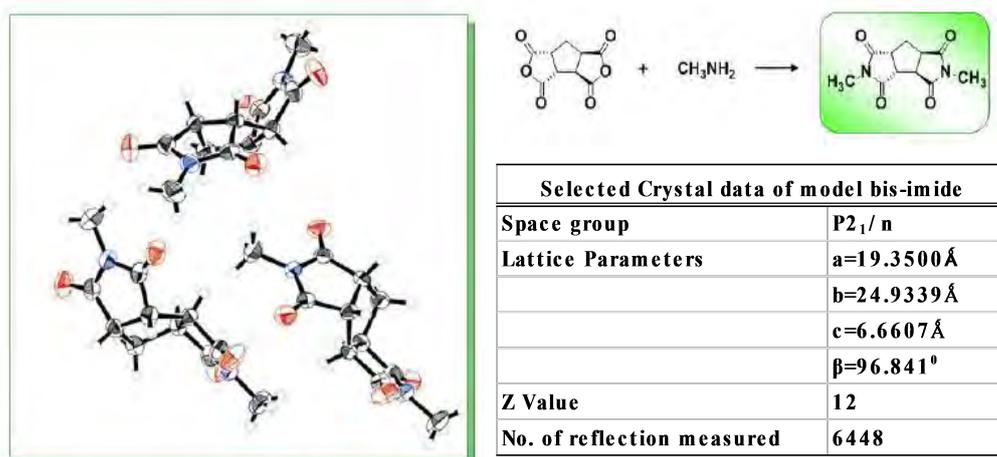


Fig. 2. A stereoview structure of bis-methylimide as a *trans*-form model compound

Herein, we describe an example of the synthesis of *t*-CPDA⁶. It was prepared by thermal isomerization of *Itcc*-tetracarboxylic acid, obtained by hydration of *c*-CPDA, at 285 °C for 5 hours in the molten state, followed by acetic anhydride-driven dehydration *via* *2tcc*- and/or *2ctt*-anhydride-dicarboxylic acids as intermediates. Purified *t*-CPDA (mp. 245 °C) was obtained in 56% yield. Structure of *trans*-form was assigned by ¹H-NMR and ¹³C-NMR. Moreover, a single-crystal X-ray diffraction analysis for bis-methylimide as a model compound also proved a *trans*-form of CPDA. Fig.2 shows molecular structure of *trans*-bisimide by X-ray diffraction.

2) Preparation of PIs

(1) PIs from TCA

PI from TCA is expected to be soluble and possessing higher T_g owing to unsymmetrical and polycyclic structure.

We compared the transparency, T_g and solubility of PIs from TCA with a series of PIs derived

from aliphatic butane 1,2,3,4-tetracarboxylic dianhydride (BTDA), alicyclic cyclobutane 1,2,3,4-tetracarboxylic dianhydride (CBDA) and aromatic 2,2'-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA) as representative examples of transparent PIs.

PIs were prepared from the above dianhydrides and selected aromatic diamines which varied electron density at amino-substituted benzene ring, such as 2,2'-bis(trifluoromethyl)benzidine (TFMB), bis(3-(3-aminophenoxy)phenyl)sulfone (BAPS-M), bis(4-(4-aminophenoxy)phenyl)sulfone (BAPS), 2,2-bis(4-(4-aminophenoxy)phenyl)propane (BAPP) and 4,4'-diaminodiphenylether (DDE).

Experimental results are shown in Fig.3. In case of aromatic PIs with 6FDA, transparency was exhibited only by PIs with TFMB and BAPS-M, in which electron density of amino-substituted benzene ring was lower compared with other aromatic diamines studied here. Among them, transparent PIs with 6FDA and TFMB have been commercialized earlier under trade name FLUPI® by NTT.

On the other hand, PIs with aliphatic and alicyclic dianhydrides in combination with aromatic diamines showed transparency, except for DDE. Introduction of non-aromatic moiety reduces coloring owing to cancellation of charge transfer (CT) complex formation between benzene ring with each monomer unit. However, PI with alicyclic CBDA appeared to be insoluble in organic solvents, while PIs with BTDA showed lower T_g. Among studied dianhydrides, only TCA showed balanced characteristics, such as transparency, T_g higher than 260°C (measure of reflow soldering temperature) and solubility. TCA takes advantage of its unsymmetrical and polycyclic structure.

In order to understand qualitatively relations between PI with alicyclic and aromatic dianhydrides, absorption spectra of each PIs were compared. TCA was used as a representative of alicyclic dianhydrides, as 6FDA did as aromatic one. Absorption spectra of each PI are shown in Fig.4. The difference in cut-off wavelengths of absorbance between TCA PI and 6FDA PI is obvious. In case of aromatic 6FDA PIs, cut-off of absorbance shifted to shorter wavelengths with the lowering electron density at amino-substituted benzene rings, reaching ca. 330 nm. On the other hand, that of TCA PIs has converged to ca. 280 nm, even for diamines with different electron density at amino-substituted benzene ring, namely TFMB and BAPP.

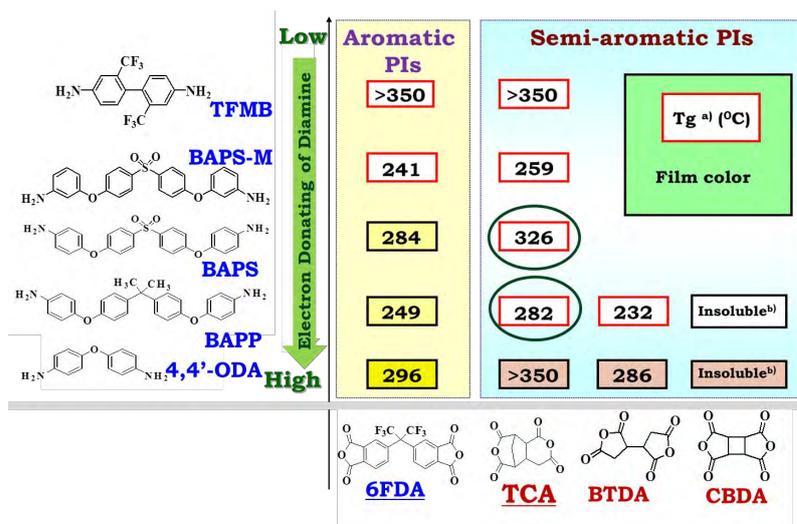


Fig. 3. Thermal and optical properties of PIs

This is owing to cancellation of CT complex formation by introducing alicyclic moiety. These numerical values of cut-off wavelengths are compatible with those of results by Matsumoto⁵⁾. Option of

aromatic diamines is extended by using alicyclic dianhydride with shifting cut-off wavelength to shorter wavelengths, as preferable for transparency

(2) PIs from *t*-CPDA

Commercially available CPDA exists in *3ccc:cis*-form. It has a problem to get higher molecular weight enough to film preparation owing to apparent steric hindrance around dianhydride group at five-membered ring.

Table 1 shows representative characteristics of PI using *3ctt:t*-CPDA. One can compare molecular weight of soluble transparent PI with BAPP for CPDA isomer, that (Mw by GPC) of PI with *t*-CPDA was ca 150,000, which is much higher than 4,700 of *c*-CPDA. As a result of Mw *t*-CPDA is able to prepare film enough to measure other characteristics with higher Tg >350 °C.

Table 1. Representative characteristics of transparent PI using *t*-CPDA

Monomer		Mw (GPC)	Solubility	Transmittance %	Tg °C	CTE ppm/°C	Elastic Modulus GPa	Tensile strength MPa	Elongation %	Water Absorption %
Dianhydride	Diamine									
TCA	BAPP	11.2×10 ⁴	○	89	280	60	2.5	108	66	3.0
<i>t</i> -CPDA	BAPP	15.0×10 ⁴	○	89	>350	56	3.5	120	82	1.9
<i>c</i> -CPDA	BAPP	0.47×10 ⁴	○	impossible to measure	212	impossible to measure				
<i>t</i> -CPDA	MBCHA	12.0×10 ⁴	○	91	>350	58	2.7	96	48	1.8

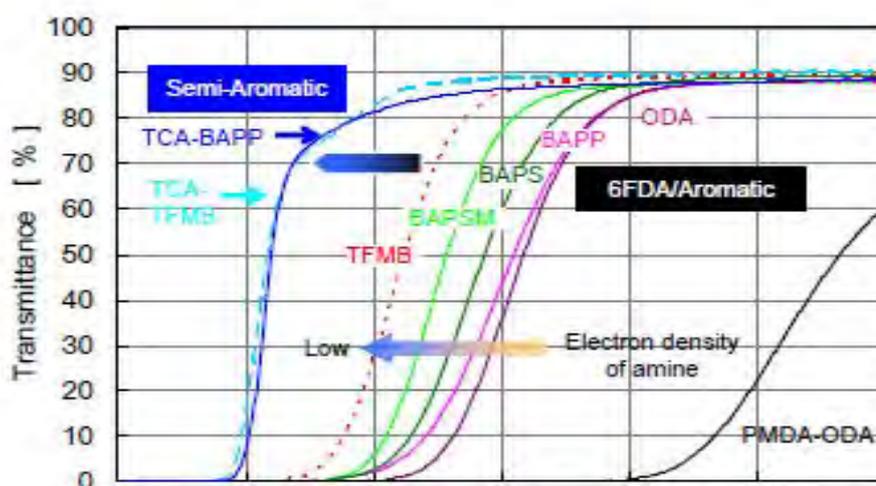


Fig.4 UV-visible spectra of 20µm thick polyimide films derived from aromatic diamines and TCA or 6FDA.

Wholly aliphatic PI was prepared by the combination of *t*-CPDA and 4,4'-methylene bis(cyclohexylamine) (MBCHA). This PI was soluble, transparent and having high Tg >350 °C.

Interestingly, PIs with *t*-CPDA had a tendency to absorb less water than those with TCA, while

comparing the same concentration of imide groups in PI. It is believed to depend on different imidization rates in PIs with *t*-CPDA and TCA. In Alicyclic PI, high imidization rate (near 100%) is one of important factors to control the characteristics.

t-CPDA has a crank-shaft structure as shown in Fig.2. It seems to promote a rod-like structure along the direction of anhydride functional group through its five-membered rings. Known dianhydrides of similar crank-shaft structure can be represented by *t*-CBDA⁸⁾, *trans-endo-endo- α -clopentanone- α' -spiro-2''-norbornane-5,5'',6,6''-tetracarboxylic dianhydride (CpODA)⁹⁾ and aromatic 2,2',3,3'-biphenyltetracarboxylic dianhydride (*i*-BPDA)¹⁰⁾. In combination with rigid aromatic diamines, corresponding PIs exhibited low coefficients of thermal expansion (CTE). *t*-CPDA is also expected as a candidate monomer for PIs with low CTE .*

3. Conclusions

Two types of alicyclic dianhydrides, derived from cyclopentadiene contained in C₅ major fraction of petroleum; TCA with unsymmetrical structure, and *t*-CPDA with a crank-shaft structure, were synthesized. TCA was prepared by oxidation *via* HO-DCPD with nitric acid. *t*-CPDA was obtained by thermally driven isomerization of commercially available *cis*-isomer. Using *t*-CPDA yielded PI with higher Mw enough to prepare film, while *cis*-isomer was not able to prepare high Mw of corresponding PI. Both monomers afforded soluble transparent PIs in combination with aromatic diamines with keeping high Tg. Lower water absorption was observed in PI with *t*-CPDA than that with TCA. This was attributed to different imidization rate in PIs. In alicyclic PI, high imidization rate (near 100%) is one of important requirements to control the characteristics. Cut-off wavelengths of absorption spectra of a series of PIs with aromatic diamines were compared with alicyclic TCA and aromatic 6FDA. As a result, coloring of PI by formation or achromatizing by cancellation of CT complex was verified with or without non-aromatic alicyclic moiety.

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