Colorless polyimides derived from 1S,2S,4R,5R-cyclohexanetetra
carboxylic dianhydride, self-orientation behavior during solution
casting, and their optoelectronic applications

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A novel cycloaliphatic monomer for polyimides (PI), 1S,2S,4R,5R-cyclohexanetetra
carboxylic dianhydride (H-PMDA) is proposed in this work. H-PMDA shows high polymerizability with various diamines in contrast to its isomer, i.e., conventional hydrogenated pyromellitic dianhydride (H-PMDA) and leads to highly flexible and colorless PI films with very high Tg’s. In particular, the combinations with rigid structures of diamines give rise to PI films with significantly decreased coefficients of thermal expansion (CTE) owing to high extents of in-plane chain orientation induced by thermal imidization, whereas the H-PMDA-based counterparts do not. The decreased CTE reflects structural rigidity/linearity of the H-
PMDA-based diimide units as supported by liquid crystallinity observed in the corresponding model compound. Solution casting of a chemically imidized PI derived from H-PMDA and 2,2'-bis(tri-
fluoromethyl)benzidine (TFMB) results in a lower CTE than that of the thermally imidized counterpart, suggesting the presence of a self-orientation phenomenon during solvent evaporation. The mechanism is proposed in this work. H-PMDA/TFMB and its copolymer systems can be useful as plastic substrates in image display devices and/or novel coating-type optical compensation films.

1. Introduction

The importance of optically transparent high-temperature polymeric materials has been increasing for their extensive applications as optical components, e.g., plastic substrates of image display devices, liquid crystal alignment layers, color filters, optical compensation films, optical fibers, light-guiding plates, and optical lenses. One of the recent key projects is to replace current fragile inorganic glass substrates (300–700 μm thick) in flat panel displays by plastic substrates (<50 μm thick), thereby the display devices become drastically light and flexible. However, it is very difficult to obtain the substrate materials simultaneously possessing the merits of inorganic glass (i.e., excellent optical transparency, ultrahigh heat resistance, and high dimensional stability against thermal cycles undergoing in the device fabrication processes) and organic polymeric systems (flexibility and processability). Poly(ether sulfone) (PES) is known to possess the highest level of physical heat resistance (Tg = 225 °C) among current colorless engineering plastics, however, it is not enough for applications to the plastic substrate materials. Polymeric materials with very high Tg exceeding 300 °C are practically limited to polyimide (PI) systems, which are widely used in a variety of electronic devices for their simple two-step manufacturing processes, excellent electric insulation ability based on an extremely high purity (the absence of volatile organic compounds and metallic/ionic contaminations), non-flammability, and thermo-oxidative stability (long-term heat resistance) in addition to considerably high Tg’s overcoming the solder-reflowing processes (short-term heat resistance) [1–13]. However, conventional aromatic PI films are in general not suitable for optoelectronic applications because of their intensive coloration arising from charge-transfer (CT) interactions [14].

Much effort has been devoted to erase the PI film coloration. The most effective strategy is to use aliphatic monomers (usually, cycloaliphatic ones for avoiding significant Tg decrease) either in diamines or tetracarboxylic dianhydrides or both [15–23]. However, most of cycloaliphatic monomers do not lead to PI films with...
low linear coefficients of thermal expansion (CTE) indispensable for good dimensional stability because their non-linear/non-planar steric structures disturb the PI chain alignment along the film plane (X-Y) direction (called in-plane orientation) during the thermal imidization process. Cycloaliphatic monomers with relatively high structural linearity effective for low CTE generation are limited to 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) and trans-1,4-cyclohexanediamine (t-CHDA) at the present time. However, the use of aliphatic diamines such as t-CHDA causes the formation of insoluble salt at the initial stage in the polymerization process of PI precursors [poly(amic acid)s (PAAs)], by which the reaction is completely inhibited in some cases or needs prolong periods until the reaction mixtures are completely homogenized [21,22]. In contrast, the combinations between cycloaliphatic tetracarboxylic dianhydrides and aromatic diamines can easily produce colorless PIs without such salt formation problem. CBDA is also advantageous from the viewpoints of the polymerizability with aromatic diamines [23-26], whereas conventional cycloaliphatic tetracarboxylic dianhydrides [e.g., bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BTA)] often lead to insufficient molecular weights of PAAs without film-forming ability [21,22,27]. However, CBDA-based PIs basically possess no solution-processability [16]. Thus, cycloaliphatic tetracarboxylic dianhydrides suitable for obtaining practically useful plastic substrate materials are very limited.

The present work proposes a novel cycloaliphatic tetracarboxylic dianhydride with a relatively linear/planar structure, i.e., 1S,2S,4R,5R-cyclohexanetetracarboxylic dianhydride (H0-PMDA) [28] and illustrates some distinctive properties of H0-PMDA-based PIs [29]. As the hydrogenated forms of pyromellitic dianhydride (PMDA), two isomers have been so far reported: 1S,2R,4S,5R-cyclohexanetetracarboxylic dianhydride (H1-PMDA) [30] and 1R,2S,4S,5R-cyclohexanetetracarboxylic dianhydride (H2-PMDA) [31]. H0-PMDA is an additional stereoisomer. In the present work, isomer effects on the polymerizability and the PI film properties are also discussed. To the best of our knowledge, this is the earliest

**Fig. 1.** Molecular structures of monomers used in this work.
report described in detail on the properties of H'-PMDA-based PIs and their optoelectronic applications.

2. Experimental

2.1. Materials

The structures, abbreviations, sources, and pre-treatment conditions of the monomers used in this work are summarized in Fig. 1 and Table 1. H'-PMDA was synthesized as follows [28]; PMDA was first hydrolyzed with a NaOH aqueous solution. The pyromellitic acid tetratsodium salt formed was hydrogenated in a high-pressure hydrogen atmosphere at 160 °C in the presence of a ruthenium catalyst. After hydrogenation was completed, the solution was additionally heated at a precisely controlled temperature for several hours, and cooled to room temperature. The solution was then neutralized by slowly adding conc. HCl. The white precipitation yielded (tetracarboxylic acid, 1) was collected by filtration, recrystallized from water, and dried in vacuum at 80 °C for 5 h. A small portion of 1 was quantitatively converted into tetramethyl ester to analyze the purity of 1 by gas chromatography (GC). The GC chart for the tetramethyl ester of 1 showed a single peak at a different elution time from that of the tetramethyl ester counterpart derived from conventional H-PMDA, suggesting the difference of the steric structures. The tetracarboxylic acid (1) was finally dehydrated with acetic anhydride (Ac2O) to form tetracarboxylic dianhydride (2). Product 2 was difficult to form a sufficient size of single crystal by recrystallization from Ac2O for the X-ray structural analysis. Instead, the corresponding tetracarboxylic acid (1) was used for this purpose. The results revealed that product 1 is 1,2,5,4,8,5r-cyclohexanetetracarboxylic acid with a chair form of the central cyclohexane unit as depicted in Fig. 2 [32]. Fig. 3 shows the powder X-ray diffraction patterns for 1 and a compound yielded by hydrolyzing 2 with water. A good agreement between them suggests that the steric structure of 1 is maintained even after dehydration with Ac2O. Therefore, product 2 can be identified as 1,2,5,4,8,5r-cyclohexanetetracarboxylic dianhydride (H'-PMDA). The most probable steric structure of H'-PMDA is shown in Fig. 4 (c) together with those of H-PMDA and H2-PMDA which were directly determined by the single-crystal X-ray diffraction measurements [30,31].

PAAs were prepared by equimolar polyaddition of tetracarboxylic dianhydrides and diamines as shown in Fig. 5. A typical procedure is as follows; tetracarboxylic dianhydride powder (10 mmol) was added in a dry N,N-dimethylacetamide (DMAc) or N,N-dimethylformamide. CHX — cyclohexane.

* Compound repeatedly recrystallized from acetic anhydride (Ac2O).

Table 1

<table>
<thead>
<tr>
<th>Monomer Source</th>
<th>Solvent for recrystallization</th>
<th>Vacuum-drying condition</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2,3,4-Cyclobutanetetracarboxylic dianhydride (CBD)</td>
<td>Ethyl acetate</td>
<td>30 °C/24 h</td>
<td>142</td>
</tr>
<tr>
<td>p-Phenylene diamine (p-PDA)</td>
<td>Tohoku University</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>4,4'-Oxydianiline (4,4'-ODA)</td>
<td>Wako Chemical</td>
<td>Toluene/DMF (10/1, v/v)</td>
<td>50 °C/24 h</td>
</tr>
<tr>
<td>3,4'-Oxydianiline (3,4'-ODA)</td>
<td>JFE Chemical</td>
<td>Toluene/DMF (10/1, v/v)</td>
<td>50 °C/24 h</td>
</tr>
<tr>
<td>Bis(4-amino-2-trifluoromethylphenyl) ether (TFODA)</td>
<td>Ibara Chemical</td>
<td>EtOH/H2O (11/5, v/v)</td>
<td>145 °C/12 h</td>
</tr>
<tr>
<td>m-Tolidine (m-TOL)</td>
<td>Wakayama Seika</td>
<td>Toluene/CHX (7/3, v/v)</td>
<td>70 °C/24 h</td>
</tr>
<tr>
<td>o-Tolidine (o-TOL)</td>
<td>Wakayama Seika</td>
<td>Toluene</td>
<td>80 °C/24 h</td>
</tr>
<tr>
<td>2,2'-Bis(trifluoromethyl) benzidine (TFMB)</td>
<td>Wako Seika</td>
<td>—</td>
<td>50 °C/24 h</td>
</tr>
<tr>
<td>1,4-Bis(4-aminophenoxy) benzene (TPEQ)</td>
<td>Wako Seika</td>
<td>Toluene/DMF (15/1, v/v)</td>
<td>100 °C/24 h</td>
</tr>
<tr>
<td>4-Aminophenyl-4'-aminobenzoate (APAB)</td>
<td>Wako Seika</td>
<td>—</td>
<td>50 °C/24 h</td>
</tr>
<tr>
<td>4,4'-Diaminobenzonitrile (DABA)</td>
<td>TCI</td>
<td>—</td>
<td>50 °C/24 h</td>
</tr>
<tr>
<td>4,4'-Bis(4-aminophenoxy) biphenyl (BAPB)</td>
<td>Wako Seika</td>
<td>Toluene/DMF (15/1, v/v)</td>
<td>50 °C/24 h</td>
</tr>
<tr>
<td>2,2'-Bis[4-(4-aminophenoxy)pheny]</td>
<td>Wako Seika</td>
<td>—</td>
<td>50 °C/24 h</td>
</tr>
<tr>
<td>propane (BAPP)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2,2'-Bis[4-(4-aminophenoxy)pheny] hexafluoropropane (HFAPP)</td>
<td>Wako Seika</td>
<td>—</td>
<td>50 °C/24 h</td>
</tr>
<tr>
<td>Trans-1,4-cyclohexanedicarboxylic acid (t-CHDA)</td>
<td>Iwatani Industrial Gases</td>
<td>—</td>
<td>30 °C/24 h</td>
</tr>
<tr>
<td>4,4'-Methylenebis(cyclohexylamine) (MBCHA) (mixture of cis/trans isomers)</td>
<td>New Japan Chemical</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>4,4'-Methylenebis(2-methylcyclohexylamine) (M-MBCHA) (mixture of cis/trans isomers)</td>
<td>Aldrich</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
N-methyl-2-pyrrolidone (NMP) solution of diamine (10 mmol) at an initial total solid content of 30 wt% with continuous stirring at room temperature. The reaction mixture was stirred with a magnetic spinner at room temperature in a sealed bottle until it becomes homogeneous with a maximum solution viscosity (typically for 72 h). In this case, if necessary, the reaction mixture was gradually diluted with a minimum quantity of the same solvent to ensure effective magnetic stirring. The polymerization conditions are listed in Table 2. The formation of PAAs was confirmed by the transmission-mode FT-IR spectroscopy (Jasco, FT/IR 4100 infrared spectrometer) using separately prepared thin cast films (4–5 μm thick) with non-uniform thickness to erase interference fringes. A typical FT-IR spectrum is shown in Fig. 6 (a). The spectrum includes some specific bands (cm⁻¹): 3318 (amide, N–H), 3119 (C–H), 2948 (C–H), ~2600/1715 (hydrogen-bonded carboxylic acid, O–H/C=O), 1675/1535 (amide, C=O), 1489 (1,4-phenylene), and 1323 (C–F).

PI films were prepared by different methods (thermal and chemical imidization). The reaction schemes are shown in Fig. 5. PI films were prepared upon thermal imidization as follows; PAA solution was bar-coated on a glass substrate and dried at 60 °C/2 h for DMAc solutions (80 °C/1 h for NMP solutions) in an air-convection oven. We first attempted thermal imidization under a relatively mild condition (e.g., at 250 °C in vacuum) for suppressing PI film coloration. However, the PI films obtained were somewhat brittle in many cases. This is probably due to partial retro-polyaddition although the generated terminal functional groups can recombine by additional heating at higher temperatures [33]. Then, to obtain flexible PI films while avoiding film coloration, thermal imidization was carried out typically at 200 °C/20 min + 250 °C/30 min + 320 (or 300) °C/1 h in vacuum as adhered on the substrate, and successively annealed in vacuum at 10–20 °C lower temperatures than the Tg’s after peeling them off from the substrate to eliminate residual stress without undesirable significant film deformation. The imidization and annealing conditions were properly adjusted to obtain better quality of PI films. The thermally imidized film samples are represented as “(T)” from now on. On the other hand, chemical imidization was conducted by gradually adding a mixed solution of Ac₂O/pyridine (7/3, v/v) to adequately diluted PAA solutions at a fixed molar ratio of [Ac₂O]/[COOH]PAA = 5 with continuous vigorous stirring at room temperature. The reaction mixture was additionally stirred at room temperature for 12 h in a sealed bottle while carefully monitoring the solution homogeneity. After the chemical imidization process, the homogeneous reaction mixture was adequately diluted with the same solvent, and very slowly poured into a large quantity of methanol or water as a poor solvent. The fibrous white precipitate obtained was repeatedly washed with methanol/water, collected by filtration, and dried at 80 °C in vacuum for 12 h. The excess of the chemical imidization reagent is completely eliminated on this procedure, which is important for avoiding undesirable film coloration as observed in some cases. The dried precipitate was redissolved in a fresh solvent [typically, cyclopentanone (CPN)] at a solid content of 10 – 15 wt%. The homogeneous PI solution formed was coated on a glass substrate and dried typically at 60 °C/2 h + 150 °C/2 h on the substrate, and at 200 °C/1 h in vacuum without the substrate. The PI films were additionally annealed at
1. Reaction schemes of polyaddition and imidization of PAAs and predicted end-capping reaction of terminal amino groups during chemical imidization process.

2. Results of polyaddition of H'-PMDA with various diamines.

<table>
<thead>
<tr>
<th>Category of diamine</th>
<th>System no.</th>
<th>Diamine</th>
<th>Solid content (init−final) (wt%)</th>
<th>Solvent</th>
<th>( \eta_{in} ) (PAA) (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic-flexible (I)</td>
<td>1</td>
<td>4,4-ODA</td>
<td>30 → 16.9</td>
<td>DMAc</td>
<td>1.52</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>TPEQ</td>
<td>30 → 15.4</td>
<td>DMAc</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>BAPP</td>
<td>30 → 14.4</td>
<td>DMAc</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>BAPS</td>
<td>30 → 18.8</td>
<td>DMAc</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>TDOA</td>
<td>30 → 15.3</td>
<td>DMAc</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>HFBAPP</td>
<td>30 → 19</td>
<td>DMAc</td>
<td>1.10</td>
</tr>
<tr>
<td>Aromatic-rigid (II)</td>
<td>7</td>
<td>p-PDA</td>
<td>30 → 8.8</td>
<td>DMAc</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>o-TOL</td>
<td>30 → 12.2</td>
<td>NMP</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>m-TOL</td>
<td>30 → 10</td>
<td>DMAc</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>APAB</td>
<td>30 → 12.6</td>
<td>DMAc</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>DABA</td>
<td>30 → 15</td>
<td>DMAc</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>TMDB</td>
<td>30 → 13</td>
<td>DMAc</td>
<td>2.43</td>
</tr>
<tr>
<td>Cycloaliphatic-flexible (III)</td>
<td>13</td>
<td>MBCHA</td>
<td>30 → 17.6</td>
<td>DMAc</td>
<td>0.67</td>
</tr>
<tr>
<td>Cycloaliphatic-rigid (IV)</td>
<td>14</td>
<td>M-MBCHA</td>
<td>30 → 12.8</td>
<td>DMAc</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>t-CHDA</td>
<td>20 → 18</td>
<td>NMP</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>t-CHDAa</td>
<td>15 → 6.8</td>
<td>NMP</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>t-CHDAb</td>
<td>15 → 9.7</td>
<td>DMAc</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>t-CHDAc</td>
<td>15</td>
<td>DMAc</td>
<td>–</td>
</tr>
</tbody>
</table>

3.  Inhomogeneous mixture.

4.  Formation of insoluble salt.

5.  Gelation.

6.  Diffuse transmittance (\( T_{\text{diff}} \), JIS K 7361–1) and the diffuse transmittance (\( T_{\text{diff}} \), JIS K 7136) of PI films.
were measured on a double-beam haze meter equipped with an integrating sphere (Nippon Denshoku Industries, NDH 4000). Haze (turbidity) of PI films was calculated from the relation:

\[
Haze = \frac{I_{\text{diff}}}{I_{\text{tot}}} \times 100
\]

The in-plane \((n_{\text{in}} \text{ or } n_b = n_y)\) and out-of-plane \((n_{\text{out}} \text{ or } n_z)\) refractive indices of PI films were measured with a sodium lamp at 589.3 nm (D-line) on an Abbe refractometer (Atago, 4T, \(n_D\) range: 1.47–1.87) equipped with a polarizer by using a contact liquid (sulfur-saturated methylene iodide with \(n_D = 1.78–1.80\) or 1-bromonaphthalene with \(n_D = 1.658\) when the samples were swollen by \(\text{CH}_2\text{I}_2\)) and a test piece (\(n_D = 1.92\)). The birefringence of PI films, which represents a relative extent of chain alignment along the film plane \((X-Y)\) direction, was calculated from the relation:

\[
\Delta n_{\text{th}} = n_{\text{in}} - n_{\text{out}}
\]

The dielectric constants were estimated from the optical data on the basis of an empirical relation:

\[
e_{\text{opt}} = 1.1 n_{\text{av}}^2
\]

where \(n_{\text{av}}\) denotes the average refractive indices expressed as

\[
n_{\text{av}} = (2n_{\text{in}} + n_{\text{out}})/3
\]

The \(e_{\text{opt}}\) values are known to be approximate to the dielectric constants directly determined with a precision LCR meter at a frequency of 1 or 10 MHz for PI systems [25,34].

\[
\Delta n_{\text{th}}
\]

was also measured as a function of wavelength in the visible range on an Abbe refractometer (Atago, 1T, \(n_D\) range: 1.30–1.70). Monochromatic light was introduced to the refractometer from a Xe lamp source in a fluorescence spectrometer (Hitachi, F-2000) with a 10 nm bandpass of a monochromator through an optical fiber cable. In this case, the color compensation dial of the refractometer was set at 30 for measuring at different wavelengths from the D-line. The raw data were corrected using a formula supplied by Atago Co., Ltd.

2.2.3. Linear coefficient of thermal expansion

The CTE along the \(X-Y\) direction for PI films \((15 \text{ mm long, 5 mm wide, and typically 20 } \mu\text{m thick})\) in the glassy region was measured by thermomechanical analysis (TMA) as an average in the range of 100–200 °C at a heating rate of 5 K min\(^{-1}\) on a thermomechanical analyzer (Bruker-AXS, TMA 4000) with a fixed load \((0.5 \text{ g per unit film thickness in } \mu\text{m, typically 10 g load for 20 } \mu\text{m-thick films})\) in a dry nitrogen atmosphere. In this case, after the preliminary first heating run up to 120 °C and successive cooling to room temperature in the TMA chamber, the data were collected from the second heating run for removing an influence of adsorbed water.

2.2.4. Glass transition temperature

The storage modulus \((E')\) and the loss energy \((\epsilon''\text{)}\) of PI films were measured by the dynamic mechanical analysis (DMA) at a heating rate of 5 K min\(^{-1}\) on the same TMA instrument. The measurements were conducted at a sinusoidal load frequency of 0.1 Hz with an amplitude of 15 gf in a nitrogen atmosphere. The \(T_g\)'s of PI films were determined from a peak temperature of the \(E''\) curve. In this instrument, the heating runs undergo an automatic stop when the irreversible elongation (\(\Delta l\)) of the specimens exceeded 3000 \(\mu\text{m}\) by softening above the \(T_g\)'s.

2.2.5. Thermal stability at elevated temperatures

Thermal stability of PI films was evaluated from the 5% weight loss temperatures \((\text{T}_{5\%})\) by thermogravimetric analysis (TGA) on a thermo-balance (Bruker-AXS, TG-DTA2000). TGA was performed at a heating rate of 10 K min\(^{-1}\) in nitrogen or air atmosphere. For the measurements in \(N_2\), the preliminary first heating run up to 150 °C was carried out to eliminate adsorbed water, and the samples were cooled to room temperature while mounting in the sample chamber under a continuous dry \(N_2\) flow. After the data resetting to 0% weight loss, TGA data were collected from the second heating run.

2.2.6. Mechanical properties

The tensile modulus \((E)\), tensile strength \((\sigma_b)\), and elongation at break \((\epsilon_b)\) of PI specimens \((30 \text{ mm long, 3 mm wide, typically 20 } \mu\text{m thick})\) were measured on a mechanical testing machine (A & D, Tensilon UTM-II) at a cross head speed of 8 mm min\(^{-1}\) at room temperature. The data were averaged for 10–15 samples. In this case, the specimens were taken from high-quality large film samples \((10 \text{ cm } \times 10 \text{ cm})\) without any defects such as fine bubbles. For some systems, it was difficult to carry out the mechanical stretching test because of film brittleness or the difficulty of high-quality large film preparation.

2.2.7. Solubility

The solubility of thermally imidized film or chemically imidized powder samples was evaluated by observing the immersed samples \((10 \text{ mg})\) in various solvents \((1 \text{ mL})\) in a test tube.
2.2.8. Heat of combustion

The heats of combustion $Q_c$ (gross calorific value) for three hydrogenated PMDA isomers were measured by a custom analysis center (Ibiden Engineering Co.) on an advanced adiabatic bomb calorimeter (Yoshida Seisakusho Co., JIS M8814) calibrated with benzoic acid as a standard sample. In this case, the $Q_c$ values correspond to the internal energy change of combustion ($\Delta U_g$). The enthalpy change of combustion ($\Delta H_g$) was calculated from the relation: $\Delta H_g = \Delta U_g + P\Delta V = \Delta U_g + \Delta n_g RT$ ($P$ is pressure, $\Delta V$ volume change, $R$ the gas constant, and $T$ absolute temperature). $\Delta n_g$ (in mol) is a change in the amount of substance for the gaseous phases in the following combustion reaction: $C_{10}H_{8}O_{6}\left(s\right) + 9 \, O_2 \left(g\right) = 10 \, CO_2 \left(g\right) + 4H_2O \left(l\right)$ ($\Delta n_g = 1$ in the present case). To compare thermodynamic stability of three hydrogenated PMDA isomers, each standard enthalpy of formation at 25 °C ($\Delta H_f^{298}$) for the stereoisomers was estimated from the thermochemical equations with the $\Delta H_g$ values of the stereoisomers, graphite, and $H_2\left(g\right)$.

2.2.9. Liquid crystallinity

Liquid crystallinity of low molecular weight model compounds was examined on an Olympus BX51 polarizing optical microscope (POM) equipped with a digital camera (Nikon Coolpix 950) and a temperature-controllable hot stage (Mettler Toledo, FP82HT hot stage and FP 90 central processor).

3. Results and discussion

3.1. Polymerizability of H'-PMDA with diamines and isomer effect

The polyaddition reactivity of tetracarboxylic dihydrides with diamines can be represented by the second-order rate constants in a homogeneous state. However, the PAA polymerization actually proceeds in an inhomogeneous mixture composed of tetracarboxylic dihydride powder fed into diamine solutions. Thus, instead of the rate constants, we simply compared the polymerizability of three hydrogenated PMDA isomers on the basis of the $\eta_{inh}$ Values of the finally obtained PAAs in the present work. This parameter is practically useful because it is closely related to the PI film flexibility as often represented by the elongation at break ($\varepsilon_b$) [35]; in many cases, the film specimens become very brittle at both stages of PAA and PI when the $\eta_{inh}$ values are rather low (empirically speaking, $< - 0.3$ dL g$^{-1}$) owing to poor chain entanglement. For example, the BTA/4,4'-ODA system leads to a PAA without film-forming ability as a result of a rather low $\eta_{inh}$ value (0.19–0.38 dL g$^{-1}$) [21,22,27], which is attributed to insufficient polymerizability of BTA. The use of H'-PMDA instead of BTA slightly increases the $\eta_{inh}$ value (0.57 dL g$^{-1}$). The insufficient polymerizability of BTA and H-PMDA can be explained in terms of self-steric hindrance during the polymerization, which is related to an all-exo configuration for the four C=O groups; once one functional group reacted with a terminal amino group, the other surviving functional group may undergo steric hindrance arising from “covering/shielding” by the adjacent growing chain, consequently, the approaching/attack of other terminal amino groups to the remaining functional is disturbed [22]. On the other hand, the reaction of H'-PMDA and 4,4'-ODA gave rise to a sufficiently high $\eta_{inh}$ of 1.52 dL g$^{-1}$, which is somewhat lower than $\eta_{inh} = 2.26$ dL g$^{-1}$ for CBDA/4,4'-ODA. The strikingly improved polymerizability of H'-PMDA compared to H-PMDA probably results from a unique configuration of H'-PMDA as depicted in Fig. 4 (c) where the functional groups orient almost opposite directions each other as in PMDA and CBDA, thereby the self-steric hindrance mentioned above becomes less effective. Thus, when 4,4'-ODA was used as a fixed diamine, the $\eta_{inh}$-based polymerizability of the cycloaliphatic tetracarboxylic dihydrides tends to increase as follows: BTA < H'-PMDA << H'-PMDA < CBDA.

A strained structure of the five-membered anhydride rings in H'-PMDA may also contribute to its enhanced polymerizability. The bomb calorimetry determined: $\Delta U_g = -1.87 \times 10^4\, \text{J g}^{-1}$ for H'-PMDA, $-1.82 \times 10^4\, \text{J g}^{-1}$ for H'-PMDA, and $-1.80 \times 10^4\, \text{J g}^{-1}$ for H'-PMDA. Using these experimental data, the heats of formation were estimated: $\Delta H_f^{298} = -8.88 \times 10^3\, \text{kJ mol}^{-1}$ for H'-PMDA, $-1.00 \times 10^4\, \text{kJ mol}^{-1}$ for H'-PMDA, and $-1.05 \times 10^4\, \text{kJ mol}^{-1}$ for H'-PMDA. The results suggest that H'-PMDA is somewhat thermodynamically less stable than the other isomers, probably relating to a strained structure of the former.

Table 2 lists the results of the polyaddition between H'-PMDA and different categories of diamines. In the aromatic diamine systems, the reactions smoothly proceeded and led to homogeneous/viscous PAA solutions with high $\eta_{inh}$ Values (0.9–3.2 dL g$^{-1}$) except for the cases using p-PDA and o-tolidine (o-TOL). The reactions between H'-PMDA and these rigid diamines in DMAc disturbed the formation of homogeneous PAA solutions. This is probably attributed to partial precipitation of the initially formed rigid amic acid oligomers with poor solubility. The PAA chains for H'-PMDA/p-PDA most likely possess a mixed sequence of cis-1,3- and trans-1,4-cyclohexanedicarboxamide units, in which the central cyclohexane moieties take a chair form (Fig. 7), as suggested from the fact that PMDA/diamine systems provide PAAs with a composition of meta(60)/para(40) [36]. Therefore, the trans-1,4-cyclohexanedicarboxamide units greatly contribute to enhancing the main chain rigidity, as a result, decreasing the PAA solubility. On the other hand, neither the PAA counterpart from H'-PMDA nor H'-PMDA contains such rigid structural unit, corresponding to the fact that these isomers cause no precipitation problem during the polymerization process even when very rigid diamines such as p-PDA were used. A similar precipitation problem as in the H'-PMDA/p-PDA system was observed in a comparative reaction system, i.e., polymerization of a polyamide from pure trans-1,4-cyclohexanedicarboxylic chloride (t-1,4-CHDC) and TFMB in DMAc in the presence of pyridine as an acid acceptor. In contrast, the use of trans(24)/cis(76) mixture of 1,4-CHDC, instead of pure t-CHDC, allowed the formation of a homogeneous polyamide solution. This also supports that the trans-1,4-cyclohexanedicarboxamide moiety (Fig. 7(a)) behaves indeed as a very rigid structural unit. In the present work, a pronounced solvent effect was observed in the H'-PMDA/p-PDA system; the reaction mixture was homogenized in NMP in contrast to DMAc and provided a PAA with a sufficiently high $\eta_{inh}$ Value of 1.6 dL g$^{-1}$. This is probably attributed to better affinity between the PAA and NMP (namely, higher solubility) than CBDA. The strikingly improved polymerizability of H'-PMDA compared to H-PMDA probably results from a unique configuration of H'-PMDA as depicted in Fig. 4 (c) where the functional groups orient almost opposite directions each other as in PMDA and CBDA, thereby the self-steric hindrance shown above becomes less effective. Thus, when 4,4'-ODA was used as a fixed diamine, the $\eta_{inh}$-based polymerizability of the cycloaliphatic tetracarboxylic dihydrides tends to increase as follows: BTA < H'-PMDA << H'-PMDA < CBDA.

![Fig. 7. Structures of cyclohexanamide units in the PAA main chains for H'-PMDA/p-PDA system: (a) trans-1,4-cyclohexanedicarboxamide and (b) cis-1,3-cyclohexanedicarboxamide.](image-url)
PAA/DMAc. However, even the use of NMP was less effective to obtain a homogeneous PAA solution for the H\textsuperscript{0}-PMDA/o-TOL system.

TFMB is somewhat inferior in the reactivity to common aromatic diamines such as 4,4'-ODA owing to the presence of the electron-withdrawing CF\textsubscript{3} substituents in TFMB. Nonetheless, the reaction between H\textsuperscript{0}-PMDA and TFMB led to a PAA with a high molecular weight enough for flexible film formation \(M_w = 1.2 \times 10^5\), \(M_n = 5.2 \times 10^4\) for the chemically imidized powder sample with \(\eta_{inh} (\text{PI}) = 1.23 \text{ dL g}^{-1}\) in contrast to the absence of film-forming ability for the isomeric H-PMDA/TFMB system. The use of specially purified H\textsuperscript{0}-PMDA by repeated recrystallization produced a PAA with an extremely high \(\eta_{inh}\) of 9.04 dL g\textsuperscript{-1} as a maximum value.

The reactions between H\textsuperscript{0}-PMDA and flexible cycloaliphatic diamines (category III) caused salt formation in the initial stage as generally observed when aliphatic diamines were used. However, the reaction mixtures were finally homogenized by gradual dissolution of the salt during stirring at room temperature for several days. The system derived from H\textsuperscript{0}-PMDA and t-CHDA (category IV) is greatly expected to display valuable combined properties (low CTE, transparency, and low birefringence as discussed later). However in fact, the polymerization was completely inhibited by the formation of quite insoluble salt. In this system, neither the silylation method \[37\] nor the addition of acetic acid \[38\] was successful. The success/failure of the reactions between t-CHDA and various tetracarboxylic dianhydrides can be roughly classified into three categories as shown in Fig. 8; in Group 1, the initially formed salt gradually dissolves just by stirring at room temperature, and homogeneous PAA solutions are formed after stirring for several days. The tetracarboxylic dianhydrides of this group (e.g., H-PMDA and H\textsuperscript{00}-PMDA) commonly consist of non-planar/non-linear structures. In Group 2, the reaction mixtures including the salt become homogeneous by heating at 80–120 °C for a short period. The tetracarboxylic dianhydrides of this group possess relatively rigid crank-shaft-like structures. In Group 3, once the salt was initially formed, it does not dissolve any longer even though the reaction mixtures were diluted and heated. The tetracarboxylic dianhydrides of this group consist of “rod-like” structures. The classification of Fig. 8 suggests that the insolubility of the initially formed salt is closely related to the structural rigidity of the tetracarboxylic dianhydride monomers used, consequently, overall rigidity of the low molecular weight amic acids formed in the initial stage. The present work revealed that H\textsuperscript{0}-PMDA belongs to Group 3 as shown in Table 2, suggesting that it behaves in the reaction with t-CHDA as an extremely rigid monomer like as PMDA and 2,3,6,7-naphthalenetetracarboxylic dianhydride (NTDA) \[39\].

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Fig_8.png}
\caption{Classification based on polymerizability between t-CHDA and various tetracarboxylic dianhydrides in DMAc.}
\end{figure}
We compared the polymerizability for three hydrogenated PMDA isomers as shown in Fig. 9. When ether-linked flexible aromatic diamines (category I) were used, the $\eta_{inh}$-based polymerizability tends to increase as follows: H-PMDA $\leq$ H$^\circ$-PMDA $\leq$ H$^\circ$-PMDA except for some diamines (#4 and #5). When a less reactive sulfone-containing diamine (BAPS, #4) was used, H$^\circ$-PMDA was roughly comparable to that of H$^\circ$-PMDA. On the other hand, in the reactions with rigid aromatic diamines (category II), the polymerizability of H$^\circ$-PMDA was roughly comparable to that of H$^\circ$-PMDA except for the o-TOL system (#8). H$^\circ$-PMDA was somewhat superior to H$^\circ$-PMDA in the polymerizability with very rigid diamines (p-PDA and m-TOL). This feature is desirable for our current aim addressed to lowering CTE as discussed later.

3.2. Properties of H$^\circ$-PMDA-based Pls and isomer effects

3.2.1. Heat resistance

The $T_g$ values of the H$^\circ$-PMDA-based PI films are listed in Table 3. The systems obtained from H$^\circ$-PMDA and rigid aromatic diamines (category II) showed considerably high $T_g$ ranging 340–420 °C. Even when ether-linked flexible aromatic diamines (category I) were chosen, the resultant PI films maintained still high $T_g$ ranging 280–310 °C. The results are probably related to the structural rigidity/planearity of the H$^\circ$-PMDA-based diimide (H$^\circ$-PMDI) moieties in the PI chains, which probably contributes to intermolecular face-to-face stacking between the diimide units for activating the dipole–dipole interactions between the imide C=O groups.[40, 41].

As suggested from the steric structure of H$^\circ$-PMDA monomer in Fig. 4 (c), the molecular planarity of the H$^\circ$-PMDI unit must be rather high, although it is somewhat inferior to that of aromatic PMDI. The impact of the diimide molecular planarity on the $T_g$ is illustrated in the following comparisons: case (1) $T_g$ = 256 °C for H$^\circ$-PMDA/BAPP vs. 287 °C for PMDA/BAPP[42] ($\Delta T_g$ = 31 °C), and case (2) $T_g$ = 287 °C for H$^\circ$-PMDA/HFBAPP vs. 327 °C for PMDA/HFBAPP[42] ($\Delta T_g$ = 40 °C).

Fig. 10 shows an isomer effect on the $T_g$'s for the Pls derived from three hydrogenated PMDA isomers. The H$^\circ$-PMDA-based Pls tend to possess comparable to (or slightly higher $T_g$'s than) those of the H$^\circ$-PMDA-based counterparts except for some diamine systems. The results also suggest that H$^\circ$-PMDA is the most effective for enhancing the $T_g$ among these isomers. This predominance may be related to the molecular shape of the H$^\circ$-PMDI unit just like a “dish”, which is more suitable for stacking. Thus, the order of $T_g$ can be represented in the following: H$^\circ$-PMDA $\leq$ ( = ) H$^\circ$-PMDA $\leq$ H$^\circ$-PMDA.

As shown in Table 3, the H$^\circ$-PMDA-based Pls derived from aromatic diamines also possess relatively good thermal stability (chemical heat resistance) as suggested from the $T_d$ values (in N2) exceeding 450 °C, although a decrease in $T_d$ is inevitable when cycloaliphatic diamines were used. The H$^\circ$-PMDA-based Pls still maintain high $T_d$ values even in a thermo-oxidative atmosphere (in air), e.g., 451 °C for H$^\circ$-PMDA/4,4'-ODA.

3.2.2. Thermal expansion properties

One of our greatest interests concerns the dimensional stability of PI films as represented by CTE. The CTE values of the thermally imidized H$^\circ$-PMDA-based PI films (T) are summarized in Table 3. The Pl systems derived from flexible ether-containing diamines (category I), as well as methylene-linked cycloaliphatic diamines (mixture of cis/trans isomers, category III), show a common level of CTE values ranging 50–62 ppm K$^{-1}$. The results are attributed to a

---

**Table 3**

<table>
<thead>
<tr>
<th>No.</th>
<th>Diamine</th>
<th>Tune$^a$</th>
<th>$\eta_{inh}$ (g/L)</th>
<th>$\chi$ (nm)</th>
<th>$\Delta \eta_{inh}$</th>
<th>$\Delta T_g$ (°C)</th>
<th>CTE (ppm/°C)</th>
<th>$E$ (GPa)</th>
<th>$\epsilon_{inh,max}$ (%)</th>
<th>$\sigma$ (MPa)</th>
<th>$T_d$ (N2) (°C)</th>
<th>$T_d$ (air) (°C)</th>
</tr>
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<tr>
<td>1</td>
<td>4,4'-ODA</td>
<td>T</td>
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<td>0.0003</td>
<td>2.88/294</td>
<td>50.2</td>
<td>2.42</td>
<td>94/13.5</td>
<td>95</td>
<td>453</td>
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</tr>
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<td>2</td>
<td>TPEQ</td>
<td>T</td>
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<td>298</td>
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<td>2.91/278</td>
<td>57.2</td>
<td>2.60</td>
<td>11.2/14.4</td>
<td>93</td>
<td>459</td>
<td>434</td>
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<tr>
<td>3</td>
<td>BAPP</td>
<td>T</td>
<td>79.0</td>
<td>294</td>
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<td>2.91/256</td>
<td>59.3</td>
<td>1.99</td>
<td>41.4/115</td>
<td>71</td>
<td>456</td>
<td>427</td>
</tr>
<tr>
<td>4</td>
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<td>T</td>
<td>80.5</td>
<td>303</td>
<td>0.0000</td>
<td>2.93/284</td>
<td>59.6</td>
<td>1.89</td>
<td>8.9/25.4</td>
<td>90</td>
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<td>422</td>
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<td>C</td>
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<td>2.65/310</td>
<td>59.2</td>
<td>2.38</td>
<td>93.9/119</td>
<td>110</td>
<td>453</td>
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<td>295</td>
<td>0.0005</td>
<td>2.74/287</td>
<td>61.7</td>
<td>2.42</td>
<td>74.3/119</td>
<td>110</td>
<td>453</td>
<td>411</td>
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<td>8</td>
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<td>D</td>
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<td>39.1</td>
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<td>452</td>
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<tr>
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<td>C</td>
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<td>291</td>
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<td>0.0001</td>
<td>2.62/303</td>
<td>62.8</td>
<td>1.83</td>
<td>116/14.6</td>
<td>76</td>
<td>450</td>
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<td>M-MBCHA</td>
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<td>5.5/8.1</td>
<td>84</td>
<td>439</td>
<td>366</td>
</tr>
</tbody>
</table>

$^a$ Imidization (cure) processes: T, thermal imidization; C, chemical imidization in homogeneous solutions, and D: imidization by dipping PAA film into Ac$_2$O/pyridine at room temperature for 24 h and successive annealing at 350 °C/1 h in vacuum.

$^b$ CPN-cast PI film formed under a slow drying condition at 30 °C/1 h $>$ 60 °C/10 min + 100 °C/10 min + 150 °C/15 min in air $+$ 300 °C/1 h in vacuum. PAA with $\eta_{inh}$ = 3.75 dl g$^{-1}$ was used for chemical imidization.

$^c$ CPN-cast PI film formed under the slow drying condition. PAA with $\eta_{inh}$ = 9.04 dl g$^{-1}$ was used for chemical imidization.
low degree of in-plane orientation as suggested from their very low birefringence ($\Delta n_{th} < 0.001$). On the other hand, the use of rigid diamines (category II) caused suppressed thermal expansion behavior, e.g., CTE = 30.6 ppm K$^{-1}$ for H'-PMDA/DABA and 39.1 ppm K$^{-1}$ for H'-PMDA/p-PDA. A good correlation is observed in Fig. 11; CTE decreases with increasing $\Delta n_{th}$ for H'-PMDA/aromatic diamine systems. Thus, the distinctly decreased CTE for the H'-PMDA/rigid diamine systems (T) results from an enhanced in-plane chain orientation, which was induced upon thermal imidization [43,44]. Fig. 12 shows the comparisons of CTE between H'-PMDA-based PIs and other isomeric systems (H-PMDA- and H'-PMDA-based PIs). When flexible ether-containing diamines were used, the data points were plotted near the $Y = X$ line or slightly below, thus indicating no prominent effect of H'-PMDA on reducing CTE. The results mean that CTE is governed by not “local” structural rigidity/linearity of the diimide units but “overall” main chain linearity; a positive contribution of H'-PMDA to an increase in the structural rigidity/linearity was almost canceled by incorporating the highly flexible units from the diamines. On the other hand, when H'-PMDA was combined with rigid diamines (typically DABA, #11), the plots obviously deviate downward from the $Y = X$ line, indicating that the H'-PMDA/DABA system shows a much lower CTE than the corresponding isomeric systems. In this case, there exists distinct differences of the overall chain linearity; in contrast to H'-PMDA, the use of H-PMDA and H'-PMDA spoils a great effect of DABA on enhancing the structural rigidity/linearity because of their distorted steric structures. Thus, H'-PMDA is an outstandingly effective monomer for reducing CTE. The magnitude of in-plane chain orientation as an origin of the suppressed thermal expansion behavior is closely related to the PI backbone structures; Fig. 13 depicts schematic illustrations of the extended chain forms for the isomeric PI systems derived from three hydrogenated PMDA isomers and p-PDA as a typical rigid diamine for simplicity. The H'-PMDA-based system possesses a backbone structure with high linearity as depicted in Fig. 13 (b), which arises from the above-mentioned specific steric structure of H'-PMDA [Fig. 4 (c)]. A similar correlation between the low CTE property and the main chain linearity is also observed in the crank-shaft-shaped CBDA-based PI systems depicted in Fig. 13 (d) [23]. On the other hand, the non-planar steric structures of H-PMDA and H'-PMDA are responsible for a significant decrease in the overall PI chain linearity as shown in Fig. 13 (a) and (c), which corresponds to the increased CTE values for their systems. Thus, the overall chain linearity in the extended forms can be a useful indicator for predicting the possibility of low CTE generation. This criterion conforms well to not only the present semi-cycloaliphatic PI systems but also conventional wholly aromatic PLS [43] and poly(ester imide) systems [45].

The high structural rigidity/linearity of the H'-PMDI unit is also supported by a model compound approach; a low molecular weight diimide compound was prepared from H'-PMDA and 4-$n$-octylaniline in a similar manner to a previously reported procedure [22]. This compound exhibited a liquid crystalline morphology in the temperature range of 121.1—128.0 °C in the heating process and 127.7—103.2 °C in the cooling process on POM as shown in Fig. 14, whereas the H'-PMDA-based counterpart did not. Thus, the N,N'-diphenyl-substituted H'-PMDI unit can behave as a mesogenic structure.

For the H'-PMDA-based systems derived from non-fluorinated common diamines, the PI film specimens (T) were essentially insoluble in various solvents [NMP, DMAC, DME, DMSO, m-cresol, CPN, $\gamma$-butyrolactone (GBL), and THF]. Therefore, it was difficult to complete chemical imidization while keeping a homogeneous state. In contrast, the use of CF$_3$-containing diamines (TFODA, HFBAPP, and even rigid TFMB) made it possible, and their PI powder samples (C) were highly soluble in various solvents at room temperature. The properties of the CF$_3$-containing H'-PMDA-based PI films (C) are also summarized in Table 3. A positive effect of the chemical imidization process was observed: the PI films (C) showed lower CTE values by approximately 10 ppm K$^{-1}$ than those of the

---

**Fig. 10.** Comparisons of $T_g$ for thermally imidized PI films from hydrogenated PMDA isomers: (left: black bar) H'-PMDA, (center: red bar) H'-PMDA, and (right: blue bar) H'-PMDI systems. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 11.** Relationship between CTE and $\Delta n_{th}$ for H'-PMDA/aromatic diamine systems: PI films prepared via (●) thermal and (▲) chemical imidization processes.

**Fig. 12.** Comparisons of CTE for thermally imidized PI films from H'-PMDA-based and other isomeric systems: (●) H'-PMDA vs. H'-PMDA and (▲) H'-PMDA vs. H'-PMDA. The dotted line denotes the relation: $Y = X$. 
thermally imidized counterparts for the systems using TFODA and HFBAPP. The decreased CTE for the former results from an increased degree of in-plane chain orientation (Fig. 11) as suggested from the increased $D_{nth}$ values (Table 3).

For the rigid H$_0$-PMDA/p-PDA system which was not compatible to the homogeneous chemical imidization process, we attempted to prepare the PI film by dipping the PAA film formed on a substrate into an Ac$_2$O/pyridine solution, followed by rinsing with water and heat treatment in vacuum. This procedure provided a decreased CTE of 27.4 ppm K$^{-1}$ compared to the thermally imidized counterpart.

3.2.3. Self-chain orientation behavior during solution casing process

The relatively high $D_{nth}$ values for the H$^*$-PMDA-based PI films (C) also mean the presence of a self-orientation phenomenon during the simple solution casting process without structural transformation from PAAcs into PIs [46]. The present results look curious because solution casting of common soluble polymers usually causes no significant in-plane orientation; for example, we observed almost zero $D_{nth}$ and a common level of CTE (65.0 ppm K$^{-1}$) for an NMP-cast PES film. We propose a possible

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**Fig. 13.** Schematic illustrations for simplified extended PI chains: (a) H-PMDA, (b) H$^*$-PMDA, (c) H$^{00}$-PMDA, and (d) CBDA systems. For simplicity, p-phenylene unit is depicted as a typical rigid diamine fragment. The diimide units are represented as edge-view.

**Fig. 14.** POM photograph for H$^*$-PMDA-based model compound at 123.3 °C in the cooling process.
mechanism for the self-orientation behavior in the H'-PMDA-based systems (C); as schematically depicted in Fig. 15 (a), no orientation occurs yet just after the PI solutions were coated onto a substrate. The coating viscosity increases with solvent evaporation and must be abruptly enhanced near the rubbery state at a solid content $C^*$. Above $C^*$, the coating probably begins to undergo shrinkage stress [47]. For the present PI systems, we hypothesize that such shrinkage stress (in other words, apparent stretching effect) may act as a trigger for the “permanent” in-plane chain orientation occurring at the drying temperatures ($T_{dry}$). When the coatings on the substrate were cooled from $T_{dry}$ to room temperature, the thermal stress arising from the film/substrate CTE difference also contributes “temporally” to the total in-plane orientation. However, in our PI film specimens, such contribution from the thermal stress is canceled by removal of the substrate. Besides, it is most likely that there exists a good correlation between the shrinkage stress and the tensile modulus of the PI systems chosen. This corresponds well to our empirical rule that the stiff/linear chain structures, which generally increase the modulus, are indispensable for drastically reducing CTE of the PI films. Therefore, we challenged to further decrease the CTE for the rigid H'-PMDA/TFMB system. The PI molecular weight can be also an important factor for this purpose [48]; as schematically depicted in Fig. 15 (b, left), an increase in the molecular weight ($M_1 > M_2$) raises the coating viscosity, as a result, should contribute to an increase in the shrinkage stress owing to a greater thickness decrement between $C_{PI} = C^*$ and 100 wt%. Flexible PI systems are probably disadvantageous to induce higher shrinkage stress because of their originally lower modulus. Another possible factor is the drying temperature. A slow drying process by elevating $T_{dry}$ little by little and holding at each step for a period, which corresponds to a drying program with a lower temperature ramp, provides a higher coating viscosity (i.e., a higher shrinkage stress) than a rapid drying process as schematically depicted in Fig. 15 (b, right). In addition, an increase in $T_{dry}$ (or increase in the heating rate) may also contribute to orientational relaxation harmful for low CTE generation. Indeed, the combination of a molecular weight increase and very slow drying caused to a further decrease in CTE (to 29.8 ppm K$^{-1}$) for H'-PMDA/TFMB as shown in Table 3. To apply such slow drying process, adequately volatile and less hygroscopic solvents (e.g., CPN) are more desirable than frequently used amide solvents with higher boiling points (e.g., NMP). The H'-PMDA/TFMB powder sample (C) allowed to form a

![Fig. 15.](image)

(a) Schematic illustration for film formation processes via coating/drying of PI solution and (b) influences of PI molecular weight (left, $M_1 > M_2$) and heating rate in the drying processes (right) on the viscosity of the coatings and predicted internal stress at the drying temperatures. $\eta^*$ denotes a viscosity at a rubbery state where the solid content ($C_0$) is represented as $C^*$. 
highly stable CPN solution at room temperature with a high solid content (10 wt%) enough for applying common casting processes.

However, the shrinkage stress effect independently seems to be less active as the driving force for inducing the actual high level of in-plane chain orientation (recall the fact that PES and other flexible PI systems never show prominent in-plane orientation by solution casting in a similar manner). Therefore, an additional factor relating to attractive intermolecular interactions and chain rigidity/linearity should be considered; i.e., the formation of a local ordered structure consisting of highly oriented chains (probably with a very small domain size undetectable by POM) [see Fig. 15(a)]. This idea comes from our previous experience; a partially imidized PAA of s-BPDA/p-PDA (s-BPDA: 3,3′,4,4′-biphenyltetraarboxylic dianhydride) forms a liquid crystal-like ordered structure in NMP, and thermal imidization of the cast PAA film including the ordered structure results in an appreciably lower CTE than that of the counterpart from the ordinary PAA [49]. The fact that liquid crystallinity was observed in the H′-PMDA-based model compound [Fig. 14] suggests that a similar local ordered structure may exist even in the actual H′-PMDA/rigid diamine PI films. Such local ordering should be much more advantageous in rigid/linear PI systems such as H′-PMDA/TFMB than in non-rigid systems. On this assumption, we propose the self-orientation mechanism; each domain can be forcibly aligned along the X–Y direction by a flow field from the apparent stretching effect as schematically depicted in Fig. 15(a).

### 3.2.4. Other properties

The H′-PMDA-based systems provides very clear (non-turbid) PI films (e.g., $T_{\text{opt}} = 88.7\%$ and Haze = 1.7% for the H′-PMDA/4,4′-ODA film imidized at 300 °C/0.5 h in vacuum). The H′-PMDA-based PI films (T) show slightly lower $T_{\text{opt}}$ values than the H′-PMDA-based counterparts [22], however, the formers are essentially colorless as illustrated from a low YI value less than 5 (e.g., 4.3 for H′-PMDA/4,4′-ODA). As listed in Table 3, a positive effect of the film preparation process via homogeneous chemical imidization on the optical transparency was also observed; the H′-PMDA-based PI films (C) tend to show appreciably higher light transmittance than the corresponding PI films (T) as shown particularly in the HFBAPP system. The improved transparency for the PI films (C) may be attributed to an end-capping effect of the unstable terminal amino groups by Ac2O during the chemical imidization process (Fig. 5). In particular, the transparency of the H′-PMDA/TFMB film (C) is so high as illustrated from its optical data ($T_{\text{opt}} = 90.5\%$, YI = 1.8, and Haze = 2.0%) that this system is suitable for some optical applications as proposed later.

The H′-PMDA-based PI films are expected to show low dielectric constants as suggested from the optically estimated ones ($r_{\text{opt}}$) ranging 2.8–2.9 even when common aromatic diamines were used. The incorporation of CF3 groups and complete removal of the aromatic units were both very effective to significantly reduce $r_{\text{opt}}$ (2.59–2.65) in accordance with previous reports [8,50].

Table 3 also summarizes the mechanical properties of the H′-PMDA-based systems. Essentially flexible PI films were formed upon thermal imidization. In particular, the use of BAPP and HFBAPP was very effective to enhance the film toughness as suggested from their very high $\varepsilon_p$ values. Even if the molecular weights were sufficiently high, the combinations of rigid tetracarboxylic dianhydrides and rigid diamines generally lead to brittle PI films owing to insufficient chain entanglement as typically observed in PMDA/p-PDA system ($\varepsilon_p < 3\%$ [51]). Against this general criterion, the H′-PMDA/p-PDA system with a stiff/linear backbone structure exhibited sufficient film flexibility as shown in Table 3. It should be noted that the H′-PMDA/TFMB system with less polarized and bulky CF3 groups displayed a further enhanced $\varepsilon_p$ value (>50%), which is much higher than that of the aromatic counterpart (PMDA/TFMB, $\varepsilon_p < 20\%$ [39]). Thus, the film toughness was prominently improved by exchanging aromatic PMDA for non-aromatic H′-PMDA and exchanging p-PDA for CF3-containing TFMB. The results may reflect an effect of chain slippage in the plastic deformation region during the stretching test, which can be allowed when intermolecular forces were significantly weakened. In contrast to the good film toughness of H′-PMDA/TFMB, the H′-PMDA/TFMB system possessed no film-forming ability because of its insufficient molecular weight from the polymerizability problem, namely, insufficient chain entanglement.

### 3.3. Performance balance and applicability as plastic substrate materials for H′-PMDA-based systems

Fig. 16 shows spider charts for the present target properties, which represent performance balance for the hydrogenated PMDA isomers. The chars for CBDA and aromatic PMDA are also depicted for a comparison. The each property was evaluated with five levels on the basis of criteria listed in Table 4. Two fixed diamines, 4,4′-ODA and TFMB were chosen as a typically flexible and a rigid diamine, respectively. The 4,4′-ODA systems are highly transparent (except the combination with PMDA) but commonly not suitable for low CTE generation owing to the absence of the overall chain linearity. In addition, these are essentially less soluble in common solvents except H′-PMDA/4,4′-ODA. As evaluated from a relatively spread shape of the spider chart for the H′-PMDA/4,4′-ODA system [Fig. 16(c)], H′-PMDA possesses comparatively good performance balance although it is difficult to achieve low CTE. On the other hand, the TFMB systems display quite different performance balance. The combination of CBDA and TFMB is suitable for low CTE generation but not for enhancing the solubility and the film toughness as shown in Fig. 16(h). It should be noted that H′-PMDA/TFMB [Fig. 16(f)] possesses an outstanding performance balance among the TFMB systems, although there is room for further improvement of low CTE property.

Our first attempt for further decreasing the CTE of H′-PMDA/TFMB by copolymerization using DABA was less effective because of a gelation problem at a high DABA content during the chemical imidization process. This motivated us to develop a novel CF3-containing rigid diamine [52]. The combination of this diamine with H′-PMDA led to a solution-processable colorless PI with a further decreased CTE (16 ppm K–1). The results will be reported elsewhere in detail. Thus, the present work revealed how H′-PMDA is a promising tetracarboxylic dianhydride monomer for obtaining novel plastic substrate materials. However, there seems to be a problem in its application as the plastic substrates in liquid crystal displays (LCD) with a backlight transmission mode, that is, relatively high birefringence ($\Delta n_{\text{th}}$). The plastic substrates for LCDs are in general desirable to possess zero $\Delta n_{\text{th}}$ like current inorganic glass substrates because $\Delta n_{\text{th}}$ is responsible for optical retardation ($R_{\text{th}} = \Delta n_{\text{th}} \times d$, where d is film thickness), which may cause a decrease in the image contrast at a high viewing angle. However, as shown in Fig. 11, there seems to be in principle a sort of “trade-off” relationship between low CTE and low $\Delta n_{\text{th}}$, suggesting great difficulty of obtaining ideal plastic substrate materials for LCDs. Instead, the present H′-PMDA-based low-CTE colorless PI systems can be applied as the substrates for bottom-emission-type flexible organic emitting diode (OLED) displays without the optical retardation problem mentioned above and/or electronic paper displays with an external light reflection mode.

### 3.4. Potential application as optical compensation layer

We investigated the potentiality of H′-PMDA/TFMB as a novel coating-type optical compensation film material (negative-C plate,
\( n_x > n_y > n_z \), i.e., \( \Delta n_{th} > 0 \) with low wavelength dependence of \( R_{th} \) for vertical alignment-mode LCDs. In this case, higher \( \Delta n_{th} \) is preferable because thinner compensation films can be used to obtain an aimed \( R_{th} \) value. Another merit is that the H'-PMDA/TFMB layer can be directly formed on a triacetylcellulose (TAC) film as a standard protective layer for iodine-doped poly(vinyl alcohol) polarizers from a CPN solution of this PI without corrosion of TAC. In this case, thermal deformation of TAC can be also avoided by simply drying at lower temperatures than \(-150\) °C without subsequent thermal imidization process at elevated temperatures (>250 °C). The wavelength dependence of \( \Delta n_{th} \) (or \( R_{th} \)) is usually a normal dispersion type, that is, \( \Delta n_{th} \) decreases with increasing wavelength (\( \lambda \)) as expressed by an asymptotic empirical equation: 
\[
\Delta n_{th} = A + B/\lambda^2 - C \]
where \( A, B, \) and \( C \) are constants depending on the materials \[53\]. The birefringence ratio at \( \lambda = 450 \) and 550 nm, i.e., \( \Delta n_{450}/\Delta n_{550} \) (\( = R_{450}/R_{550} \)) can be a good indicator for representing a slope in the \( \Delta n_{th} - \lambda \) curves. Our goal is to achieve an ultimately low wavelength dispersion property with \( \Delta n_{450}/\Delta n_{550} \) values close to 1.00. However, this subject is not easy because \( \Delta n_{450}/\Delta n_{550} \) ranges \( 1.07 - 1.16 \) for most of colorless PI systems (e.g., 1.11 -1.12 for 6FDA/TFMB). This parameter is sensitive to not only the PI chemical structure but also the drying temperature program, solvent, and PI molecular weight. We observed that the parameter \( \Delta n_{450}/\Delta n_{550} \) tends to reduce with decreasing \( \lambda_{cut} \) which is probably closely related to the extents of electronic conjugation through the main chains. In this context, the H'-PMDA/TFMB system with a low \( \lambda_{cut} \) may be suitable for achieving a low wavelength dispersion property. For the present purpose, H'-PMDA/TFMB was modified with a minor content of a non-conjugated cycloaliphatic diamine, isophoronediamine (IPDA). Fig. 17 shows a \( \Delta n_{th} - \lambda \) curve for a CPN-cast H'-PMDA/TFMB(80):IPDA(20) copolyimide film. Indeed, this system exhibited a low wavelength dispersion property \( \Delta n_{450}/\Delta n_{550} \).
\( \Delta n_{550} = 1.03 \). The partial incorporation of 1,3-dimethyl-substituted CBDA (DM-CBDA) as a comonomer into \( H^-\text{PMDA/TFMB} \) desirably enhanced \( \Delta n_{550} \), while maintaining a low wavelength dispersion property, excellent transparency \( (T_{200} = 89.2\%) \), a relatively low CTE \( (30.3 \text{ ppm K}^{-1}) \), and a very high \( T_g \) \( (335 \text{ °C}) \). The results give us an idea: although high \( \Delta n_{550} \) is generally an undesirable property for the plastic substrates in LCDs as mentioned above, we propose that \( H^-\text{PMDA/TFMB} \) and the modified systems with the relatively high \( \Delta n_{550} \) values can be applied to a new type of LCD substrates possessing both of good dimensional stability based on their low CTE property and the optical compensation functionality.

4. Conclusion

This work proposed a cycloaliphatic tetracarboxylic dihydride monomer, \( H^-\text{PMDA} \), useful for obtaining novel optoelectronic materials. \( H^-\text{PMDA} \) showed much higher polymerizability with various diamines than conventional \( H^-\text{PMDA} \) and led to PAAs with high molecular weights. Consequently, even the combination with TFMB including electron-withdrawing \( CF_3 \) groups provided a highly flexible PI film in contrast to the absence of film-forming ability for \( H^-\text{PMDA/TFMB} \). The enhanced polymerizability of \( H^-\text{PMDA} \) is attributed to its unique steric structure. Exceptionally, the polyaddition with t-CHDA did not proceed by insoluble salt formation, which is probably related to the structural rigidity of the oligomers formed. The thermally imidized \( H^-\text{PMDA-based PI films} \) were essentially colorless regardless of diamines owing to inhibited CT interactions. The PIs also possessed relatively high \( T_g \)'s \( (e.g., 294 \text{ °C for } H^-\text{PMDA/(4,4')-ODA}) \). The use of some flexible diamines \( (e.g., \text{BAPP}) \) was effective to drastically enhance the film toughness. The combinations of \( H^-\text{PMDA} \) and rigid diamines \( (\text{typically, } \text{DABA}) \) caused a prominent decrease in CTE owing to an activated imidization-induced in-plane chain orientation phenomenon, whereas the counterparts from \( H^-\text{PMDA} \) and \( H^-\text{PMDA} \) did not. The results suggest how the \( H^-\text{PMDA-based diimide moiety behaves as a rigid/linear structural unit as supported by the fact that the } H^-\text{PMDA-based model compound showed liquid crystallinity. Some of the } H^-\text{PMDA-based PI films} \) were also prepared via the chemical imidization process in a homogeneous state. For example, the PI powder sample for \( H^-\text{PMDA/TFMB} \) was highly soluble in common solvents \( (even \ in \ some \ hygroscopic \ solvents \ such \ as \ CPN) \). This procedure was more advantageous for increasing transparency and decreasing CTE of the PI films than the conventional thermal imidization process. The CTE for \( H^-\text{PMDA/TFMB} \) further decreased \( (to 29.8 \text{ ppm K}^{-1}) \) by increasing the molecular weight and drying the coatings more slowly. The results suggest the presence of a self-orientation phenomenon during solution casting. The mechanism was discussed in this work. A potential application was also proposed as novel coating-type optical compensation film materials with low wavelength dispersion of \( R_{th} \) for vertical alignment-mode LCDs. The CPN-cast \( H^-\text{PMDA/TFMB/80} \) \( ; \text{IPDA/20} \) copolyimide film achieved a low wavelength dispersion property \( (\Delta n_{550}/\Delta n_{550} = 1.03) \) in addition to non-coloration and a high \( \Delta n_{th} \) value exceeding 0.03. Thus, the \( H^-\text{PMDA-based PI systems} \) can be useful materials for high-temperature transparent plastic substrates with high dimensional stability and/or novel coating-type optical compensation films.

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References

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