Solution-Processable Colorless Polyimides Derived from Hydrogenated Pyromellitic Dianhydride with Controlled Steric Structure

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ABSTRACT: This work presents novel colorless polyimides (PIs) derived from 1R,2S,4S,5R-cyclohexanetetracarboxylic dianhydride (H"-PMDA). Isomer effects were also discussed by comparing with PI systems derived from conventional hydrogenated pyromellitic dianhydride, that is, 1S,2R,4S,5Rcyclohexanetetracarboxylic dianhydride (H-PMDA). H"-PMDA was much more reactive with various diamines than H-PMDA, and the former led to PI precursors with much higher molecular weights. The results can be explained from the quite different steric structures of these isomers. The thermally imidized H"-PMDA-based films were colorless regardless of diamines because of inhibited charge-transfer interaction. In particular, the H"-PMDA/4,4'-oxydianiline system simultaneously achieved a very high T_g exceeding 300 °C, high toughness (elongation at break > 70%), and good solution processability. In contrast, the H-PMDA-based counterparts were essentially insoluble. The outstanding solubility of the former probably results from

INTRODUCTION Recently, colorless high-temperature polymeric materials are greatly required as various optical component materials, for example, plastic substrates in various display devices, liquid crystal alignment layers, color filters, optical compensation films, antireflection films, core/clad materials in light waveguides, and optical lenses. If current fragile inorganic glass substrates were replaced by plastic substrates, flat panel displays can be lightened. However, it is not easy to develop practically useful plastic substrates simultaneously possessing excellent optical transparency (noncoloration) and sufficiently high heat resistance ($T_{\rm g}$ > 250 °C, more desirably > 300 °C) overcoming some thermal processes such as thin-film transistor formation; even poly (ether sulfone) (PES), which possesses the highest heat resistance among current colorless engineering plastics $(T_{\rm g} = 225$ °C), is not applicable for this purpose. Polymeric materials with very high T_g exceeding 300 °C are practically limited to polyimides (PI) and polybenzazoles [polybenzoxazoles (PBO), polybenzimidazoles, and polybenzthiazoles]. PIs

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Materials

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disturbed chain stacking by its nonplanar steric structure. An advantage of chemical imidization process is also proposed. In some cases, a copolymerization approach with an aromatic tetracarboxylic dianhydride was effective to improve the thermal expansion property. The results suggest that the H"-PMDAbased PI systems can be promising candidates for novel hightemperature plastic substrate materials in electronic paper displays. A potential application as optical compensation film materials in liquid crystal displays (LCD) is also proposed in this work. © 2012 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 575–592

KEYWORDS: coefficient of thermal expansion (CTE); cycloaliphatic tetracarboxylic dianhydride; optical compensation films; plastic substrates; polyimides; solution processability; toughness; transparency

are widely used in electric and microelectronic devices for their simple two-step manufacturing processes, excellent electric insulation ability, an extremely high purity (the absence of volatile organic compounds and metallic/ionic contaminations), nonflammability, thermo-oxidative stability (long-term heat resistance), and considerably high T_g 's overcoming the reflow soldering processes (short-term heat resistance).^{1–12} However, intensive coloration intrinsic to conventional aromatic PI films often disturbs their optical applications.

No attention has been paid to the development of colorless polybenzazole films in industrial standpoints, probably owing to their complicated manufacturing processes, poor processability, and limited commercial sources of the monomers. We have previously reported that novel PBO systems polycondensed in hot polyphosphoric acid from aromatic bis(*o*-aminophenol)s and cycloaliphatic (alicyclic) dicarboxylic acids are highly soluble in various common organic solvents (solution processable) and provides colorless cast films with good toughness.¹³ However, the results also revealed that most of commercially available aliphatic dicarboxylic acids show no sufficient polymerizability with bis(*o*-aminophenol)s except for 1,4- or 1,3-cyclohexanedicarboxylic acids. This means a narrow width of structural modification in colorless PBO systems.

On the other hand, much effort has been devoted to erase PI film coloration from academic and industrial interests. The most effective strategy is to use nonaromatic (cycloaliphatic) monomers either in diamines or tetracarboxylic dianhydrides or both,¹⁴⁻¹⁷ thereby charge-transfer (CT) interactions are inhibited.¹⁸ However, a serious problem occurs when aliphatic diamines were used, that is, the formation of insoluble salt at the initial stage in the polymerization process of PI precursors [poly(amic acid)s (PAAs)].^{14,15} In particular, trans-1,4-cyclohexanediamine (t-CHDA) tends to form the "tightest" salt, for example, the polyaddition with pyromellitic dianhydride (PMDA) is completely inhibited,^{19,20} although even reaction systems using other flexible cycloaliphatic diamines need very long reaction times until the salt is completely dissolved. This situation causes poor productivity/reproducibility for the PAA polymerization process, which must be a great obstacle for commercialization of colorless PI systems using aliphatic diamines. In contrast, the combinations of cycloaliphatic tetracarboxylic dianhydrides and aromatic diamines can provide colorless PIs without the salt formation in the PAA polymerization processes. However, cycloaliphatic tetracarboxylic dianhydrides [e.g., commercially available bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BTA)] are often not highly reactive with aromatic diamines,^{21,22} as a result, tend to give PAAs with lower molecular weights, which reduce chain entanglement closely related to film flexibility (formability). Exceptionally, 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA)²³ shows very high polymerizability with diamines like common aromatic tetracarboxylic dianhydrides,^{19,20,24} probably owing to a strain in the acid anhydride ring of CBDA. Therefore, it leads to colorless PIs with very high molecular weights.^{14,19,20,23} However, CBDA-based PIs essentially possess no solution processability.¹⁴

To solve such crucial problems in acquiring useful colorless PI materials, we have previously developed cycloaliphatic tetracarboxylic dianhydrides derived from hydrogenated trimellitic anhydride (HTA) and various diols.²² The HTA-derived tetracarboxylic dianhydrides showed high polymerizability with diamines and led to colorless poly(ester imide)s (PEsIs), which also possess outstanding solution processability, relatively high T_{g} , and good toughness. The incorporation of rigid biphenyl units into the colorless PEsI main chains was capable of enhancing the T_g up to 295 °C.²² However, it was difficult to obtain T_g 's exceeding 300 °C as far as the HTA-derived tetracarboxylic dianhydrides were used.

In the present article, we proposes novel colorless PI materials derived from a cycloaliphatic tetracarboxylic dianhydride with a controlled steric structure, that is, 1R,2S,4S,5R-cyclohexanetetracarboxylic dianhydride (H"-PMDA),^{25–27} which show excellent combined properties compatible to plastic

substrate materials. Steric structure effects on the polymerizability with diamines and the PI film properties are also discussed by comparing with isomeric systems using conventional hydrogenated PMDA, that is, 1S,2R,4S,5Rcyclohexanetetracarboxylic dianhydride (H-PMDA).²⁸ A potential application for the H"-PMDA-based PIs is also proposed in this work.

EXPERIMENTAL

Materials

Monomers, Polyaddition, Imidization, and Film Preparation

The abbreviations, sources, purification methods, and melting points of the monomers used in this work are shown in Table 1 and Figure 1. H"-PMDA and H-PMDA were supplied by Iwatani Industrial Gases and New Japan Chemical, respectively. The oak ridge thermal ellipsoid plot program (ORTEP) diagrams obtained by the single-crystal X-ray diffraction measurements for H"-PMDA²⁵ and H-PMDA²⁸ are also depicted in Figure 1. The central cyclohexane unit of H"-PMDA in crystal takes an intermediate conformation between a boat and a twist-boat form. H"-PMDA was synthesized as previously described;²⁵ PMDA was hydrolyzed with an NaOH aqueous solution. The pyromellitic acid tetrasodium salt formed was hydrogenated in a high-pressure hydrogen atmosphere at 160 °C in the presence of a ruthenium/carbon catalyst. The reaction mixture was heated at a precisely controlled temperature and neutralized with conc. HCl. The precipitated tetracarboxylic acid was collected by filtration and washed with toluene. The white precipitate was dissolved in acetic anhydride (Ac₂0) and refluxed at an established temperature, then recrystallized by cooling to room temperature.

PAAs were prepared by equimolar polyaddition of tetracarboxylic dianhydrides and diamines as shown in Figure 2. A typical procedure is as follows: tetracarboxylic dianhydride powder (10 mmol) was added in a dry *N*,*N*-dimethylacetamide (DMAc) solution of diamine (10 mmol) at an initial total solid content of 30 wt % with continuous stirring. The reaction mixture was stirred with a magnetic spinner at room temperature 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 stirring. The polymerization conditions and the results are listed in Table 2. The PAA solutions were stored in a sealed bottle at -20 °C without dilution to avoid a gradual molecular weight decrease.

PI films were prepared upon different methods (thermal and chemical imidization). The reaction schemes are shown in Figure 2. PI films were prepared by the conventional two-step process; PAA solution was bar-coated on a glass substrate and dried at 60 °C/2 h for DMAc solutions or 80 °C/2 h for *N*-methyl-2-pyrrolidone (NMP) solutions in an air-convection oven. We first attempted thermal imidization under a relatively mild condition with a maximum temperature of 250 °C from the viewpoints of the film transparency.

TABLE 1 The Conditions of Pretreatment and Purification for Monomers

| Monomers | Source | Solvent for Recrystallization | Vacuum-Drying Condition | Melting Point (°C) |
|---|----------------------------------|---|----------------------------|-------------------------|
| 1R,2S,4S,5R-Cyclohexanetetracarboxylic dianhydride (H"-PMDA) | lwatani Industrial Gases | - | 150 °C/24 h | 267 (273 ^a) |
| 1S,2R,4S,5R-Cyclohexanetetracarboxylic dianhydride (H-PMDA) | New Japan Chemical | - | 150 °C/24 h | 303 |
| Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BTA) | Tokyo Chemical Industry (TCI) | Ac ₂ O/DMF (3/1, v/v) | 150 °C/24 h | - |
| 1,2,3,4-Cyclobutanetetracarboxylic dianhydride (CBDA) | Nissan Chemical Industries | - | 150 °C/12 h | 241 |
| p-Phenylenediamine (p-PDA) | TCI | Ethyl acetate ^b | 30 °C/24 h | 142 |
| 4,4'-Oxydianiline (4,4'-ODA) | Wako Chemical | Toluene/DMF (10/1, v/v) ^b | 50 °C/24 h | 191 |
| 3,4'-Oxydianiline (3,4'-ODA) | JFE Chemical | - | 50 °C/24 h | 74 |
| Bis(4-amino-2-trifluoromethylphenyl) ether (TFODA) | Ihara Chemical | EtOH/H ₂ O (11/5, v/v) | 145 °C/12 h | 129 |
| <i>m</i> -Tolidine (<i>m</i> -TOL) | Wakayama Seika | Toluene/CHX (7/3, v/v) | 70 °C/24 h | 86 |
| <i>o</i> -Tolidine (<i>o</i> -TOL) | Wakayama Seika | Toluene | 80 °C/24 h | 129 |
| 2,2'-Bis(trifluoromethyl)benzidine (TFMB) | Wakayama Seika | - | 50 °C/24 h | 184 |
| 2,2-Bis(4-aminophenyl)hexafluoropropane (BA6F) | ТСІ | - | 50 °C/24 h | 198 |
| 1,4-Bis(4-aminophenoxy)benzene (TPEQ) | Wakayama Seika | Toluene/DMF (15/1, v/v) | 100 °C/24 h | 172 |
| 1,3-Bis(4-aminophenoxy)benzene (TPER) | Wakayama Seika | Ethanol/H ₂ O (11/9, v/v) | 50 °C/24 h | 115 |
| 4-Aminophenyl-4'-aminobenzoate (APAB) | Wakayama Seika | - | 50 °C/24 h | 185 |
| 4,4'-Diaminobenzanilide (DABA) | TCI | - c | 50 °C/24 h | 205 |
| 4,4'-Bis(4-aminophenoxy)biphenyl (BAPB) | Wakayama Seika | Toluene/DMF (15/1, v/v) | 50 °C/24 h | 197 |
| Bis[4-(4-aminophenoxy)phenyl] sulfone (BAPS) | Wakayama Seika | Toluene | 50 °C/24 h | 194 |
| 2,2-Bis[4-(4-aminophenoxy)phenyl] propane (BAPP) | Wakayama Seika | - | 50 °C/24 h | 129 |
| 2,2-Bis[4-(4-aminophenoxy)phenyl] hexafluoropropane (HFBAPP) | Wakayama Seika | - | 50 °C/24 h | 159 |
| trans-1,4-Cyclohexanediamine (t-CHDA) | lwatani Industrial Gases | - | 30 °C/24 h | 70 |
| 4,4'-Methylenebis(cyclohexylamine) (MBCHA) (mixture of isomers) | New Japan Chemical | - | - | none |
| 4,4'-Methylenebis(2-methylcyclohexylamine) (M-MBCHA) (mixture of isomers) | Aldrich | - | - | - |

^a Repeatedly recrystallized from acetic anhydride (Ac₂O).

^b Vacuum sublimated for complete decoloration after recrystallization.

^c It contains a colored contamination which is difficult to remove even

by recrystallization in the presence of activated carbon. DMF, *N*,*N*-dime-thylformamide; CHX, cyclohexane.

However, the PI films obtained were often somewhat brittle. This is probably due to partial retro-polyaddition although the generated terminal functional groups can recombine by additional heating at higher temperatures.²⁹ Then, to obtain flexible PI films while avoiding film coloration, thermal imidization was carried out typically at 200 °C/0.5 h + 320 °C/1

h in vacuum as adhered on the substrate, and successively annealed in vacuum at 10–20 °C lower temperatures than the T_{g} '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 form better quality of PI films. The



Tetracarboxylic dianhydrides



FIGURE 1 Molecular structures of monomers and ORTEP diagrams of H"-PMDA and H-PMDA.

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 Ac_2O/pyr -idine (7/3, v/v) to adequately diluted PAA solutions at a feed molar ratio of $[Ac_2O]/[COOH]_{PAA} = 5$ with continuous vigorous stirring at room temperature. The reaction mixture was additionally stirred at room temperature for 12 h in a sealed flask while monitoring the solution homogeneity. This

procedure is effective to suppress an undesirable significant $\eta_{\rm inh}$ decrease, for example, $\eta_{\rm inh} = 1.25$ dL g⁻¹ (PAA) and $\eta_{\rm inh} = 1.32$ dL g⁻¹ (PI) for H"-PMDA/2,2'-bis(trifluoromethyl)-benzidine (TFMB) system in contrast to simple thermal imidization in solution. In some systems using aromatic diamines with rigid structures, chemical imidization was not applicable because of inhomogenization such as gelation due to insufficient solubility of the imidized forms, by which



FIGURE 2 Reaction schemes of polyaddition and imidization of PAAs.

imidization is not completed. 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 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 added should be eliminated to avoid undesirable film coloration as observed in some cases. The dried precipitate was redissolved in pure DMAc at a solid content of 10–15 wt %. The homogeneous solution formed was coated on a glass substrate and dried at 60 °C/2 h + 250 °C/1 h in vac-

uum. After peeling them off from the substrate, the PI films (typically 20 μ m thick) were additionally annealed in a similar manner. The samples prepared via chemical imidization (powder or film) are denoted as "(C)".

In this work, the chemical compositions of PAA and PI systems are represented with the abbreviations of the monomer components used [tetracarboxylic dianhydrides (X) and diamines (Y)] as X/Y for homopolymers and $X_1;X_2/Y_1$ for copolymers.

Model Compounds

A model compound was prepared as follows; aniline (22 mmol) was dissolved in dry DMAc in a three-necked flask

| Category of Diamine | Diamine | Solid Content (wt %) | Solvent | Reaction Time (h) | η _{inh} (PAA) (dL g ⁻¹) |
|-------------------------------|---------------|-------------------------|---------|----------------------|---|
| Aromatic-flexible (I) | 4,4'-ODA | 30→17 | DMAc | 72 | 2.47 |
| | 3,4'-ODA | 30→21 | DMAc | 72 | 2.44 |
| | TPEQ | 30→11 | DMAc | 72 | 3.76 |
| | TPER | 30→11 | DMAc | 72 | 2.21 |
| | BAPP | 30→12 | DMAc | 72 | 3.63 |
| | BAPB | 30→12 | DMAc | 72 | 3.89 |
| | BAPS | 30 | DMAc | 72 | 0.60 |
| | TFODA | 30→22 | DMAc | 72 | 1.21 |
| | BA6F | 30→25 | DMAc | 72 | 1.22 |
| | HFBAPP | 30→17 | DMAc | 72 | 4.02 |
| Aromatic-rigid (II) | <i>p</i> -PDA | 30→8 | DMAc | 72 | _a |
| | <i>p</i> -PDA | 10→8 | NMP | 120 | 1.21 |
| | o-TOL | 30→15 | DMAc | 72 | 1.62 |
| | <i>m</i> -TOL | 30→12 | DMAc | 72 | 3.01 |
| | APAB | 30→17 | DMAc | 72 | 1.55 |
| | DABA | 30→14 | DMAc | 72 | 1.35 |
| | TFMB | 30→15 | DMAc | 72 | 1.25 |
| Cycloaliphatic-flexible (III) | MBCHA | 20→16 | DMAc | 96 | 1.25 |
| | M-MBCHA | 20→18 | DMAc | 96 | 1.83 |
| Cycloaliphatic-rigid (IV) | t-CHDA | 20→15 | DMAc | 96 | 0.61 |

TABLE 2 Results of polyaddition of H"-PMDA with various diamines

^a Gelation.



with a nitrogen inlet and a condenser. H"-PMDA powder (10 mmol) was added in the solution and stirred at room temperature for 24 h, then refluxed in an oil bath regulated at 190 °C for 3 h while keeping nitrogen bubbling. The reaction mixture was cooled to room temperature and slowly poured into a large amount of water. The white precipitate obtained was repeatedly washed with fresh water, collected by filtration, and dried at 100 °C in vacuum for 12 h. The product purified by recrystallization from toluene provided white plate crystal with a very sharp endothermic peak (m.p. 266.6 °C) by differential scanning calorimetry (DSC, Bruker-AXS, DSC3100) at a heating rate of 5 K min⁻¹.

IR (Jasco FTIR 5300, KBr): 3065 cm⁻¹ (C_{arom}—H stretching), 2936 cm⁻¹ (C_{aliph}—H), 1779/1709 cm⁻¹ (imide C=O), 1497 cm⁻¹ (phenyl group). ¹H NMR [JEOL, JNM-ECP400, 400 MHz, dimethyl sulfoxide (DMSO)- d_6 , δ , ppm]: 7.5–7.2 (10H, *N*-phenyl group, relative integrated intensity: 10.00), 3.2–2.3 (m, 8H, central cyclohexane unit, relative integrated intensity: 8.00). Anal. Calcd (%) for C₂₂H₁₈N₂O₄ (374.40): C, 70.58; H, 4.85; N, 7.48. Found: C, 70.86; H, 4.90; N, 7.29.

The H-PMDA-derived model compound was also synthesized in a similar manner. Recrystallization from ethanol led to a white needle crystal with a very sharp endothermic peak at m.p. 240.3 $^{\circ}$ C by DSC.

IR (KBr): 3065 cm⁻¹ (C_{arom} —H), 2984/2915 cm⁻¹ (C_{aliph} —H), 1769/1709 cm⁻¹ (imide C=O), 1497 cm⁻¹ (phenyl). ¹H NMR (400 MHz, DMSO- d_6 , δ , ppm): 7.5–7.25 (10H, *N*-phenyl group, relative integrated intensity: 10.00), 3.2–2.0 (m, 8H, central cyclohexane unit, relative integrated intensity: 7.87). Anal. Calcd (%) for C₂₂H₁₈N₂O₄ (374.40): C, 70.58; H, 4.85; N, 7.48. Found: C, 70.24; H, 4.86; N, 7.40. The chemical imidization method led to essentially the same product as that obtained by thermal imidization.

Measurements

Inherent Viscosities and Gel Permeation Chromatography

The reduced viscosities (η_{red}) of PAAs were measured at a solid content of 0.5 wt % at 30 °C on an Ostwald viscometer. The measurements were conducted as prompt as possible to avoid the depolymerization of PAAs, which immediately proceeds by dilution. An extrapolation to zero concentration for determination of the inherent viscosities (η_{inh}) is difficult due to an abnormal increase in the η_{red} values in the lower concentration range, which arises from a polyelectrolyte effect of PAAs. Instead, the η_{red} values measured at 0.5 wt % can be practically regarded as η_{inh} as often similarly dealt with in the literature.

The molecular weights for some soluble PIs were determined by gel permeation chromatography (GPC) using tetrahydrofuran (THF) as an eluent at room temperature on a Jasco, LC-2000 Plus HPLC system with a GPC column (Shodex, KF-806L) and an UV detector (Jasco, UV-2075) at a flow rate of 1 mL min⁻¹. The calibration was carried out with standard polystyrenes (Shodex, SM-105).

Monitoring of Imidization

Full imidization for the chemically imidized samples was confirmed from complete disappearance of the proton sig-



FIGURE 3 FTIR spectrum of thin PI film for H"-PMDA/BAPP.

nals for the NHCO ($\delta = 10.0$ ppm) and the COOH groups (12.3 ppm) in the ¹H NMR spectra. Imidization was also monitored using separately prepared thin films (4–5 μ m thick) to avoid spectral over-saturation by the transmissionmode IR spectroscopy (Jasco FTIR 5300 infrared spectrometer). In this case, it is preferable to use thin film samples with nonuniform thickness to erase significant interference fringes, which deform the IR spectra. A typical FTIR spectrum of a thin PI film is shown in Figure 3. The spectrum indicate that imidization was completed on the basis of the perfect disappearance of the $1660/1540 \text{ cm}^{-1}$ bands (amide C=0 stretching) and the $\sim 2600/\sim 1700$ cm⁻¹ broad bands (hydrogen-bonding carboxylic acid, O-H/C=0) inherent to PAAs, in addition to the appearance of some specific bands originating from the imide ring formation at 1779 cm^{-1} (C=0, imide-I) and 1715 cm⁻¹ (C=0, imide-II), and 1387 cm⁻¹ (N-C_{arom}, imide-III). Other IR bands are also observed at 3054 cm⁻¹ (C_{arom}—H), 2969 cm⁻¹ (C_{aliph}—H), 1503 cm⁻¹ (1,4-phenylene group), and 1242 cm⁻¹ (C_{arom}-0-C_{arom}).

Thermomechanical Analysis

The linear coefficients of thermal expansion (CTE) along the film plane direction for PI specimens (15 mm long, 5 mm wide, and typically 20 μ m thick) in the glassy region were measured 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, thermomechanical analysis (TMA) 4000] with a fixed load (0.5 g per a unit film thickness in μ m, typically, 10 g load for 20 μ 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 elimination of adsorbed water.

Dynamic Mechanical Analysis

The storage modulus (E') and the loss energy (E'') of PI films were measured 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 (ΔL) of the specimens exceeded 3000 μ m by softening above the T_g 's.

Mechanical Properties

Tensile modulus (*E*), tensile strength (σ_b), and elongation at break (ε_b) of PI specimens (film dimension: 30 mm long, 3 mm wide, typically 20 μ m thick, specimen numbers > 15) 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. In this case, the specimens were taken from high-quality large film samples (10 × 10 cm²) without any defects such as fine bubbles. For some systems, it was difficult to carry out the mechanical stretching test owing to considerable film brittleness or the difficulty of high-quality large film preparation.

Extent of Water Absorption

The water absorption % (W_A) of PI films was determined from the relation:

$$W_A = [(W - W_0)/W_0] \times 100$$

where W_0 is the weight of film samples just after vacuum drying at 50 °C for 24 h, *W* denotes the weight of the films that were immersed in water at 23 °C for 24 h and carefully blotted dry with a tissue paper. In this case, large film specimens (> 0.1 g) were used to minimize the experimental errors.

Refractive Indices, Birefringence, and Optically Estimated Dielectric Constants

The in-plane $(n_{\rm in} \text{ or } n_x = n_y)$ and the out-of-plane $(n_{\rm out} \text{ or } n_z)$ refractive indices of PI films were measured with a Na lamp at 589.3 nm on an Abbe refractometer (Atago, 4T, $n_{\rm D}$ range: 1.47–1.87) equipped with a polarizer by using a contact liquid (sulfur-saturated methylene iodide $n_{\rm D} = 1.78$ –1.80) and a test piece $(n_{\rm D} = 1.92)$. The birefringence of PI films, which represents a relative extent of in-plane chain orientation (chain alignment parallel to the film plane), was calculated from the relation:

$$\Delta n_{\rm th} = n_{\rm in} - n_{\rm out}$$

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

$$\varepsilon_{\rm opt} = 1.1 n_{\rm av}^2$$

where $n_{\rm av}$ represents the average refractive indices expressed as

$$n_{\rm av} = (2n_{\rm in} + n_{\rm out})/3$$

The $\varepsilon_{\rm opt}$ values are known to be approximate to the dielectric constants determined with a precision LCR meter at a frequency of 1 or 10 MHz for PI systems.^{20,30}

 $\Delta n_{\rm th}$ was also measured at some wavelengths in the visible range on an Abbe refractometer (Atago, 1T, $n_{\rm D}$ range: 1.30–1.70); monochromatic light was introduced from a Xe lamp in a fluorescence spectrometer (Hitachi, F-2000) with a



10 nm bandpass of a monochromator through an optical fiber cable.

Thermogravimetric Analysis

Thermal stability of PI films was evaluated from the 5% weight loss temperatures (T_d^5) on a thermo-balance (Bruker-AXS, TG-DTA2000). Thermogravimetric analysis (TGA) was performed at a heating rate of 10 K min⁻¹ in nitrogen or air atmosphere. For the measurements in N₂, 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 N₂ flow. After the data resetting to 0% weight loss, TGA data were collected from the second heating run.

Solubility

The solubility of chemically imidized powder samples or thermally imidized film samples was examined by immersing these samples (20 mg) in various solvents (1 mL) in a test tube at room temperature. When the samples were insoluble at room temperature, they were heated at 60 °C for THF or at 100 °C for other solvents.

Film Transparency

The optical transparency of PI films (20 μ m thick) was evaluated from the light transmittance (%) at a wavelength (λ) of 400 nm (T_{400}) and the cutoff wavelength (λ_{cut} , λ at $T \sim$ 0%) on a Jasco V-530 UV/vis spectrophotometer. The total light transmittance (T_{total} , JIS K 7361-1) and the diffuse transmittance (T_{diff} , JIS K 7136) of PI films were measured on a double-beam haze meter with an integrating sphere (Nippon Denshoku Industries, NDH 4000). The haze (turbidity) of PI films was calculated from the relation:

Haze =
$$(T_{\rm diff}/T_{\rm total}) \times 100$$

RESULTS AND DISCUSSION

Polymerizability of H"-PMDA with Diamines and Effect of Steric Structure

The reactivity of tetracarboxylic dianhydrides with diamines can be represented strictly by the second-order rate constants. However, in actual PAA polymerization processes, it is difficult to determine the rate constants since the reaction mixtures are inhomogeneous in the initial stage; the amic acid formation proceeds with gradual dissolution of tetracarboxylic dianhydride powder fed into diamine solutions. Therefore, in the present work, the polymerizability was discussed on the basis of the $\eta_{\rm inh}$ values of the finally obtained polymers. This parameter (η_{inh} -based polymerizability) is more important in the practical viewpoints because the η_{inh} of PAAs is closely related to the PI film flexibility as represented by $\varepsilon_{\rm b}$;³¹ empirically speaking, PI films usually become very brittle in systems with very low η_{inh} values (<0.3 dL g^{-1}) owing to poor chain entanglement. Insufficient polymerizability, which increases unreacted functional groups at the chain ends, may also cause another negative result, that is, undesirable film coloration arising from partial decomposition of the terminal amino groups as mentioned later.



FIGURE 4 Comparisons of polymerization reactivity for H"-PMDA systems with other systems: (\bullet) H-PMDA, (\times) BTA, and (\blacktriangle) CBDA systems. The dotted line denotes the relation: Y = X.

Table 2 shows the results of polyaddition of H"-PMDA and various diamines. When aromatic diamines were used, the polyaddition smoothly proceeded and led to homogeneous/ viscous PAA solutions with high η_{inh} values (1.2–4.0 dL g⁻¹) except for the systems using 1,4-phenylenediamine (p-PDA, in DMAc) and bis[4-(4-aminophenoxy)phenyl] sulfone (BAPS) with an electron-withdrawing sulfone group. The reaction with TFMB also proceeded without the polymerizability problems predicted from the presence of the electronwithdrawing CF3 substituents and led to a sufficiently high $\eta_{\rm inh}$ value of 1.25 dL g $^{-1}$ ($M_{\rm w}=$ 1.8 imes 10 5 , $M_{\rm n}=$ 6.3 imes 10 4 for the chemically imidized powder sample). On the other hand, the use of cycloaliphatic diamines caused salt formation in the initial stage. However, the salt formed in the H"-PMDA systems was not so tight; the salt started to dissolve after several hours, consequently, the reaction mixtures were almost homogenized by stirring at room temperature for 12-24 h. In contrast, the conventional hydrogenated PMDA, that is, H-PMDA shows much lower polymerizability; for example, $\eta_{inh}=$ 0.57 dL g^{-1} even when highly reactive 4,4'-ODA was selected as a diamine. In particular, the systems using less reactive or rigid diamines give rise to a crucial problem, that is, poor film-formability, corresponding to very low η_{inh} values (e.g., 0.1–0.3 dL g^{-1} for the H-PMDA/TFMB system). The significant difference of the polymerizability between H"-PMDA and H-PMDA is observed independent of the categories of the diamines used (aromatic/cycloaliphatic and flexible/rigid) as illustrated in Figure 4. One also notices that BTA is less reactive than H-PMDA. In contrast, CBDA shows comparable or higher polymerizability than H"-PMDA.

Thus, we observed a prominent steric structure effect on the PAA polymerizability between H"-PMDA and H-PMDA. However, there are no clear descriptions on this effect for other cycloaliphatic dianhydride systems in the literature. For example, Matsumoto et al.³² reported that the polyaddition of bicyclo[2.2.2]octane-2-*endo*,3-*endo*,5-*exo*,6-*exo*-tetracarbox-

1,3-bis(4-aminophenoxy)benzene dianhydride and vlic (TPER) led to a PAA with $\eta_{\rm inh} = 0.18$ dL g⁻¹, on the other hand, that with $\eta_{inh} = 0.20 \text{ dL g}^{-1}$ when the all-exo isomer was used. The prominent isomer effect observed in the present work can be explained on the basis of the significantly different steric structures as schematically depicted in Figure 5; in the H-PMDA system with the all-exo configuration, after one functional group reacted, the another surviving functional group may be partially "covered/shielded" by the adjacent growing chain, thereby the approaching/attack of other reactants to the surviving functional group is prevented. In contrast, such steric hindrance is probably less effective in the H"-PMDA system since the functional groups orient almost opposite directions each other. An alternative possible interpretation for the present isomer effect is based on the difference of cyclic oligomer formability. A previous article reported that the cyclic oligomers can be formed in the reaction of mellophanic dianhydride (MLPDA) and nonsubstituted flexible diamines with a symmetric structure (e.g., 4,4'methylenedianiline and 4,4'-ODA),³³ although the reactions using asymmetric or rigid diamines at considerably high monomer concentrations most likely lead preferably to the corresponding linear polymers.³⁴ In this context, one may imagine that the chain structure of H-PMDA/4,4'-ODA (η_{inh} $= 0.57 \text{ dL g}^{-1}$) may be more suitable for the cyclic oligomer formation than the asymmetric H"-PMDA counterpart ($\eta_{inh} =$ 2.47 dL g⁻¹). However, as far as H-PMDA was used, no drastic η_{inh} enhancement was observed even under an established reaction condition unfavorable for the cyclic oligomer formation; for example, the η_{inh} remained rather low (0.22) dL g^{-1}) even in the reaction of H-PMDA and rigid/highly reactive 4,4'-diaminobenzanilide (DABA) at a high solid content. This result suggests that the cyclic oligomer formation is probably not the primary reason why H-PMDA possesses much lower polymerizability than H"-PMDA.

Properties of H"-PMDA-based PI films Prepared on Thermal Imidization

Optical Properties

As shown in Table 3, H"-PMDA was very effective to completely erase PI film coloration for all systems examined as suggested from very high light transmittance ($T_{400} > 80\%$), unlike that the degree of PI film coloration usually strongly depends on the diamines when common aromatic tetracarboxylic dianhydrides were used. The H"-PMDA-based PI films (T) tend to be somewhat superior in the film transparency to the H-PMDA-based counterparts, for example, $T_{400} =$ 83.4% (H"-PMDA/TPEQ) versus 79.4% (H-PMDA/TPEQ), and 83.9% (H"-PMDA/BAPP) versus 74.7% (H-PMDA/BAPP). The slightly decreased transparency of the H-PMDA-based systems may be due to partial deterioration of a trace amount of the terminal amino groups, which probably becomes practically negligible when the molecular weights are considerably high as in the H"-PMDA-based systems.

The cutoff wavelength (λ_{cut}) is an index representing the transparency in the ultraviolet range. The λ_{cut} values (244–319 nm) for the H"-PMDA/aromatic diamine systems (T) were much lower (i.e., higher uv transmittance) than those



FIGURE 5 Predicted steric hindrance for polyaddition reaction by the growing chains adjacent to the functional groups for H"-PMDA and H-PMDA systems. A model reaction with aniline is depicted here for simplicity.

of another type of semiaromatic PI systems derived from aromatic tetracarboxylic dianhydrides and cycloaliphatic diamines (e.g., $\lambda_{cut} = 330$ nm for PMDA/4,4'-methylenebis(cyclohexylamine) (MBCHA) system and 366 nm for 3,3',4,4'biphenyltetracarboxylic dianhydride (s-BPDA)/MBCHA system, where there exists electronic conjugation between the imide C=O groups and the adjacent aromatic ring. The present results originate from a combined effect of an overall decrease in the π electrons and the nonextended conjugation in the H"-PMDA-based diimide unit.



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TABLE 3 Film Properties of H"-PMDA-Based Homo-Pls

| No. | Diamine | Cure ^a | T ₄₀₀ (%) | λ _{cut} (nm) | $\Delta n_{\rm th}$ | ε _{opt} | <i>T</i> g (°C) | CTE (ppm K ⁻¹) | W _A (%) | <i>E</i> (GPa) | ^ε ь (%) | σ _b (MPa) | 7 ⁵ d (N₂) (°C) | 7 ⁵ (air) (°C) |
|-----|---------------|-------------------|-------------------------|--------------------------|---------------------|------------------|--------------------|-------------------------------|-----------------------|-------------------|-----------------------|-------------------------|-------------------------------|------------------------------|
| 1 | 4,4'-ODA | Т | 86.0 | 292 | 0.0012 | 2.89 | 328 | 54.9 | 2.32 | 2.87 | 73 | 114 | 484 | 455 |
| | | С | 92.9 | 306 | 0.0099 | 2.82 | 302 | 57.1 | 2.91 | 2.31 | 65 | 145 | - | - |
| 2 | 3,4'-ODA | Т | 86.0 | 288 | 0.0007 | 2.88 | 277 | 54.5 | 2.83 | 2.10 | 74 | 86 | 449 | 451 |
| | | С | 87.8 | 306 | 0.0090 | 2.86 | 253 | 52.1 | 2.86 | 1.69 | 53 | 86 | - | - |
| 3 | TPEQ | Т | 83.4 | 305 | 0.0018 | 2.92 | 285 | 60.8 | 1.89 | 2.04 | 31 | 105 | 480 | 470 |
| 4 | TPER | Т | 81.9 | 290 | 0.0008 | 2.82 | 239 | 61.9 | 1.37 | 1.54 | 29 | 64 | - | - |
| 5 | BAPP | Т | 83.9 | 294 | 0.0007 | 2.89 | 256 | 63.1 | 1.43 | 1.68 | 70 | 80 | 477 | 457 |
| 6 | BAPB | Т | 84.5 | 315 | 0.0000 | 2.99 | 289 | 58.9 | 1.62 | 2.11 | 51 | 116 | 469 | 420 |
| 7 | BAPS | Т | 81.0 | 301 | 0.0002 | 2.93 | 283 | 56.2 | - | 2.03 | 9 | 85 | 467 | 447 |
| | | С | 83.2 | 315 | 0.0050 | 2.87 | 283 | 54.0 | - | 1.73 | 6 | 50 | - | - |
| 8 | TFODA | Т | 83.3 | 296 | 0.0010 | 2.65 | 292 | 54.8 | 1.12 | 2.43 | 56 | 122 | 463 | 421 |
| | | С | 83.8 | 297 | 0.0204 | 2.64 | 290 | 38.8 | - | 1.93 | 59 | 85 | 476 | 409 |
| 9 | BA6F | Т | 88.5 | 277 | 0.0004 | 2.66 | 327 | 56.1 | 1.75 | 2.39 | 8 | 81 | 463 | 443 |
| | | С | 88.6 | 277 | 0.0135 | 2.64 | 319 | 55.7 | - | 1.95 | 9 | 95 | 464 | 414 |
| 10 | HFBAPP | Т | 82.5 | 290 | 0.0005 | 2.73 | 264 | 63.8 | 1.41 | 2.07 | 61 | 115 | 451 | 412 |
| | | С | 87.0 | 296 | 0.0202 | 2.75 | 277 | 59.4 | - | 1.59 | 58 | 42 | 475 | 402 |
| 11 | <i>p</i> -PDA | Т | 80.5 | 278 | 0.0020 | 2.82 | 407 | 42.7 | 3.02 | 2.53 | 20 | 92 | 460 | 424 |
| 12 | <i>o</i> -TOL | Т | 83.8 | 319 | 0.0257 | 2.92 | 360 | 46.1 | 2.69 | 3.14 | 9 | 173 | 486 | 421 |
| | | С | 87.6 | 322 | 0.0306 | 2.80 | 330 | 45.6 | 2.92 | 2.95 | 6 | 116 | 486 | 404 |
| 13 | <i>m</i> -TOL | Т | 86.4 | 294 | 0.0096 | 2.87 | 369 | 47.5 | 3.31 | 3.17 | 11 | 119 | 462 | 427 |
| | | С | 86.6 | 307 | 0.0149 | 2.83 | 368 | 46.8 | 3.42 | 3.03 | 7 | 106 | 453 | 420 |
| 14 | APAB | Т | 83.5 | 313 | 0.0293 | 2.91 | 290 | 46.1 | - | 3.22 | 7 | 97 | 431 | 428 |
| 15 | DABA | Т | 78.6 | 339 | 0.0277 | 2.97 | 381 | 40.5 | 5.74 | 2.61 | 27 | 133 | 462 | 441 |
| 16 | TFMB | Т | 83.5 | 295 | 0.0016 | 2.68 | 330 | 47.2 | 1.55 | 2.22 | 18 | 108 | 463 | 422 |
| | | С | 89.5 | 291 | 0.0253 | 2.65 | 339 | 43.5 | - | 2.23 | 28 | 117 | 477 | 422 |
| 17 | MBCHA | Т | 86.6 | 244 | 0.0002 | 2.62 | 285 | 65.8 | 1.52 | 1.88 | 14 | 109 | 443 | 373 |
| 18 | M-MBCHA | Т | 84.7 | 248 | 0.0005 | 2.58 | 270 | 62.8 | 2.72 | 2.16 | 8 | 112 | 430 | 360 |
| 19 | t-CHDA | Т | 81.4 | 258 | 0.0005 | 2.66 | 346 | 56.6 | - | 2.78 | 10 | 132 | 445 | 394 |

^a Imidization (cure) processes; C, chemical imidization; T, thermal imidization.

The H"-PMDA-based PI films (T) also essentially showed very low birefringence ($\Delta n_{\rm th} < 0.002$) except for some rigid diamine systems, reflecting to the three-dimensionally random chain orientation. Lower $\Delta n_{\rm th}$ values correspond to lower optical retardation ($R_{\rm th} = \Delta n_{\rm th} d$, where d = film thickness), which is a desirable property as plastic substrates in LCDs. On the other hand, the systems using rigid diamines (*o*- and *m*-tolidine, APAB, and DABA) showed one-order higher $\Delta n_{\rm th}$ values (~0.01–0.03), although they are still in a low level. This is probably due to a certain degree of inplane chain orientation behavior, which occurs upon the thermal imidization process with a close relation to the backbone stiffness/linearity.^{35,36}

The H"-PMDA-based PI systems (T) also display relatively low ε_{opt} values ranging 2.82–2.99 even when nonfluorinated common aromatic diamines were used. The incorporation of less polar CF₃ group gave rise to a significant decrease in ε_{opt} for example, 2.65 for the H"-PMDA/TFODA system. Complete removal of π electrons was also effective for further reducing $\varepsilon_{opt'}$ for example, 2.58 for H"-PMDA/M-MBCHA. Thus, the results are attributed to the same reason as that for reducing λ_{cut} as mentioned above.

Thermal Properties

The H"-PMDA-based PIs derived from ether-containing diamines were essentially thermoplastic as suggested from an abrupt E' decrease above the T_g in the dynamic mechanical analysis (DMA) curves. When 4,4'-ODA was used as a typical flexible diamine, the PI film (T) exhibited a very high T_g of 328 °C as listed in Table 3, although the T_g inevitably decreased by incorporation of meta-linkages (3,4'-ODA) and bulky substituents (TFODA) and an increase in flexible ether linkages (TPEQ, TPER, BAPP, etc.). On the other hand, the use of rigid diamines (typically, *p*-PDA, *o*-TOL, *m*-TOL, and DABA) drastically enhanced the T_g (>360 °C). The T_g 's of H"-PMDAbased systems were compared with those of the corresponding H-PMDA-based counterparts as shown in Figure 6; the



FIGURE 6 Comparison of T_g of thermally imidized PI films for H"-PMDA-based and H-PMDA-based systems (see Table 3 for the sample numbers inserted). The dotted line denotes the relation: Y = X.

former always shows somewhat (7–24 $^{\circ}$ C) lower $T_{\rm g}$'s than the latter. The results can be explained in terms of the difference of the degree of the dipole-dipole intermolecular interaction between the imide C=0 groups, which is believed to be an origin of strong intermolecular forces acting as physical crosslinks in aromatic PIs;^{37,38} assuming the presence of a similar intermolecular interaction in the present systems, the asymmetric nonplanar steric structure of the H"-PMDA-diimide moiety is probably disadvantageous for denser chain stacking. However, it should be noted that the present trend, that is, $T_{\rm g}$ (H"-PMDA system) $< T_g$ (H-PMDA system) is limited to the cases using flexible diamines; the combinations of H-PMDA and rigid diamines (e.g., p-PDA, o- and m-TOL) caused a crucial problem, that is, poor film formability. In this viewpoint, H"-PMDA is much superior to H-PMDA in aiming at a higher level of heat resistance by using such rigid diamines. The T_{g} influencing overall structural rigidity for the H"-PMDA-based systems can be relatively speculated from the order of the $T_{\rm g}$ in analogous systems using a fixed diamine, 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP): $T_g = 287$ °C (PMDA/ BAPP) > 280 °C (MLPDA/BAPP)³⁴ > 265 °C (H-PMDA/BAPP) $> 256 \ ^{\circ}C \ (H''-PMDA/BAPP).$

As shown in Table 3, the H"-PMDA-based PIs derived from aromatic diamines also possess relatively good thermal stability (chemical heat resistance) as suggested from the T_d^5 is values (in N₂) exceeding 450 °C, although a decrease in T_d^5 is inevitable when cycloaliphatic diamines were used. The H"-PMDA-based PIs still maintain high T_d^5 values even in a thermo-oxidative atmosphere (in air), for example, 455 °C for H"-PMDA/4,4'-ODA.

The H"-PMDA-based PI systems (T) derived from flexible diamines (category I and III) provided CTE values ranging 54–66 ppm K^{-1} (Table 3), which are a common level to flexible polymer systems. The present CTE values were also comparable to those for the H-PMDA-based systems. On the other hand, the combinations of H"-PMDA and rigid diamines (category II) brought about an appreciable decrease in CTE;

for example, 40.5 ppm K⁻¹ for H"-PMDA/DABA, which is somewhat lower than for the isomeric H-PMDA/DABA system (46.7 ppm K⁻¹). However, the CTE level of the former is still far from a criterion for so-called "low-CTE systems" (< ~20 ppm K⁻¹) in contrast to a very low CTE (0.2 ppm K⁻¹) of the aromatic counterpart, that is, PMDA/DABA.³⁹ It is generally accepted that there is a good correlation between CTE and the degree of in-plane chain orientation in a fixed system.^{35,36} Therefore, the common level of the CTE values for the H"-PMDA-based systems reflect that the imidization-induced in-plane orientation phenomenon became ineffective by their highly bent/nonplanar chain structure.

Water Absorption Behavior

The H"-PMDA/4,4'-ODA film (T) showed a W_A value of 2.32% (Table 3), which is a common level to conventional PI systems. In the systems using nonfluorinated flexible diamines, W_A tends to decrease as the diamine molecular weight is increased: 2.32% (4,4'-ODA) > 1.89% (TPEQ) > 1.62% (BAPB) > 1.43% (BAPP). This trend is probably related to a decrease in the content of highly polarizing imide groups. As expected, the incorporation of CF₃ group with the lowest polarizability per a unit volume led to a further decrease in W_A (1.12% for the TFODA system). A secondary factor influencing W_A is the degree of chain packing,²² as illustrated from a higher W_A (1.55%) for a highly bent/nonplanar structure of H"-PMDA/TFMB than that for the aromatic counterpart, a rod-like structure of PMDA/TFMB ($W_A = 0.47\%^{40}$).

Mechanical Properties

The H"-PMDA-based PI films (T) provide common tensile modulus (*E*) ranging 1.54–3.22 GPa without significant difference with those of the H-PMDA-based counterparts. On the other hand, a prominent isomer effect was observed in the comparison of film toughness as shown in Figure 7; the use of ether-containing diamines led to highly tough films, for example, $\varepsilon_{\rm b} = 73\%$ for H"-PMDA/4,4'-ODA and 70% for H"-PMDA/BAPP, which are comparable to $\varepsilon_{\rm b}$ of a typical tough PI film ($\varepsilon_{\rm b} = 85\%$ for PMDA/4,4'-ODA).⁴⁰ On the one hand, the corresponding H-PMDA systems displayed further enhanced $\varepsilon_{\rm b}$ values in spite of their lower $\eta_{\rm inh}$ as shown in



FIGURE 7 Comparison of ε_b of thermally imidized films for H"-PMDA-based (blue/left bar) and H-PMDA-based PIs (red/right bar). The systems without red/right bars practically represent $\varepsilon_b = 0\%$ or difficulty of mechanical stretching test for the absence of film-forming ability.

| | | | | | Sol | vent | | | |
|---------------|--------------------|----------|----------|----------|----------|------------------|----------|----------|-----|
| Diamine | Sample Form (Cure) | NMP | DMAc | DMF | DMSO | <i>m</i> -Cresol | CPN | GBL | THF |
| 4,4'-ODA | Film (T) | + | + | <u>±</u> | ± | + | _ | ± | _ |
| | Powder (C) | ++ | ++ | ++ | ++ | + | _ | ++ | _ |
| 3,4'-ODA | Film (T) | + | ++ | ++ | + | + | + | + | _ |
| | Powder (C) | ++ | ++ | ++ | ++ | + | + | ++ | _ |
| TPEQ | Film (T) | <u>+</u> | <u>+</u> | <u>+</u> | <u>+</u> | <u>+</u> | _ | ± | _ |
| TPER | Film (T) | - | - | _ | - | _ | _ | _ | _ |
| BAPP | Film (T) | ± | ± | <u>+</u> | <u>+</u> | + | <u>+</u> | <u>+</u> | _ |
| BAPB | Film (T) | ± | ± | <u>+</u> | ± | <u>+</u> | \pm | \pm | - |
| BAPS | Film (T) | + | + | + | + | + | _ | _ | _ |
| | Powder (C) | ++ | ++ | ++ | ++ | + | ++ | ++ | + |
| TFODA | Film (T) | + | + | ++ | + | + | + | + | _ |
| | Powder (C) | ++ | ++ | ++ | ++ | + | ++ | ++ | _ |
| BA6F | Film (T) | + | ++ | ++ | + | + | + | + | + |
| | Powder (C) | ++ | ++ | ++ | ++ | + | + | ++ | ++ |
| HFBAPP | Film (T) | ++ | ++ | ++ | ++ | + | + | + | + |
| | Powder (C) | ++ | ++ | ++ | ++ | + | ++ | ++ | ++ |
| <i>p</i> -PDA | Film (T) | _ | _ | _ | - | _ | _ | - | _ |
| o-TOL | Film (T) | + | + | + | + | + | - | + | - |
| | Powder (C) | ++ | ++ | ++ | ++ | + | + | + | _ |
| <i>m</i> -TOL | Film (T) | + | + | + | + | + | \pm | - | - |
| | Powder (C) | + | + | + | + | + | + | + | _ |
| APAB | Film (T) | <u>+</u> | <u>+</u> | <u>+</u> | \pm | <u>+</u> | \pm | - | _ |
| DABA | Film (T) | + | + | + | + | _ | _ | + | — |
| TFMB | Film (T) | + | + | + | + | + | + | + | - |
| | Powder (C) | ++ | ++ | ++ | ++ | + | ++ | ++ | ++ |
| MBCHA | Film (T) | - | - | _ | - | _ | - | _ | _ |
| M-MBCHA | Film (T) | _ | _ | _ | _ | _ | _ | _ | _ |
| t-CHDA | Film (T) | _ | _ | _ | _ | - | _ | _ | _ |

TABLE 4 Solubility of H"-PMDA-Based Homo-PIs

(++) Soluble at room temperature, (+) soluble upon heating, (±) deformed or swelled, and (–) insoluble. CPN, cyclopentanone; GBL, γ -butyrolactone.

Figure 7. It is also obvious how the toughening effect generated by the combination of H-PMDA and flexible diamines is prominent from a comparison: $\varepsilon_b = 236\%$ for H-PMDA/ BAPP ($\eta_{\rm inh}=$ 0.73 dL g⁻¹) versus $\varepsilon_{\rm b}=$ 169% for PMDA/ BAPP ($\eta_{inh} = 2.30 \text{ dL g}^{-1}$). Thus, H-PMDA monomer is undoubtedly effective for film toughening. This may stand for the importance of its molecular shape (see Fig. 1) which contributes to chain entanglement just like ether linkages, although the detailed mechanism is not clear. However, it should be noted that the present situation, that is, ε_b (H"-PMDA systems) $\ll~\epsilon_{\rm b}$ (H-PMDA systems) is limited to the systems using flexible diamines; when rigid diamines were used, the H-PMDA systems completely lost film-forming ability probably owing to their too low molecular weights (e.g., $\eta_{\rm inh} = 0.10 \, \, {\rm dL g^{-1}}$ for H-PMDA/TFMB). Thus, the excellent film-forming ability irrespective of diamines is a prominent feature of H"-PMDA.

Solution Processability

It is empirically known that thermally imidized film samples tend to decrease solubility compared to the corresponding chemically imidized powder samples as discussed later. Nonetheless, the H"-PMDA/4,4'-ODA system (T) possesses good solubility in hot NMP while keeping homogeneity even after cooling to room temperature. The H"-PMDA/3,4'-ODA system (T) displayed further improved solubility as shown in Table 4. Even the rigid diamine systems (DABA, o-, and m-TOL) display good solubility in hot amide solvents. In general, highly organo-soluble PIs include some solubility-promoting groups (e.g., CF₃, -SO₂-, and bulky side groups) and significantly distorted units in the structures.41-43 It should be noted that the H"-PMDA-based systems (T) show good solubility even without any solubility-promoting groups. The introduction of such solubility-promoting groups caused further solubility improvement by a combined effect. However,

| | | | | | Sol | vent | | | |
|----------|--------------------|----------|----------|----------|----------|------------------|----------|-------|-----|
| Diamine | Sample Form (Cure) | NMP | DMAc | DMF | DMSO | <i>m</i> -Cresol | CPN | GBL | THF |
| 4,4'-ODA | Film (T) | \pm | ± | \pm | <u>+</u> | + | - | - | _ |
| 3,4′-ODA | Film (T) | <u>+</u> | <u>+</u> | <u>+</u> | <u>+</u> | ± | <u>+</u> | \pm | - |
| TPEQ | Film (T) | <u>+</u> | <u>+</u> | ± | <u>+</u> | + | - | - | _ |
| TPER | Film (T) | <u>+</u> | <u>+</u> | <u>+</u> | ± | ± | - | - | - |
| BAPP | Film (T) | <u>+</u> | <u>+</u> | ± | <u>+</u> | + | - | - | _ |
| BAPS | Film (T) | ++ | ++ | + | + | + | - | - | - |
| HFBAPP | Powder (C) | ++ | ++ | ++ | ++ | ++ | ++ | ++ | ++ |
| MBCHA | Film (T) | - | - | - | - | - | - | - | - |
| M-MBCHA | Film (T) | _ | _ | - | - | - | - | _ | _ |

TABLE 5 Solubility of H-PMDA-Based Pls

(++) Soluble at room temperature, (+) soluble upon heating, (\pm) deformed or swelled, and (–) insoluble.

 $H^{\prime\prime}\text{-}\mathsf{PMDA}$ was less effective for the nonaromatic systems derived from cycloaliphatic diamines.

Comparing with the solubility of the H-PMDA-based counterparts (Table 5), a prominent isomer effect is obvious; the H-PMDA-based samples (T) are essentially insoluble. The significant difference of the solubility between these isomeric systems originates from the quite different steric structures of H"-PMDA and H-PMDA, although no distinct isomer effect on the solubility was recognized in other analogous PI systems derived from bicyclo[2.2.2]octane-2-endo,3-endo,5exo,6-exo-tetracarboxylic dianhydride and the all-exo isomer.³² The order of the solubility for the H"- and H-PMDAbased model compounds also corresponds to the present results. The much better solubility for the H"-PMDA/aromatic diamine systems than for the H-PMDA-based counterparts can be also explained by reduced intermolecular dipole-dipole interaction based on the highly bent/nonplanar steric structure at the H"-PMDA-based diimide unit. Comparing with analogous systems that we have so far investigated, the dependence of the relative solubility on the tetracarboxylic dianhydrides used can be represented by the following order: H"-PMDA \geq MLPDA³⁴ > H-PMDA \gg PMDA, reflecting their structural planarity/linearity at the diimide fragments rather than their aromaticity. We have previously investigated the property difference between MLPDA- and PMDA-based PI systems and found that the former possesses always slightly lower T_{g} 's than the latter, but the solubility difference between them was remarkable.³⁴ One notices that a very similar isomer effect are also observed between H"-PMDA and H-PMDA systems (small $T_{\rm g}$ difference but large solubility difference).

Figure 8 shows a $T_{\rm g}$ -transparency–solubility diagram. Many of conventional engineering plastics are originally colorless, however, their $T_{\rm g}$'s do not exceed 230 °C. PIs tend to lose the film transparency and the solubility as soon as $T_{\rm g}$ exceeds 300 °C in the *X*-axis, suggesting how it is difficult to achieve our target properties ($T_{400} > 80\%$, $T_{\rm g} > 300$ °C, good solution processability, and high toughness). Some semicycloaliphatic PIs (PMDA/MBCHA, H-PMDA/4,4'-ODA,

and CBDA/TFMB) are surely categorical in colorless high- T_g systems as plotted in the target area in this figure. However, in fact, these are beyond the present candidates because of their poor solution processability. The TA-BPFL/t-CHDA system (see the bottom of Figure 8 for its monomer structure) shows a high $T_{\rm g}$ exceeding 300 $\,^\circ\text{C}$, good transparency, and NMP-solubility in contrast to the fact that the t-CHDA-based PIs are usually quite insoluble. However, this PI film is somewhat brittle,30 which may be a negative feature of fluorenecontaining cardo-type PIs. On the other hand, 6FDA/TFMB system, which contains solubility-promoting CF₃ groups with a high content, is an only limited case possessing the present target properties. It should be noted that some of the present H"-PMDA-based PI systems achieved the target properties without any solubility-promoting substituents. As an representative example, the data for the H"-PMDA/4,4'-ODA system (\bigcirc) , which is also highly tough and solution processable, is plotted within the target area in Figure 8.

Effects of Chemical Imidization

If the selected PIs were originally soluble, chemical imidization process (Fig. 2) can be applied since imidization is completed without gelation/precipitation. A great merit of this process in a practical viewpoint is that PI films can be formed by simple casting (coating and drying) of homogeneous PI solutions without subsequent thermal imidization. Another advantage is that a significant molecular weight decrease is suppressed, in contrast to thermal imidization in solution. The H"-PMDA-based systems were essentially compatible to the chemical imidization process. On the other hand, this process was often not applicable to the H-PMDAbased systems owing to a trend of inhomogenization except for H-PMDA/HFBAPP and H-PMDA/BAPS. When cycloaliphatic diamines were used, a curious phenomenon is often observed, that is, chemical imidization is not completed even if the reaction mixtures remained homogeneous. No discussion has been done for the mechanism in the literature. A possible explanation is as follows; the intramolecular nucleophilic attack of the amide group to the adjacent carbonyl





FIGURE 8 T_g -transparency-solubility diagram: (\diamond , \Box , \bigcirc) soluble and (\blacktriangle) insoluble systems, 1: bisphenol A-type polycarbonate, 2: PES, 3: poly(ether imide) (Ultem[®]1000, Saudi Basic Industries), 4: HTA-44BP/o-TOL, 5: 6FDA/TFMB, 6: TA-BPFL/TFMB, 7: TA-BPFL/t-CHDA, 8: ODPA/MBCHA, 9: H-PMDA/BAPP, 10: PMDA/MBCHA, 11: H-PMDA/4,4'-ODA, 12: CBDA/TFMB, 13: s-BPDA/TFMB, 14: HQDEA/o-TOL, 15: s-BPDA/4,4'-ODA, 16: DSDA/4,4'-ODA, 17: TA-HQ/4,4'-ODA, 18: s-BPDA/p-PDA, 19: TA-HQ/m-TOL 20: PMDA/TFMB, 21: H"-PMDA/4,4'-ODA system.

group for cyclodehydration (imidization) is promoted by the electron-withdrawing —OAc group in the expected intermediate as depicted in Figure 2. If the amide groups were partially protonated by free acetic acid as a by-product arising from Ac_2O , its nucleophilic reactivity would be significantly reduced. Recall that, at the stage of aliphatic diamine monomers, they possess much higher basicity than aromatic ones. Therefore, such protonation may occur in case of the aliphatic amide groups if sufficient proton-accepting ability would remain.

Table 3 also lists the properties of the H"-PMDA-based PI films (C). The properties do not essentially depend on the imidization methods. However, one notices that the transparency of the PI films appreciably increased by adopting the

chemical imidization process as illustrated from slightly higher T_{400} values than those of the corresponding thermally imidized films. The results probably originate from an endcapping effect of the thermally less stable terminal amino groups with Ac₂O during chemical imidization as shown in Figure 2. The lower maximum temperature in the film formation process also probably contributes to the increased transparency of the films (C).

Another merit of the chemical imidization process is the drastically improved solution processability as shown in Table 4. This is probably attributed to looser chain packing in the chemically imidized samples. For example, the H"-PMDA/4,4'-ODA sample (C) became soluble in γ -butyrolactone

(GBL) without heating. In addition, H"-PMDA/TFMB (C) is highly soluble at room temperature even in GBL and cyclopentanone (CPN), which behave as poor solvents for many aromatic PI systems. A large number of previous studies on organo-soluble PIs primarily discussed the solubility in polar amide solvents,⁴¹⁻⁴³ however, it seems that no great attention has been paid for the solubility in less hygroscopic solvents such as GBL. These solvents are very useful to avoid serious troubles by moisture absorption in some applications, for example, screen-printing using PI solutions; in this case, the use of amide solvents often gives rise to jamming of screen-printing plates.

One also notices another feature of the H"-PMDA-based films (C); they tend to provide slightly lower CTE than the thermally imidized counterparts, in accordance with higher $\Delta n_{\rm th}$ values as compiled in Table 3. The results indicate that the casting process induced a certain degree of in-plane chain orientation.44 The H"-PMDA/TFODA film (C), as well as H"-PMDA/TFMB (C), displayed the lowest CTE (\sim 40 ppm K⁻¹) as shown in Table 3. However, it may be a lower limit of CTE achievable in the homo PI systems derived from H"-PMDA.

Attempts to Decrease CTE

Recently, plastic substrate materials possessing excellent dimensional stability against thermal cycles in device fabrication processes are required in some cases. Electronic components (e.g., thin-film transistor) formed on the plastic substrates inevitably undergo a positional shift accompanied with reversible expansion/contraction of the substrates in the glassy temperature region ($< T_{\sigma}$) during multiple thermal cycles. However, if such dimensional change was appreciably irreversible or hysterical, it would become a great obstacle for the device fabrication. The direct strategy is to decrease CTE (ultimately, to aim at zero CTE), although it is not easy to realize low CTE characteristics without sacrificing the target properties mentioned above. The conventional copolymerization approach with rigid comonomers for reducing CTE often brings about serious deterioration of film transparency and solution processability. In this work, we used some rigid comonomers to improve the dimensional stability. Table 6 shows the properties of the H"-PMDA/TFMBbased copolymers and the comonomer structures. In spite of a high rigid comonomer content (50 mol %), chemical imidization smoothly proceeded without gelation/precipitation. This is probably due to a still surviving influence of the originally outstanding solubility of the pristine H"-PMDA/TFMB system. The modification with PMDA caused a drastic CTE decrease (26.7 ppm K^{-1}), but accompanied with an undesirable decrease in the film transparency. On the other hand, the use of s-BPDA and TA-HQ as comonomers enabled us to reduce CTE while maintaining high transparency as shown in Table 6. These copolymers (C) retain good solubility in various solvents.

H"-PMDA was also used as a property-modifier at a minor content (30 mol %) to improve the film flexibility of originally colorless and low-CTE PI systems, that is, s-BPDA/t-CHDA (ϵ_{b} = 9%, CTE = 10 ppm K^{-1} $^{19}) and TA-HQ/t-CHDA$ $(\varepsilon_b = 4\%, CTE = 13 \text{ ppm K}^{-1 39})$. The use of H"-PMDA as a comonomer somewhat improved the film toughness (ε_b = 20%) but with an increase in CTE, although the chemical

| TABLE 6 F | -ilm Properties of H"-PMDA-B. | ased Copolyimides | (0) | | | | | | | | | | | |
|-------------|---------------------------------|---|------|-------------------------|--------------------------|--------------------|------------|------------------------|-------------------------------|------------|-----------------------|-------------------------|---|---|
| Diamine | Tetracarboxylic dianhydrides | $\eta_{ m inh}$ (PAA) (dL g ⁻¹) | Cure | T ₄₀₀ (%) | λ _{cut} (nm) | $\Delta n_{ m th}$ | c opt | τ _g (∘C) | CTE (ppm K ⁻¹) | E (GPa) | ^в ь (%) | σ _b (MPa) | <i>T</i> ⁵ _d (N₂) (°C) | T ⁵ _d (air) (°C) |
| TFMB | H"-PMDA(50) TA-HQ(50) | 1.41 | F | 70.4 | 351 | 0.0466 | 2.81 | 250 | 32.3 | 2.52 | 10 | 106 | 454 | 424 |
| | | | ပ | 81.6 | 339 | 0.0744 | 2.86 | 260 | 31.8 | 2.83 | 13 | 123 | 473 | 432 |
| | H"-PMDA(50) s-BPDA(50) | 1.44 | F | 72.6 | 369 | 0.0200 | 2.81 | 303 | 47.8 | I | I | I | 482 | 452 |
| | | | ပ | 82.8 | 357 | 0.0353 | 2.77 | 287 | 33.3 | I | I | I | 490 | 450 |
| | H"-PMDA(50) PMDA(50) | 1.22 | ပ | 52.1 | 350 | 0.0520 | 2.72 | 313 | 26.7 | I | I | I | 470 | 435 |
| t-CHDA | H"-PMDA(30) TA-HQ(70) | 2.24 (NMP) | н | 74.5 | 340 | 0.1028 | 2.98 | DN | 14.2 | I | I | I | 450 | 410 |
| | H"-PMDA(30) s-BPDA(70) | 1.43 | μ | 85.2 | 365 | 0.0450 | 2.96 | 316 | 34.3 | 3.15 | 20 | 173 | 472 | 417 |
| ND, not det | ected by DMA. | | | | | | | | | | | | | |

not detected by DMA



FIGURE 9 Relationship between CTE and Δn_{th} for H"-PMDA - based systems: (**(**) thermally imidized homo PIs, (**(**) chemically imidized homo PIs, (**(**) thermally imidized co-PIs, and (\Diamond) chemically imidized co-PIs.

imidization process remained not applicable. On the one hand, the incorporation of H"-PMDA to TA-HQ/t-CHDA maintained low CTE (14.2 ppm K^{-1}), which results from a high extent of in-plane chain orientation as illustrated from a very high $\Delta n_{\rm th}$ exceeding 0.1. The data of $\Delta n_{\rm th}$ and CTE were plotted for all the H"-PMDA-based systems investigated in this work as shown in Figure 9. The results suggest that the present approach is undoubtedly effective to decrease CTE, however, a significant increase in $\Delta n_{\rm th}$ is inevitable. Even nonaromatic PI systems with a lower polarization anisotropy were difficult to erase $\Delta n_{\rm th}$ while keeping low CTE characteristics, for example, $CTE = 26 \text{ ppm } \text{K}^{-1}$ and $\Delta n_{\text{th}} = 0.02$ for CBDA/t-CHDA PI film.²⁰ In this context, the present materials are not perfect as the plastic substrates for LCDs where backlight passes through the substrates, since the birefringence of the substrates themselves causes optical retardation as an origin of a contrast decrease at higher view angles. Instead, the present materials can be applied as the plastic substrates for electronic paper displays with an external light reflection mode.

Potential Application of H"-PMDA -based PI systems

On the basis of the aforementioned features of the H"-PMDAbased PIs, we also propose a potential application as a novel coating-type optical compensation film material (negative-C plate, $n_x = n_y > n_z$, i.e., $\Delta n_{\rm th} > 0$) with low wavelength dependence of $R_{\rm th}$ for vertical alignment-mode LCDs.⁴⁵ The target materials need to be formed by solution casting on triacetylcellulose (TAC) films as a standard protective film for iodine-doped poly(vinyl alcohol) polarizers. For this purpose, the casting solvents should be sufficiently volatile and noncorrosive to the TAC substrates [typically, CPN (b.p. 131 °C)]. The H"-PMDA/TFMB system (C) has excellent CPN-processability, that is, good solution stability even at high solid contents (≥ 10 wt % in CPN at room temperature). Other desired characteristics are noncoloration, nonturbidity, and a sufficient magnitude of $\Delta n_{\rm th}$ (desirably, > 0.02) which needs to generate by simple coating/drying at temperatures lower than 150 °C to avoid thermal deformation of TAC films. Conventional aromatic polymers other than PIs usually do not generate such high $\Delta n_{\rm th}$ values by simple solution casting as illustrated from the fact a NMP-cast PES film showed a considerably low $\Delta n_{\rm th}$ approximate to zero. Heat resistance of the optical compensation film itself is beyond the present target properties. The higher $\Delta n_{\rm th}$ values mean that even the thinner films can accomplish an aiming $R_{\rm th}$ value on the basis of the relation: $R_{\rm th} = \Delta n_{\rm th} d$. In this work, we also established another target, that is, considerably low wavelength dependence (dispersion) of $R_{\rm th}$. The magnitude of the $R_{\rm th}$ -wavelength dispersion can be simply represented by an optical retardation (birefringence) ratio: $R_{450}/R_{550} = \Delta n_{450}/\Delta n_{550}$ where the subscripts denote wavelength (λ), although actual normal wavelength dispersion curve $(\Delta n_{450}/\Delta n_{550} > 1)$ is asymptotic as represented by an empirical equation: $\Delta n_{\rm th} = a(1 + b/\lambda^2)$ $(+ c/\lambda^4)$ or $\Delta n_{\rm th} = A + B/(\lambda^2 - C^2)^{46}$ where *a*, *b*, *c*, *A*, *B*, and *C* are constants depending on the materials.

We measured the $\Delta n_{450}/\Delta n_{550}$ values for a variety of solution processable colorless PIs because it is expected to provide higher $\Delta n_{\rm th}$ by the casting-induced in-plane orientation behavior. The results revealed that the dispersion parameter distributed within 1.07-1.16 in most cases. In this case, a good correlation was observed; $\Delta n_{450}/\Delta n_{550}$ decreases with decreasing λ_{cut} . This relation is convincing from an asymptotic shape of the $\Delta n_{\rm th} - \lambda$ curves where the slope (in other words, $\Delta n_{450}/\Delta n_{550}$) decreases with increasing λ . A blue-shift of light transmission curves (i.e., a decrease in λ_{cut}) probably causes a blue-shift of the $\Delta n_{\rm th}$ - λ curves, consequently, the slope further reduces in the longer wavelength range. Indeed, a thermally imidized wholly cycloaliphatic PI film showed an ultimately low wavelength dispersion ($\Delta n_{450}/\Delta n_{550} = 1.00$) although it was not compatible to the present film formation process.

In this context, the H"-PMDA-based PI systems are advantageous owing to their low λ_{cut} values (Table 3) based on the less extended electronic conjugation. For the present purpose, the H"-PMDA/TFMB system was chosen. The PI film (12 μ m thick) was prepared by coating/drying a CPN solution (10 wt %) of the chemically imidized sample at 60 °C/1 h + 100 °C/10 min + 150 °C/15 min on a glass substrate in an air-convention oven and additional heat treatment at 150



FIGURE 10 Birefringence (Δn_{th}) as a function of wavelength for H["]-PMDA/TFMB PI film cast from cyclopentanone solution.

°C/30 min in vacuum after peeling the film off from the substrate. The PI film was sufficiently flexible and colorless without appreciable turbidity ($T_{\text{total}} = 91\%$, Haze = 0.36%, $T_{400} = 87.4\%$, $\lambda_{\text{cut}} = 291$ nm). Figure 10 shows $\Delta n_{450}/\Delta n_{550}$ as a function of λ . The H"-PMDA/TFMB film displayed low wavelength dispersion ($\Delta n_{450}/\Delta n_{550} = 1.04$), which slightly fluctuated within 1.04–1.06 depending upon the drying temperature program, the solvent used, and the PI molecular weight. This system also provided a sufficient magnitude of Δn_{th} approximate to 0.03. We also tried to further improve the low wavelength dispersion property by copolymerizing a fluorene-containing monomer while maintaining the desired properties mentioned above. The results will be reported elsewhere.

Recently, the present investigation was extended to another isomer (i.e., H'-PMDA). Studies of the basic properties and some potential applications for the H'-PMDA-based PI systems are in progress.^{26,45}

CONCLUSIONS

H"-PMDA showed much higher polymerizability with various diamines than H-PMDA. The prominent isomer effect can be explained on the basis of these steric structures.

The thermally imidized H"-PMDA-based films were essentially colorless regardless of diamines, owing to inhibited CT interaction. In addition, some of the H"-PMDA-based PI films displayed excellent combined properties, for example, $T_{g} = 328$ °C, $\varepsilon_{\rm b} =$ 73%, and good solution processability for H"-PMDA/4,4'-ODA. On the other hand, the H-PMDA-based counterparts are essentially insoluble in common organic solvents. The outstanding solubility of the former probably results from disturbed chain stacking by a highly bent/nonplanar steric structure at the H"-PMDA-based diimide fragments. Chemical imidization brought about some prominent advantages compared to thermal imidization: improved film transparency, slightly decreased CTE, and drastically enhanced solution processability. In some cases, copolymerization with rigid aromatic tetracarboxylic dianhydrides was effective to reduce CTE while maintaining the original film transparency and solution processability.

The present work also proposed another potential application as novel coating-type optical compensation film materials with low wavelength dispersion of $R_{\rm th}$ for vertical alignment-mode LCDs. The CPN-cast H"-PMDA/TFMB film achieved low wavelength dispersion ($\Delta n_{450}/\Delta n_{550} = 1.04$) in addition to noncoloration and a sufficiently high $\Delta n_{\rm th}$ value approximate to 0.03. The results of this work suggest that the H"-PMDA-based PIs can be promising candidates for novel optical components as high-temperature plastic substrates in electronic paper displays, optical compensation films in LCDs, and others.

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