

RESEARCH ARTICLE

Approaches to improve the film ductility of colorless cycloaliphatic polyimides

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This study described approaches for improving the film ductility of colorless cycloaliphatic polyimides (PIs). An unexpected toughening effect was observed when a PI derived from pyromellitic dianhydride (PMDA) and 4,4'-methylenebis(cyclohexylamine) was modified by copolymerization with a low isophoronediamine (IPDA) content of 5 to 30 mol%, despite there being no film-forming ability in the homo PMDA/IPDA system. For example, at an IPDA content of 20 mol%, the copolymer showed significantly improved film toughness (maximum elongation at break, $\epsilon_{b \text{ max}} = 57\%$), excellent optical transparency (light transmittance at 400 nm, $T_{400} = 83.7\%$), and a high glass transition temperature ($T_g = 317^\circ\text{C}$). This toughening effect can be interpreted on the basis of the concept of chain slippage. In this study, the PIs derived from bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic dianhydride (H-BTA) with various diamines were also systematically investigated to evaluate the potential of H-BTA-derived systems. The combinations of H-BTA with ether-containing diamines led to highly tough PI films ($\epsilon_{b \text{ max}} > 100\%$) with very high T_g s, strongly contrasting with the results of an earlier study. The observed excellent properties are related to the steric structure of H-BTA. Our interest also extended to the solution processability. A copolyimide derived from H-BTA with a sulfone-containing diamine and an ether-containing diamine achieved a very high optical transparency ($T_{400} = 86.8\%$), a very high T_g (313°C), and good ductility ($\epsilon_{b \text{ max}} = 51\%$) while maintaining solution processability. Thus, these approaches enabled us to dramatically improve the ductility of cycloaliphatic PI films that have, to date, been considered brittle.

KEYWORDS

cycloaliphatic (alicyclic) polyimides, film ductility, heat resistance, optical transparency, solution processability

1 | INTRODUCTION

Aromatic polyimides (PIs) have been widely recognized as the most reliable high-temperature polymers. PIs have been applied as electric insulation materials in various electronic fields because of their excellent combined properties (eg, outstanding heat resistance, mechanical properties, and non-flammability).^{1–6} However, the intense coloration of conventional aromatic PI films, which arises from charge-transfer (CT) interactions,⁷ often prevents their applications in various optical and optoelectronic components (eg, plastic substrates in image display devices, liquid crystal alignment layers, color filters, optical compensation films, optical fibers, light-guiding plates, and optical lenses). Therefore, transparent (non colored or less colored and non-hazy) PIs and related high-temperature polymers have been studied in both academia and industry.^{8–23} The most effective approach for the decoloration of PI films is to inhibit the CT interactions by choosing non-aromatic

(aliphatic) monomers, either diamines or tetracarboxylic dianhydrides or both.^{7–18} Many previous studies concerning cycloaliphatic (alicyclic) PIs have focused on their optical transparency and heat resistance (glass transition temperatures [T_g] and thermal decomposition temperatures [T_d]). However, little attention has been given to their mechanical properties (in particular, film toughness [ductility], which is often represented by the elongation at break (ϵ_b) as determined by tensile testing) in the literature, even though it is a crucial factor determining practical use of PI films. This might be due to the fact that cycloaliphatic PIs often yield brittle films, and it is not easy to overcome the embrittlement problem by processing alone. In this study, we propose some approaches for improving the ductility of cycloaliphatic PI films.

In general, the ϵ_b values for linear polymers are influenced by both chemical factors (chain structure and molecular weight) and physical factors (crystallinity and chain orientation).²⁴ In this study, we focused on the chemical factors affecting the film ductility of cycloaliphatic PIs

because the PI systems handled here are basically amorphous and non-oriented except for systems of limited flexibility with very rigid/linear chain structures. However, in our experience, PI film ductility also depends somewhat on other physical factors, ie, the thermal conditions in the imidization process (eg, one-step [rapid] heating or multi-step [slow] heating). For example, for one system, a multi-step process sometimes yields a flexible PI film more easily than a one-step process, while, for another PI system, the opposite is true; thus, there is no theoretical or empirical criterion for judging which heating process (rapid or slow) is more suitable for obtaining flexible PI films. Thus, for PI films, at present, it is very difficult to theoretically correlate the resultant ductility with the preparation methods. Therefore, in this study, we focused on the relationship between the film ductility and the chain structures of cycloaliphatic PI films that were prepared under adjusted thermal conditions.

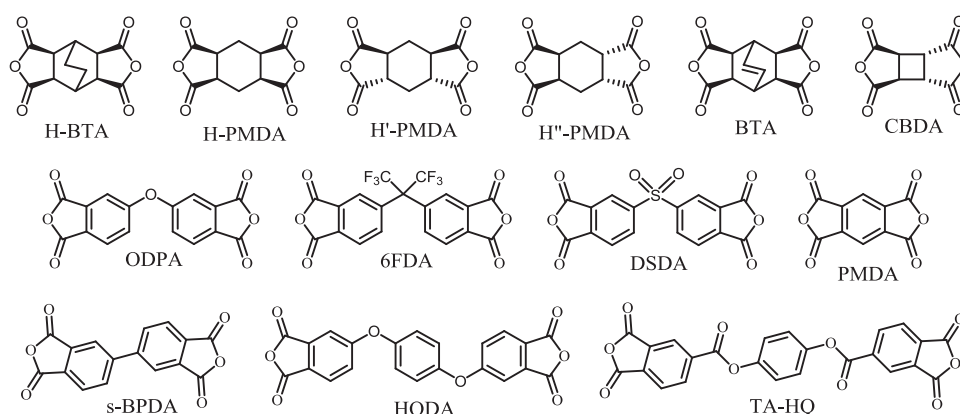
2 | EXPERIMENTAL

2.1 | Materials

The monomers used in this study are shown in Figure 1. Hydroquinone bis(trimellitate anhydride) (TA-HQ) was synthesized and characterized

according to the procedure described in our previous paper.²⁵ The sources, abbreviations, and melting points of the other monomers are summarized in Table 1. PI precursors (poly(amic acid)s) (PAAs) were prepared by equimolar polyaddition of tetracarboxylic dianhydrides and diamines according to the reaction scheme 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 established initial total solid content with continuous stirring at room temperature. The reaction mixture was stirred for 12 to 96 hours with a magnetic stirrer at room temperature in a sealed bottle until it became homogeneous with a maximum solution viscosity. If necessary, the reaction mixture was gradually diluted with a minimal quantity of the same solvent to ensure effective magnetic stirring. The formation of the PAAs was confirmed by transmission-mode FT-IR spectroscopy (Jasco, FT/IR 4100 infrared spectrometer) using separately prepared thin cast films (4–6 μm thick) with non-uniform thicknesses to prevent interference fringes; the FT-IR spectrum (eg, for the H-BTA/1,4-bis(4-aminophenoxy)benzene (1,4,4-APB) system) demonstrates specific bands (cm^{-1}): 3318 (amide N–H), 3046 ($\text{C}_{\text{arom}}\text{--H}$), 2950 ($\text{C}_{\text{aliph}}\text{--H}$), ~ 2600 (broad, hydrogen-bonded carboxylic acid O–H), 1662 (amide C=O), and 1493 (1,4-phenylene), 1211 (C–O–C).

Tetracarboxylic dianhydrides



Diamines

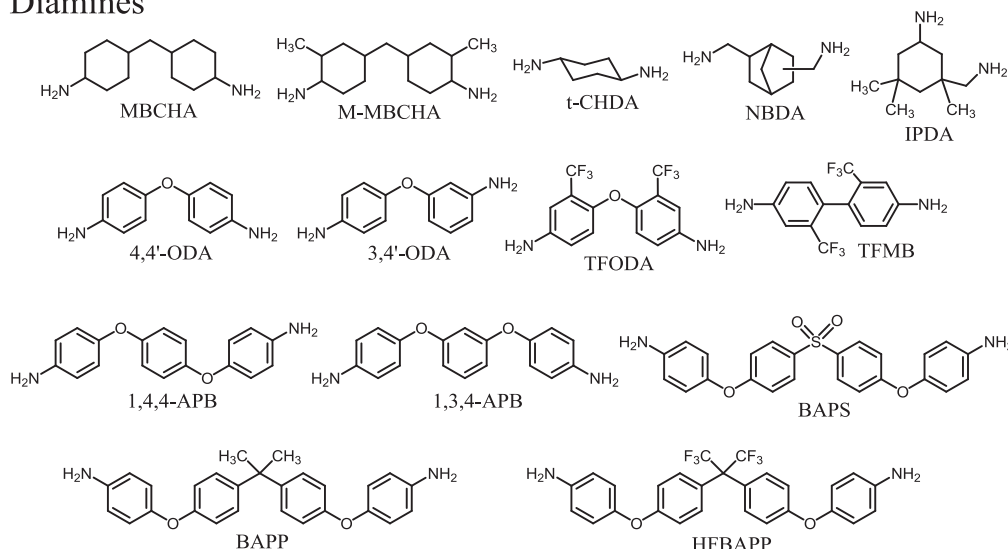
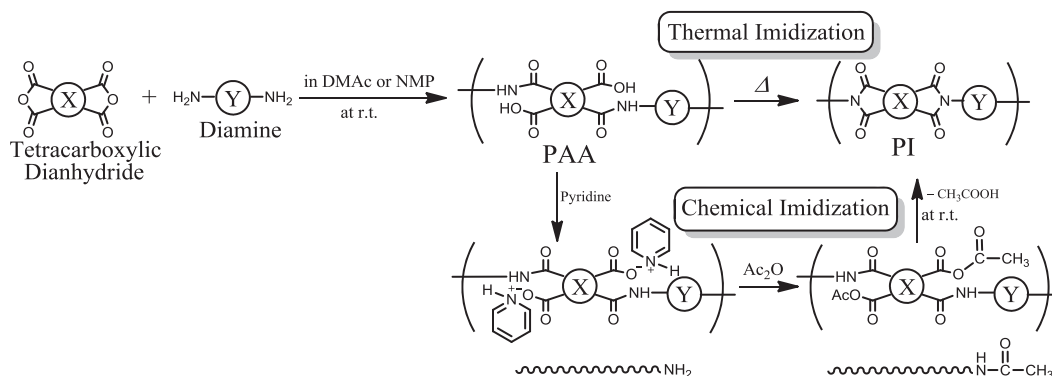


FIGURE 1 The structures of monomers used

TABLE 1 The conditions of pre-treatment and purification for monomers

Monomer	Source	Solvent for Recrystallization	Vacuum-Drying Condition	Melting Point, °C
Bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic dianhydride (H-BTA)	Iwatani Industrial Gases	-----	150°C/24 h	261
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	-----
1S,2R,4S,5R-Cyclohexanetetracarboxylic dianhydride (H-PMDA)	New Japan Chemical	-----	150°C/24 h	303
1,2,3,4-Cyclobutanetetracarboxylic dianhydride (CBDA)	Nissan Chemical Industries	-----	160°C/12 h	241
4,4'-Oxydiphthalic anhydride (ODPA)	Shanghai Research Institute of Synthetic Resins	-----	160°C/12 h	228
4,4'-(4,4'-Isopropylidenediphenoxy)bis(phthalic anhydride) (BisA-PA)	Aldrich	-----	130°C/24 h	184–187 (MSDS)
3,3',4,4'-Biphenylsulfonetetracarboxylic dianhydride (DSDA)	New Japan Chemical	-----	160°C/24 h	283 (MSDS)
Hydroquinone diphthalic anhydride (HQDA)	Chriskev Company	-----	150°C/24 h	267
Hydroquinone bis(trimellitate anhydride) (TA-HQ)	-----	1,4-Dioxane	200°C/24 h	277
4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA)	Central Glass	-----	160°C/12 h	248
3,3',4,4'-Biphenyltetracarboxylic dianhydride (s-BPDA)	TCI	-----	200°C/24 h	300
Pyromellitic dianhydride (PMDA)	TCI	-----	150°C/24 h	287
Trans-1,4-cyclohexanediamine (t-CHDA)	Iwatani Industrial Gases	-----	30°C/24 h	70
4,4'-Methylenebis(cyclohexylamine) (MBCHA) (mixture of isomers)	New Japan Chemical	-----	-----	-----
Isophoronediamine (IPDA)	TCI	-----	-----	-----
2,5(2,6)-Bis(aminomethyl)bicyclo[2.2.1]heptane (NBDA)	Mitsui Chemical	-----	-----	-----
4,4'-Methylenebis(2-methylcyclohexylamine) (M-MBCHA) (mixture of isomers)	Aldrich	-----	-----	-----
4,4'-Oxydianiline (4,4'-ODA)	Wako Chemical	Toluene/DMF (10/1, v/v)	50°C/24 h	191
Bis(4-amino-2-trifluoromethylphenyl)ether (TFODA)	Ihara Chemicals	EtOH/H ₂ O (11/5, v/v)	145°C/12 h	129
2,2'-Bis(trifluoromethyl)benzidine (TFMB)	Wakayama Seika	-----	50°C/12 h	184
3,4'-Oxydianiline (3,4'-ODA)	Wakayama Seika	-----	50°C/24 h	79
1,4-Bis(4-aminophenoxy)benzene (1,4-APB)	Wakayama Seika	-----	50°C/24 h	176
1,3-Bis(4-aminophenoxy)benzene (1,3-APB)	Wakayama Seika	-----	50°C/24 h	119
2,2-Bis[4-(4-aminophenoxyphenyl)]propane (BAPP)	Wakayama Seika	-----	50°C/24 h	130
Bis[4-(4-aminophenoxyphenyl)]sulfone (BAPS)	Wakayama Seika	-----	50°C/24 h	196

Abbreviation: DMF, N,N-dimethylformamide.

**FIGURE 2** Reaction schemes of polyaddition and imidization of poly(amic acid)s, and expected end-capping reaction of the terminal amino groups during chemical imidization

The PI films were prepared via thermal imidization as follows. The PAA solution was bar-coated on a glass substrate, dried at 60°C for 1–2 hours in an air-convection oven, heated at established imidization temperatures (T_i) under vacuum on the substrate, and finally annealed without the substrate at established annealing temperatures (T_a) for 1 hour under vacuum to eliminate residual stress. The detailed thermal conditions were mentioned in each case. The imidization and the annealing conditions were finely tuned to yield better-quality PI films in some cases.

The completion of thermal imidization was confirmed from the FT-IR spectra (Jasco, FT/IR 4100 infrared spectrometer) using the thin imidized films prepared as mentioned earlier. The FT-IR spectrum (eg, for the H-BTA/1,4,4-APB system) showed the specific bands (cm^{-1}) at 3070 ($\text{C}_{\text{arom}}-\text{H}$), 2949/2885 ($\text{C}_{\text{aliph}}-\text{H}$), 1774/1712 (imide $\text{C}=\text{O}$), 1508/1493 (1,4-phenylene), 1384 (imide $\text{N}-\text{C}_{\text{arom}}$), 1227 ($\text{C}-\text{O}-\text{C}$), and 791 (imide ring deformation).

For soluble PI systems, the PAAs were chemically imidized by adding an excess quantity of a dehydrating reagent (Ac_2O /pyridine) to the PAA solutions and stirring at room temperature for 12 hours unless stated, and the PI powder was isolated as reported in our previous papers.^{14–21} A homogeneous DMAc solution of the chemically imidized PI was coated on a glass substrate and dried for 1 hour at 60°C in an air convection oven, followed by heating at 250°C for 1 hour under vacuum. The completion of chemical imidization was confirmed by perfect disappearance of the proton signals for the COOH groups ($\delta = 12\text{--}13$ ppm) and the NHCO [$\delta \sim 10.0$ ppm in dimethyl sulfoxide ($\text{DMSO}-d_6$) originating from the PAAs in the ^1H -NMR spectra.

In this paper, the chemical compositions of PI systems are represented with the abbreviations of the monomer components used (tetracarboxylic dianhydrides [A] and diamines [B]) as A/B for homopolymers and A/B₁B₂ for copolymers.

2.2 | Measurements

2.2.1 | Inherent viscosity

The reduced viscosities (η_{red}) of PAAs just after polymerized and the chemically imidized powder samples, which can be practically regarded as the inherent viscosities (η_{inh}), were measured in DMAc at a solid content of 0.5 wt% at 30°C on an Ostwald viscometer.

2.2.2 | Linear coefficient of thermal expansion

The CTE values along the film plane (X-Y) direction for PI specimens (15 mm long, 5 mm wide, and typically 20 μm thick) in the glassy region were measured by thermomechanical analysis (TMA) as an average in the range of 100 to 200°C at a heating rate of 5°C min^{-1} on a thermomechanical analyzer (Netzsch, TMA 4000) with a fixed load (0.5 g per unit film thickness in μm , ie, 10 g load for 20- μm -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 to eliminate a bad influence of the adsorbed water.

2.2.3 | Heat resistance

The storage modulus (E') and the loss energy (E'') of PI films were measured by dynamic mechanical analysis (DMA) at a heating rate of 5°C

min^{-1} on the TMA instrument (as before). 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 of PI films was determined from the peak temperature of the E'' curve.

The thermal stability of PI films was evaluated from the 5% weight loss temperatures (T_d^5) by thermogravimetric analysis (TGA) on a thermo-balance (Netzsch, TG-DTA2000). TGA was performed at a heating rate of 10°C min^{-1} in dry nitrogen and air atmospheres. A small weight loss around 100°C in the TGA curves, which arises from the desorbed water from the samples, was compensated by off-set at 150°C to 0% weight loss for the data analysis.

2.2.4 | Optical transparency

The light transmission spectra of PI films (typically 20 μm thick) were recorded on an ultraviolet-visible spectrophotometer (Jasco, V-530) in the wavelength (λ) range of 200 to 800 nm. The light transmittance at 400 nm (T_{400}) and the cut-off wavelength (λ_{cut}) at which the transmittance becomes practically null were determined from the spectra. In this work, the transmittance data at longer wavelengths (eg, 450 and 500 nm) themselves were not discussed because they are often less informative for evaluating the film coloration; the films are not always colorless even if the T_{500} value was very high ($T_{500} > 80\%$).

2.2.5 | Birefringence

The in-plane (n_{in} or n_{xy}) and out-of-plane (n_{out} 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 $n_D = 1.78\text{--}1.80$) and a test piece ($n_D = 1.92$). The birefringence of PI films, which indicates the relative extent of chain alignment in the X-Y direction, was calculated from the relationship:

$$\Delta n_{\text{th}} = n_{\text{in}} - n_{\text{out}} \quad (1)$$

2.2.6 | Mechanical properties

The 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 μm 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 specimens were cut from high-quality film samples (10 cm \times 10 cm) free of any defects such as fine bubbles.

2.2.7 | Water uptake

The extent of water absorption (W_A , JIS K 7209) of PI films was determined from the following relationship:

$$W_A = [(W - W_0)/W_0] \times 100 \quad (2)$$

Where W_0 is the weight of film sample after vacuum-drying at 50°C for 24 hours and W denotes the weight of the films immersed in water at 23°C for 24 hours followed by carefully blotting with tissue paper.

3 | RESULTS AND DISCUSSION

3.1 | Film ductility of PIs derived from conventional tetracarboxylic dianhydrides

Before investigating the film ductility of the cycloaliphatic PIs, we surveyed those of PIs derived from conventional tetracarboxylic dianhydrides to identify which, if any, tetracarboxylic dianhydrides result in poor ductility in the resultant PI films, even when combined with flexible diamines. Figure 3 shows the comparison of the ϵ_b values for the PIs derived from conventional tetracarboxylic dianhydrides and 4,4'-oxydianiline (4,4'-ODA), which generally yields ductile films. Even when rigid structures of tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylic

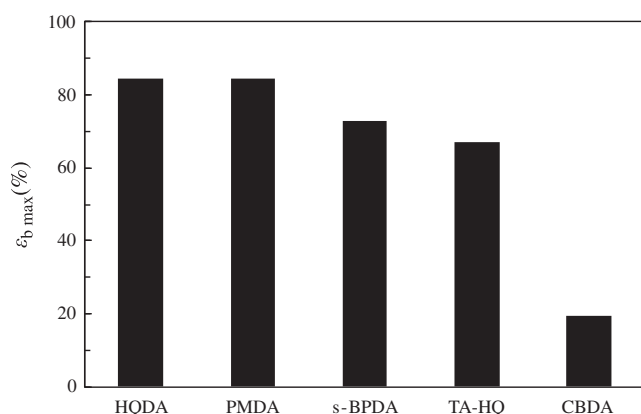


FIGURE 3 The film ductility for thermally imidized PI films derived from 4,4'-ODA and different tetracarboxylic dianhydrides

dianhydride (s-BPDA), and TA-HQ were used, highly tough PI films ($\epsilon_b \text{ max} > 60\%$) were obtained. Thus, these rigid tetracarboxylic dianhydrides did not disturb the expected effect of 4,4'-ODA. 1,2,3,4-Cyclobutanetetracarboxylic dianhydride (CBDA) also has a rigid structure similar to that of PMDA. However, the CBDA/4,4'-ODA system was inferior to the PMDA/4,4'-ODA system in terms of the film toughness as shown in Figure 3. Thus, CBDA is obviously disadvantageous for obtaining highly tough PI films, although, to date, there has been no discussion of the mechanism responsible for this apparent inferiority.

The energy necessary to stretch the film specimens until fracture corresponds to that required to pull out a portion of polymer chains from a bunch of entangled chains. Therefore, the extent of chain entanglement is the key factor influencing the fracture energy, and, consequently, the film toughness. On the basis of our previous results, we have proposed that, in addition to chain entanglement, chain slippage also affects film ductility,^{17,26} probably contributing to reducing the stress concentration, which is a trigger of film fracture during the tensile testing.

In the present study, we attempted to explain the results of Figure 3 in terms of chain slippage. Figure 4 shows a schematic diagram expressing the easiness of chain slippage in the PMDA-based and the CBDA-based PIs. It is known that there exist attractive dipole-dipole interactions between the imide C=O groups and a concomitant face-to-face stacked structure between the pyromellitimide (PMDI) units in PI fibers derived from PMDA and rigid diamines.^{27,28} Probably, a similar local structure can also be formed in the films of PMDA-based PIs. As depicted in Figure 4A, chain slippage could easily occur in the stretching process while cutting off the dipole-dipole interactions because the PMDI unit including the pendant hydrogen

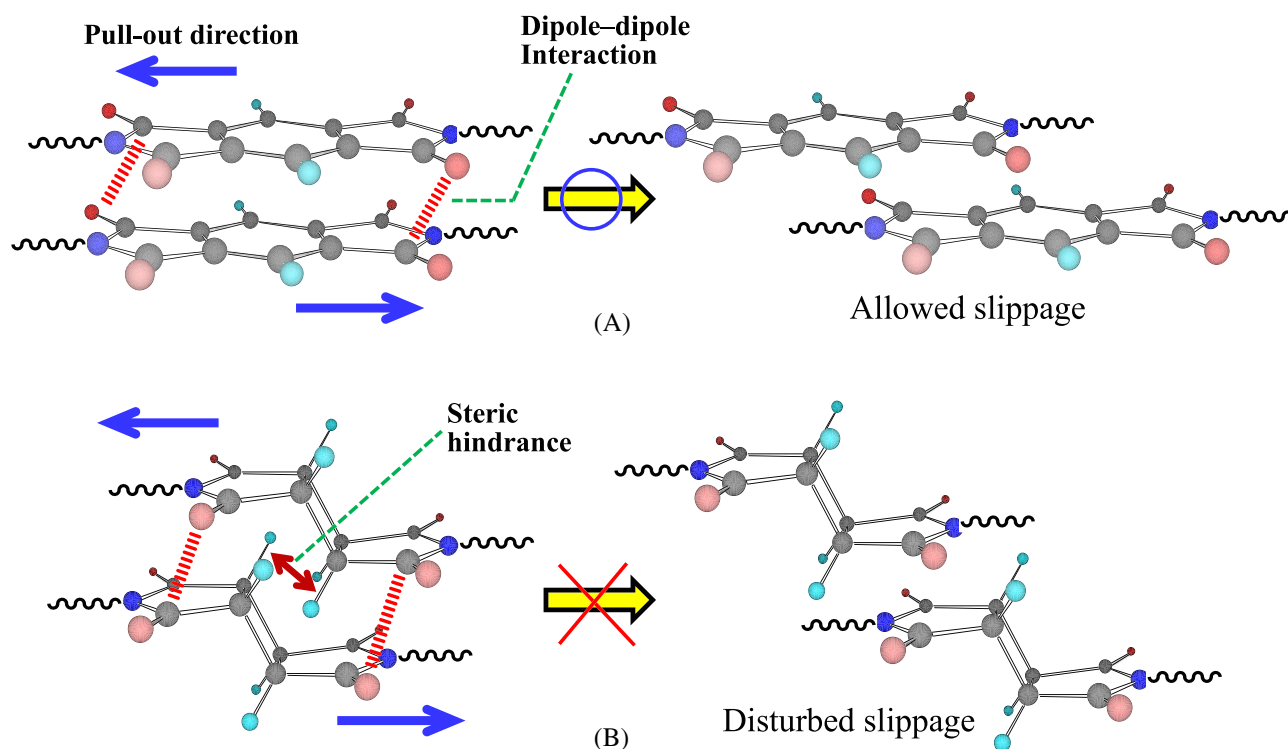


FIGURE 4 Schematic illustrations of an expected closely stacked structure between the cyclobutanetetracarboxydiimide units as arising from dipole-dipole interactions of the imide C=O groups and the easiness of chain slippage. (A) PMDA-based PIs and (B) CBDA-based PIs [Colour figure can be viewed at wileyonlinelibrary.com]

atoms has a perfectly planar structure. As for the CBDA-based PIs, similar closely stacked local structures could be formed between the CBDA-based diimide (CBDI) units, as suggested from its crank-shaft-like shape (Figure 4B). However, in this case, the shape is different from the PMDA-based systems; the laterally projecting hydrogen atoms of the CBDI units can behave like “claws”, causing steric hindrance and preventing chain slippage, as depicted in Figure 4B. The much lower ductility of the CBDA-based PI films than that of the PMDA-based counterpart can be explained by this hypothesis, suggesting the importance of chain slippage for film ductility.

3.2 | Film ductility of PIs from cycloaliphatic diamines

3.2.1 | A problem in polyaddition

As mentioned earlier, the key factor influencing the film ductility of glassy linear polymers is chain entanglement, which is closely related to the rotational flexibility and the length of the polymer chains (the degree of polymerization). For example, a previous paper reported that the ε_b values of the PMDA/4,4'-ODA PI films increased with increasing weight-average molecular weight (M_w) of the corresponding precursors, leveling off above a critical M_w (~30 000).²⁹ By contrast, the PMDA/*p*-phenylenediamine (*p*-PDA) PI film is very brittle even though its molecular weight is sufficiently high as suggested by the very high η_{inh} value of the precursor. This is undoubtedly due to the poor chain entanglement, which is predictable from its rod-like main chain structure.³⁰

Cycloaliphatic PI systems often encounter polymerizability problems, and PIs with sufficient molecular weights for chain entanglement cannot be obtained. In particular, when aliphatic diamines are reacted with an equimolar amount of tetracarboxylic dianhydrides, salt formation inevitably occurs during the polyaddition,⁹ which, in extreme cases, completely terminates PAA formation^{17,31,32} or significantly extends the reaction period required for the complete homogenization of the reaction mixture. Therefore, one of the key strategies for improving the film ductility of PIs consisting of aliphatic diamines is to maximize their molecular weights (or the η_{inh} values of the precursors for convenience) under optimum reaction conditions for controlling salt formation. Several approaches for preventing or suppressing salt formation have been reported, such as the silylation of aliphatic diamines³³ and the addition of acetic acid.³⁴ However, in our experience, these methods are not always universally effective because there are some systems where the PAA polymerization does not proceed even using these methods. Therefore, in the present study, we used the simple reactions between diamines and tetracarboxylic dianhydrides without any additional reagents, and we investigated how the initial monomer content affects the resultant η_{inh} values of the obtained PAAs.

In general, when using aromatic diamines, polyaddition is often started with a monomer content as high as possible (eg, 20–30 wt%) without heating, and a minimum quantity of the same solvent is gradually added to the reaction mixture to assist effective stirring. During this procedure, side reactions, which destroy the strict equimolar feeding ratio of the monomers, ie, the hydrolysis of tetracarboxylic dianhydrides by a small amount of water present in the reaction mixture can be kinetically suppressed. However, for the systems

consisting of PMDA and 4,4'-methylenebis(cyclohexylamine) (MBCHA), when the polyaddition was carried out at a high monomer content (eg, 13 wt%), the reaction mixture required stirring at room temperature for a prolonged period (120 hours) to achieve the complete dissolution of the formed salt. The resultant η_{inh} value of the PAA was 0.91 dL g⁻¹. Such a significant extension of the reaction period is undesirable because it increases the chance that the unreacted portion of tetracarboxylic dianhydride will undergo hydrolysis. On the other hand, the reaction at a lower monomer content (5.0 wt%) gave rise to a significantly decreased η_{inh} value (0.40 dL g⁻¹), although the reaction mixture was much more promptly homogenized than in the reaction at 13 wt%. By contrast, when the reaction was initiated at a moderate monomer content (9.0 wt%), a dramatically enhanced η_{inh} value (1.44 dL g⁻¹) was obtained after stirring at room temperature for 24 hours. In this procedure, the salt was much faster dissolved than in the case at 13 wt%, and this situation was more favorable for suppressing the hydrolysis of tetracarboxylic dianhydride.

The importance of dissolving the formed salt as quickly as possible without heating was also conveniently confirmed by an effect of high-speed stirring. Similar salt formation behavior was observed in the reaction of PMDA and isophoronediamine (IPDA). However, the salt was dissolved more smoothly than in the PMDA/MBCHA system. Then, the reaction between PMDA and IPDA was carried out at a higher monomer content (13.0 wt%). First, the reaction mixture was stirred at a minimum speed with a magnetic stirrer. This procedure led to a homogeneous PAA solution of PMDA/IPDA with a low η_{inh} value (0.28 dL g⁻¹) after stirring at room temperature for 24 hours. On the other hand, when vigorously stirred with a maximal power of the magnetic stirrer just after the salt formation, the reaction mixture rapidly became homogeneous because the salt was crushed, and the resultant η_{inh} value of the PAA increased significantly to 0.77 dL g⁻¹ after stirring at room temperature for 12 hours. In this case, the dispersion of the salt and its attachment to the inner wall of the flask should be avoided because the portion of the salt stuck to the walls is not easily dissolved. Thus, faster salt dissolution indeed brings about higher molecular weights of PAAs. However, it is very difficult to ensure the reproducibility of the resultant PAA molecular weights (or η_{inh}) by controlling the initial monomer content and stirring speed alone because the size of the salt particles also depends on many other factors (eg, the solubility of the tetracarboxylic dianhydride powder and how it is feed into the diamine solution). This is probably one of the reasons why colorless PI systems consisting of aliphatic diamines are not produced on an industrial scale.

3.2.2 | PIs derived from t-CHDA and flexible aromatic tetracarboxylic dianhydrides

In this study, non-cyclic diamines such as 1,6-hexanediamine were excluded because the resultant PIs do not maintain high heat resistance. Thus, practically useful and commercially available cycloaliphatic diamines are not so many. Among them, *trans*-1,4-cyclohexanediamine (t-CHDA) is a very limited cycloaliphatic diamine that has a semi-linear and semi-planar structure. We have previously investigated t-CHDA-based PIs with the expectation of simultaneously achieving low CTE and low dielectric constants.^{31,35} However, little attention has been paid to their mechanical properties, particularly,

film ductility. Table 2 summarizes the ϵ_b values for some t-CHDA-based PIs obtained using flexible tetracarboxylic dianhydrides, together with other properties related to high-temperature transparent materials. Our previous investigations³⁵ suggested that the *trans*-1,4-cyclohexylene units incorporated into the PI chains using t-CHDA behave like the *p*-phenylene units originating from *p*-PDA, as suggested by the fact that the T_g of s-BPDA/t-CHDA is similar to that of s-BPDA/*p*-PDA in the same way as the CTE. This means that t-CHDA, as well as *p*-PDA, is a disadvantageous diamine with respect to enhancing chain entanglement. As expected, the use of rigid tetracarboxylic dianhydrides (CBDA, s-BPDA, and TA-HQ) gave rise to brittle films. On the other hand, a certain degree of positive effect on the film ductility was observed when t-CHDA was combined with flexible ether-linked tetracarboxylic dianhydrides ie, 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) (BisA-PA), 4,4'-oxydiphthalic anhydride (ODPA), hydroquinone diphthalic anhydride (HQDA), and, particularly, BisA-PA (#4), as shown in Table 2.

In comparison between s-BPDA/t-CHDA and s-BPDA/*p*-PDA, the former ($\epsilon_b < 10\%$) was somewhat brittle compared with the latter ($\epsilon_b = 30\text{--}40\%$). This is probably related to the fact that the s-BPDA/t-CHDA film tends to have higher crystallinity than the s-BPDA/*p*-PDA film,^{36,37} which is a physical factor for reducing chain entanglement.

3.2.3 | PIs derived from MBCHA and other cycloaliphatic diamines

MBCHA is a cycloaliphatic diamine with a distorted structure, in contrast to t-CHDA. Table 3 summarizes the mechanical properties together with the thermal and optical properties of the MBCHA-based PIs. The use of rigid tetracarboxylic dianhydrides (s-BPDA [#10] and TA-HQ [#11]) gave rise to somewhat brittle PI films, as shown by the much lower ϵ_b values than those of the 4,4'-ODA-based counterparts (Figure 3), which were similar to those of the t-CHDA-derived

counterparts. According to these results, it is difficult to say that MBCHA is a "flexible" cycloaliphatic diamine in terms of the formation of ductile films. However, the inferiority of MBCHA is probably not related to the suppressed internal rotation around its central methylene linkage, as suggested by the fact the MBCHA-based PIs tend to have lower T_g s than those of the 4,4'-ODA-based counterparts (eg, $T_g = 232^\circ\text{C}$ for s-BPDA/MBCHA [#10] and $T_g = 270^\circ\text{C}$ for s-BPDA/4,4'-ODA).³⁸ Thus, these results do not eliminate our concern that, as long as MBCHA is used, the PI films will be brittle. Indeed, even when the ether-linked tetracarboxylic dianhydrides (ODPA [#6] and HQDA [#9]) were combined with MBCHA, the PI film ductility was not improved significantly, as shown in Table 3.

We also examined the effect of other cycloaliphatic diamines, ie, 2,5(2,6)-bis(aminomethyl)bicyclo[2.2.1]heptane (norbornanediamine: NBDA) and 4,4'-methylenebis(2-methylcyclohexylamine) (M-MBCHA) using a flexible ether-linked tetracarboxylic dianhydride, HQDA. The results are listed in Table 4. The HQDA/NBDA system (#12) had a slightly lower T_g than the MBCHA-based counterpart, probably owing to the presence of two rotatable connecting groups (methylene linkages) in NBDA. Unfortunately, no prominent toughening effect was observed on using NBDA. The effect of the methyl substituents was also examined by comparing HQDA/M-MBCHA and the corresponding substituent-free system. The former (#13) had a slightly higher T_g than the latter. However, the methyl-substituted system (#13) provided a much more brittle film than the substituent-free system (#9). Thus, neither NBDA nor M-MBCHA was effective in improving the film ductility, although these films showed relatively low water uptake.

3.2.4 | Unexpected effect of copolymerization on film ductility

While attempting to improve the solubility of the PMDA/MBCHA PI system by copolymerization with methyl-substituted IPDA, we

TABLE 2 Properties of thermally imidized PI films derived from flexible aromatic tetracarboxylic dianhydrides and t-CHDA

No.	Tetracarboxylic Dianhydride	η_{inh} (PAA), dL g ⁻¹	T_{400} , %	λ_{cut} , nm	T_g , °C	CTE, ppm K ⁻¹	E, GPa	σ_b , GPa	ϵ_b av/max, %
1	ODPA	1.21	80.7	344	319	54.6	3.34	0.141	15/21
2	DSDA	1.43	64.4 83.2 ^a	330	366	55.0	3.51	0.110	14/16
3	6FDA	0.67	88.0	315	333	57.9	2.63	0.112	8.6/11
4	BisA-PA	0.68	79.0	361	229	68.1	2.05	0.090	26/38
5	HQDA	0.81	69.7	350	291	62.9	2.95	0.110	13/15

^aData of the PI film obtained using recrystallized DSDA. The typical thermal conditions: $T_i = 250^\circ\text{C}$ for 1 h + 300°C for 1 h and $T_a = 300^\circ\text{C}$ for 1 h.

TABLE 3 Properties of thermally imidized PI films derived from aromatic tetracarboxylic dianhydrides and MBCHA

No.	Tetracarboxylic Dianhydride	η_{inh} (PAA), dL g ⁻¹	T_{400} , %	λ_{cut} , nm	T_g , °C	E, GPa	σ_b , GPa	ϵ_b av/max, %
6	ODPA	1.28	71.0	350	244	2.28	0.100	15/23
7	DSDA	0.80	77.0	320	280	2.54	0.129	12/17
8	6FDA	0.89	78.9	320	267	2.47	0.106	7.1/8.6
9	HQDA	1.50	71.7	360	217	1.90	0.077	19/27
10	s-BPDA ^a	1.40	63.5	366	232	2.91	0.108	9.6/11
11	TA-HQ ^a	1.64	51.9	340	ND ^b	3.40	0.117	4.1/5.3

^aTurbid films

^bND: Not detected by DMA.

The typical thermal conditions: $T_i = 250^\circ\text{C}$ for 1 h + 300°C for 1 h and $T_a = 300^\circ\text{C}$ for 1 h.

TABLE 4 Properties of thermally imidized PI films derived from aromatic tetracarboxylic dianhydrides and the other cycloaliphatic diamines

No.	Tetracarboxylic Dianhydride	Diamine	η_{inh} (PAA), dL g ⁻¹	T_{400} , %	λ_{cut} , nm	T_g , °C	CTE, ppm K ⁻¹	E , GPa	σ_b , GPa	ϵ_b av/max, %	W_A , %
12	HQDA ^a	NBDA	1.17	72.4	362	209	68.6	2.53	0.12	9.6/13	0.30
13	HQDA ^b	M-MBCHA	1.17	67.0	360	226	63.1	2.50	0.12	6.6/7.8	0.38

^aThermal conditions: T_i = 350°C for 1 h and T_a = 200°C for 1 h.

^bThermal conditions: T_i = 180°C for 0.5 h + 250°C for 0.5 h + 300°C for 1 h and T_a = 200°C for 1 h.

observed an unexpected effect. Figure 5 shows the relationship between the ϵ_b values and the copolymer composition in PMDA/MBCHA/IPDA. As in the PMDA/IPDA homo PI system, the copolyimides with high IPDA contents (≥ 70 mol%) yielded very brittle films that contained fine cracks after thermal imidization. The ϵ_b values of these films can be regarded as practically zero because of the difficulty in tensile testing. The formation of cracks is probably related to the depolymerization (molecular weight decrease) that occurs in the moderate temperature range of 170 to 200°C,³⁸⁻⁴⁰ although the extent of depolymerization depends on the systems. In spite of the absence of the film-forming ability of PMDA/IPDA, a prominent toughening effect was observed by copolymerization with a small amount of IPDA (5–30 mol%), where the measured values significantly deviated from the additivity rule between the ϵ_b values and the copolymer composition. These toughened copolymers had other excellent properties; for example, excellent optical transparency (T_{400} = 83.7%) and a very high T_g (317°C) at an IPDA content of 20 mol%, although the CTE value was normal (52.2 ppm K⁻¹).

The observed toughening effect may result from the increased PI molecular weights. However, no correlation was observed between the η_{inh} values of the PAAs and the ϵ_b values of the resultant PI films. This suggests that factors other than the PI molecular weights must be considered to explain the observed toughening effect. Considering the positions of the functional groups in IPDA, it is highly possible that the incorporation of IPDA into the PMDA/MBCHA chains by copolymerization distorts the chains dramatically even with a minor

IPDA content, and the number of PMDI-PMDI face-to-face stacked sites are reduced. This situation is probably advantageous concerning chain slippage.

Based on this hypothesis, instead of PMDA, the use of CBDA possessing an undesirable structure for the chain slippage is predicted to cancel the favorable copolymerization effect. Indeed, no significant toughening effect was observed in the CBDA/MBCHA(90);IPDA(10) copolymer (ϵ_b av = 11% and ϵ_b max = 13%).

3.3 | H-BTA-derived PIs

3.3.1 | Earlier studies on H-BTA-derived PIs and related systems

As mentioned earlier, the reactions of cycloaliphatic tetracarboxylic dianhydrides and aromatic diamines lead to transparent PI films without the salt formation and, consequently, with good reproducibility in terms of the molecular weight (practically, the η_{inh} values) of the resultant PAAs. An early study using cycloaliphatic tetracarboxylic dianhydrides concerned the synthesis of bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BTA) by the Diels-Alder reaction and the thermal stability of the BTA-derived PIs. However, these PIs suffer thermal decomposition at elevated temperatures ($>360^\circ\text{C}$), undergoing the retro-Diels-Alder reaction.⁴¹ BTA also suffers a polymerizability problem in the reactions with common diamines; as a result, we could not obtain the films.¹⁴ A previous paper⁴² reported the synthesis of two isomers of bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic dianhydride (hydrogenated BTA: H-BTA), where the retro-Diels-Alder reaction no longer occurs, and the properties of the H-BTA-derived PIs using limited diamines. However, even when highly flexible 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB) was combined with H-BTA, the obtained PI film was brittle (ϵ_b = 4% by TMA⁴²). Thus, we wonder if H-BTA might be an essentially inadequate cycloaliphatic dianhydride for the formation of tough PI films in the same way as CBDA. However, to date, there have been no studies properly evaluating the potential of H-BTA-based PIs. Thus, in the present work, we systematically investigated the H-BTA-based systems using a variety of diamines to understand their potential.

3.3.2 | Steric structure of H-BTA

H-BTA used in this study was synthesized by the catalytic reduction of the double bond after the hydrolysis of BTA.⁴³ BTA (purchased from TCI) was the starting material and has the 2-*exo*, 3-*exo*, 5-*exo*, 6-*exo*-carbonyl configuration.⁴⁴ The ¹H-NMR spectrum (CD₃CN, Jeol, JNM-ECP400) of the H-BTA used in this work showed that it also consists of the all *exo*-carbonyl configuration with the central cyclohexane unit in the boat form, as suggested by a singlet proton peak at δ = 3.38 ppm

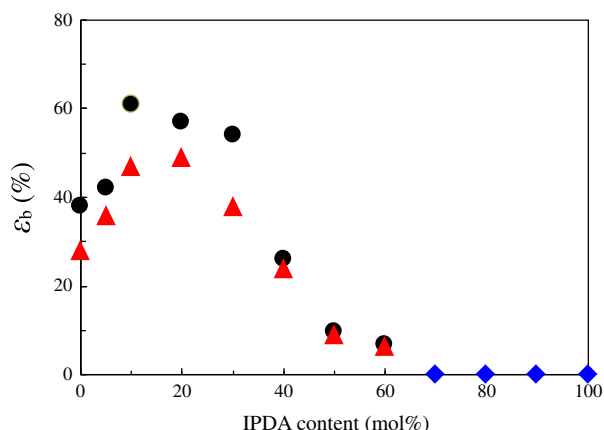


FIGURE 5 Influence of the copolymer composition in PMDA/MBCHA/IPDA on the film ductility. (●) ϵ_b max, (▲) ϵ_b av, and (◆) crack-including films not applicable to the tensile test. The typical thermal conditions: T_i = 200°C for 0.5 h + 250°C for 0.5 h + 300°C for 1 h and T_a = 300°C for 1 h [Colour figure can be viewed at wileyonlinelibrary.com]

with a reasonable integrated intensity (4H),⁴³ which indicates the presence of four equivalent 2-*endo*, 3-*endo*, 5-*endo*, 6-*endo* protons in H-BTA. Thus, H-BTA used in this study has the same steric structure as 1S,2R,4S,5R-cyclohexanetetracarboxylic dianhydride (H-PMDA),⁴⁵ except for the presence of the bridging unit.

3.3.3 | Polymerizability of H-BTA with various diamines

As mentioned earlier, attention should be paid to enhancing the molecular weights (or η_{inh}) of PAAs as much as possible to improve the film ductility. As shown in Table 5, the polyaddition of H-BTA with common aromatic diamines led to PAAs with moderate η_{inh} values ranging from 0.5 to 0.8 dL g⁻¹, except when diamines with electron-withdrawing -CF₃ and -SO₂- groups were used [eg, bis(4-amino-2-trifluoromethylphenyl)ether (TFODA, #16), 2,2'-bis(trifluoromethyl)benzidine (TFMB, #17), and bis[4-(4-aminophenoxyphenyl)]sulfone (BAPS, #21)]. Figure 6 shows a comparison of the η_{inh} -based polymerizability between H-BTA and H-PMDA when using the same diamines. In the reactions of these cycloaliphatic tetracarboxylic dianhydrides with aromatic diamines, we could not conclude if H-BTA is generally more reactive than H-PMDA because the plots were not always biased above the Y = X line. On the other hand, a prominent feature was observed when cycloaliphatic diamines were used; specifically, the plots significantly deviated upward from the Y = X line. Thus, H-BTA was superior to H-PMDA in terms of its polymerizability with cycloaliphatic diamines. This is probably related to the bulkier structure in bicyclic H-BTA than in H-PMDA, which is expected to increase the salt solubility because of the loosely formed salt originating from the presence of bulky bridging units. A similar effect was also observed in the comparison between the reaction systems of 1,3-dimethyl-CBDA/t-CHDA and CBDA/t-CHDA, where the former, which has bulky methyl substituents, can be polymerized in DMAc at room temperature by prolonged stirring.¹⁶ By contrast, for the latter, the polyaddition is terminated under the same conditions.³¹

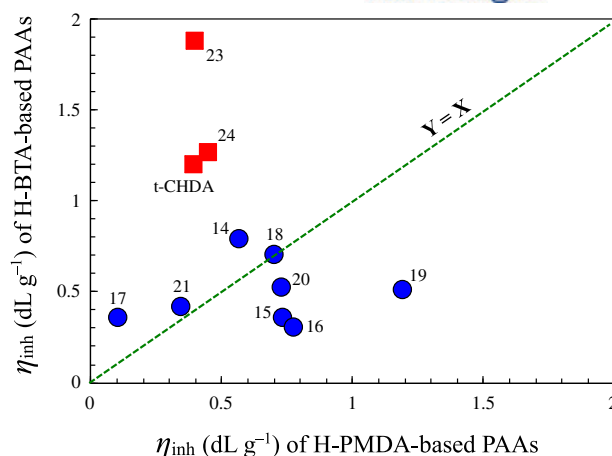


FIGURE 6 The comparison of the η_{inh} -based polymerizability between H-BTA-derived and H-PMDA-derived systems from different diamines: (●) aromatic diamines and (■) cycloaliphatic diamines. The numbers inserted denote the sample number listed in Table 5. The broken line represents the relation: Y = X [Colour figure can be viewed at wileyonlinelibrary.com]

3.3.4 | Properties of H-BTA-derived PIs

The film properties of H-BTA-derived PIs are summarized in Table 5. PI films of good quality and ductility were obtained except when TFMB was chosen as the diamine. The H-BTA/TFMB system (#17) yielded a very brittle film with fine cracks after thermal imidization, probably owing to the low molecular weight of the PAA. As expected, many of the H-BTA-based PI films had excellent optical transparency, as suggested by the high T_{400} values, which exceeded 80%. They also showed common CTE values (~50 ppm K⁻¹ or higher), which is attributed to the almost three-dimensionally random chain orientation (the absence of in-plane orientation [chain alignment along the film plane]), corresponding to their very low Δn_{th} values. Generally, in-plane chain orientation occurs during the thermal imidization of PAA films on the

TABLE 5 Properties of PI films derived from H-BTA and various diamines

No.	Diamine	Cure ^c	η_{inh} (PAA), dL g ⁻¹	T_{400} , %	λ_{cut} , nm	Δn_{th}	T_g , °C	CTE, ppm K ⁻¹	E, GPa	σ_b , GPa	ε_b av/max, %	T_d^5 (N ₂), °C	T_d^5 (air), °C	W_A , %
14	4,4'-ODA ^d	T	0.80 0.34 ^a	72.2	295	0.001	379 385 ^a	48.4	2.28	0.094	12/13 11.0 ^a	499 447 ^a	434	2.02
15	3,4'-ODA	T	0.36	83.7	293	0.002	340	50.0	2.23	0.098	66/110	500	499	---
16	TFODA	T	0.31	84.2	293	0.001	349	57.3	2.55	0.093	16/24	488	425	---
17	TFMB	T	0.36	88.1	289	0.001	---	---	---	---	---	---	---	---
18	1,4,4-APB	T	0.71	85.5	303	0.003	340	55.3	2.13	0.087	67/104	498	433	2.05
19	1,3,4-APB ^b	T	0.51 0.20 ^a	37.5	295	0.000	302 225 ^a	55.5	2.57	0.091	37/62 4.0 ^a	481 491 ^a	418	---
20	BAPP	T	0.53	83.6	294	0.001	305	62.8	1.83	0.074	74/137	497	448	---
21	BAPS	T	0.42	82.3	302	0.002	337	55.0	1.75	0.068	27/68	482	435	---
22	BAPS (70) 1,4,4-APB (30)	C	0.45 0.25 ^e	86.8	299	0.012	313	49.4	1.97	0.070	27/51	487	459	---
23	MBCHA ^d	T	1.88	87.2	250	0.002	306	56.7	1.65	0.076	16/27	463	384	2.03
24	M-MBCHA ^d	T	1.27	87.5	244	0.002	312	56.2	2.16	0.091	5.2/6.6	441	382	1.47

^aData from ref. 42.

^bTurbid film.

^cImidization process. T: thermal imidization (two-step process), the typical thermal conditions: T_i = 350°C for 2 h and T_a = 300°C for 1 h, C: chemical imidization.

^dThe PI film was prepared by thermal imidization in a free state.

^eData for PI powder sample.

substrates only when the PI backbones are highly stiff and linear.^{46–48} This suggests that, as long as H-BTA is used as a cycloaliphatic tetracarboxylic dianhydride, it is difficult to obtain a low CTE because the non-linear and non-planar steric structure of H-BTA causes a significant decrease in the overall chain linearity. This is also true in systems using H-PMDA,^{16,17,31} corresponding to the fact that H-PMDA has the same steric structure as H-BTA except for the absence of the bridging unit in the former.⁴⁵

The H-BTA-based PI films also possessed relatively high thermal stability, even though they contain thermally less stable non-aromatic units in the structures, as suggested by the relatively high T_d^5 values (in N_2) of approximately 500°C. Figure 7 shows a comparison of the T_d^5 (N_2) between H-BTA- and H-PMDA-based PI systems consisting of the same diamines. As indicated by the fact that the plots are all positioned above from the $Y = X$ line, the H-BTA-based PIs are superior to the H-PMDA-based counterparts in terms of the thermal stability.

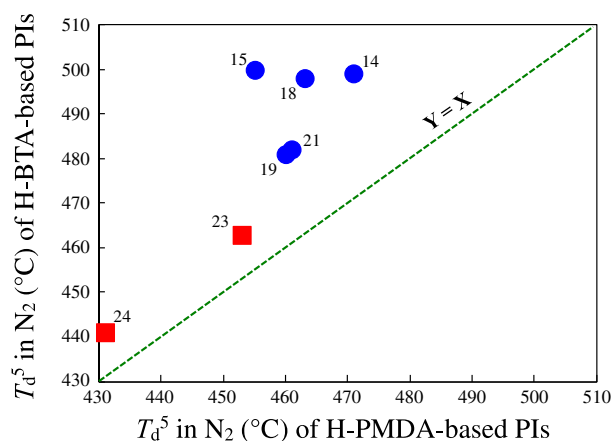


FIGURE 7 The comparison of the thermal stability based on T_d^5 (N_2) between H-BTA-derived and H-PMDA-derived systems from different diamines: (●) aromatic diamines and (■) cycloaliphatic diamines. The numbers inserted denote the sample number listed in Table 5. The broken line represents the relation: $Y = X$ [Colour figure can be viewed at wileyonlinelibrary.com]

This probably reflects the fact that the bicyclic structure of H-BTA is more advantageous in suppressing weight loss arising from the fragmentation at elevated temperatures than the mono-cyclic structure of H-PMDA.

Another prominent feature observed in the H-BTA-derived PIs is their high- T_g behavior. For example, when 4,4'-ODA was used as a diamine, the resultant PI film (#14) displayed an extremely high T_g of 379°C. Even when the more flexible 2,2-bis[4-(4-aminophenoxyphenyl)]propane (BAPP) was chosen as the diamine, the PI film (#20) still maintained a high T_g of 305°C. Figure 8 shows a comparison of the T_g s for H-BTA-derived PIs with those of other related systems (H-PMDA, H''-PMDA, and H'-PMDA). We have previously reported that H-PMDA is most effective in enhancing the T_g among these isomers.^{15,17} The present results show that H-BTA is clearly superior to H-PMDA in terms of the T_g -based physical heat resistance. However, the results cannot be explained only by the difference in the diimide-dimide interactions because the bulky bridging groups of H-BTA are not favorable for intermolecular close stacking between the diimide units. This bridging group also probably has an inhibitory effect on the internal rotations at the central cyclohexane units (ring wagging motion). This is a convincing explanation for the higher- T_g behavior of the H-BTA-derived PIs if the local motion at the cyclohexane units is closely related to the overall rotational motions of the chains necessary for the glass transition.

The H-BTA-derived PIs also possessed excellent toughness. When some ether-containing diamines were used, the PI films became very tough, as shown by their very high ϵ_b values (Table 5), in contrast to the results previously reported in the literature (eg, $\epsilon_b = 4\%$ for H-BTA/1,3,4-APB⁴²). Table 5 also shows that the H-BTA/BAPP system (#20) yielded the toughest film ($\epsilon_{b \max} = 137\%$) of the H-BTA-derived systems examined here, and this is comparable to that of PMDA/BAPP ($\epsilon_{b \max} = 133\%$ ⁴⁹), a typically tough PI system. Thus, these results clearly demonstrate that, using H-BTA, we can prepare very tough, colorless PI films, even though H-BTA has been believed to yield brittle films.

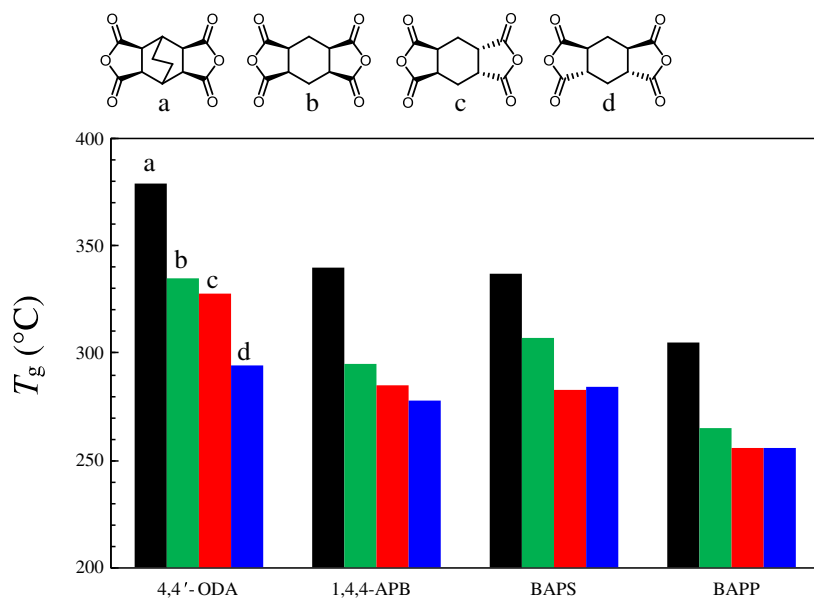


FIGURE 8 Comparisons of T_g for thermally imidized PI films obtained using relevant cycloaliphatic tetracarboxylic dianhydrides: (a) H-BTA (black bars), (b) H-PMDA (green bars), (c) H''-PMDA (red bars), and (d) H'-PMDA (blue bars) [Colour figure can be viewed at wileyonlinelibrary.com]

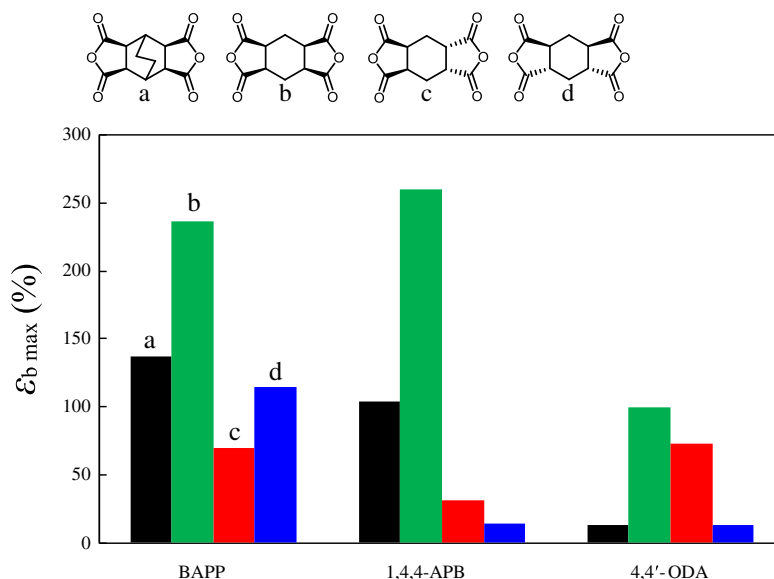


FIGURE 9 Comparisons of the film toughness ($\epsilon_{b \max}$) for thermally imidized PI films obtained using relevant cycloaliphatic tetracarboxylic dianhydrides: (a) H-BTA (black bars), (b) H-PMDA (green bars), (c) H''-PMDA (red bars), and (d) H'-PMDA (blue bars) [Colour figure can be viewed at wileyonlinelibrary.com]

The film toughness of the H-BTA-derived PIs was compared with that of other related systems using the H-PMDA isomers in Figure 9. Among the H-PMDA analogs examined here, H-PMDA was the most effective cycloaliphatic tetracarboxylic dianhydride for enhancing the film toughness, although H-BTA has a sufficient toughening effect. The superiority of H-PMDA is probably related to the absence of the rigid bridging side group in H-PMDA; thus, slippage is not impeded. Roughly speaking, H-BTA and H-PMDA are especially effective in enhancing the toughness of these H-PMDA analogs. Considering the structural similarity between H-BTA and H-PMDA, it is possible that their unique molecular shape (steric structure), which, edge-on, looks like a “lemon squeezer” with a “W” shape, plays a significant role in generating the high film toughness.

The H-BTA-derived PI films prepared via thermal imidization were basically insoluble in common aprotic solvents, indicating that casting processes using stable PI solutions cannot be used (ie, they are not solution processable). The exceptions were the systems using CF₃-containing TFMB and TFODA and sulfone-containing BAPS. These PIs were soluble in common solvents such as DMAc and *N*-methyl-2-pyrrolidone (NMP) at room temperature, as listed in **Supporting Information 1**. The results of the solubility tests were very similar to those for the H-PMDA-derived PIs.¹⁵

Our interests also extend to solution processability from the viewpoint of the practical application of these PI films. Generally, chemically imidized powder samples are more soluble than the corresponding thermally imidized film samples. Stable PI solutions obtained from the chemically imidized powder can be directly applied to a simple solution casting (coating and drying) process without imidization. In addition, the film preparation process via chemical imidization has the advantage of enhancing the optical transparency of the PI films compared with the conventional two-step process via thermal imidization, probably owing to the end-capping reaction of the less stable terminal amino groups by acetic anhydride during chemical imidization (Figure 2).^{19,20} Therefore, we attempted the chemical imidization of the H-BTA/BAPS system by adding the dehydrating reagent to the PAA solution and stirring at room temperature for 12 hours. However, on using this procedure, we found that the

chemical imidization did not complete, as shown by the fact that the amide proton peak still remained in the ¹H-NMR spectrum. Instead, chemical imidization was accelerated by heating at 150°C for 2 hours in a nitrogen atmosphere after the addition of the dehydrating reagent and, subsequently, stirring at room temperature for 3 hours, whereby the imidization reaction completed. The isolated PI powder sample had a decreased η_{inh} value of 0.21 dL g⁻¹. However, it was difficult to form a ductile film from the stable PI solution, probably owing to its decreased molecular weight during chemical imidization. Subsequently, we carried out copolymerization with 1,4,4'-APB (30 mol%) with the expectation of a dramatic improvement of the film ductility. The chemical imidization was carried out under the same conditions as those used for the homo H-BTA/BAPS system. The chemically imidized powder of the copolymer had a η_{inh} value of 0.25 dL g⁻¹ and formed a stable DMAc solution with a high solid content of 27.7 wt%. As listed in Table 5, the copolymer (#22) successfully achieved excellent combined properties, ie, a very high optical transparency ($T_{400} = 86.8\%$), a very high T_g (313°C), and good ductility ($\epsilon_{b \max} = 51\%$), all while maintaining practically useful solution processability. Thus, these approaches enabled us to dramatically improve the ductility of the cycloaliphatic PI films that have been believed to be essentially brittle.

4 | CONCLUSIONS

This paper describes the approaches for improving the film ductility of colorless PIs derived from cycloaliphatic monomers. The great difference in film ductility between CBDA/4,4'-ODA and PMDA/4,4'-ODA can be explained on the basis of the ease of chain slippage, which is affected by steric hindrance. The systems using cycloaliphatic diamines suffered problems related to salt formation during the PAA polymerization. This caused termination of the PAA polymerization, an extension of the reaction period, and a significant decrease in the molecular weights of the resultant PAAs, which made the films brittle because of the concomitant decrease in chain entanglement. An effective procedure for solving this problem and enhancing the molecular weights of PAAs is proposed in this work. The systems derived from

t-CHDA with rigid tetracarboxylic dianhydrides (eg, s-BPDA and TA-HQ) resulted in brittle PI films owing to poor chain entanglement, although the PI films showed high optical transparency and low CTE values. On the other hand, a certain result of improving the film ductility was observed when t-CHDA was combined with ether-linked tetracarboxylic dianhydrides (BisA-PA, ODPA, and HQDA), in particular, BisA-PA. MBCHA, which has a much more flexible structure than t-CHDA, was also used as another cycloaliphatic diamine. However, no significant improvement in the ductility was observed against our initial expectation, even when ether-containing ODPA and HQDA were combined with MBCHA. On the other hand, an unexpected toughening effect was observed when PMDA/MBCHA was modified by copolymerization with the minor IPDA contents of 5 to 30 mol%, in spite of the absence of the film-forming ability in the homo PMDA/IPDA system. For example, the copolymer with an IPDA content of 20 mol% showed significantly improved film toughness ($\epsilon_{b \text{ max}} = 57\%$), excellent optical transparency ($T_{400} = 83.7\%$), and a very high T_g (317°C). This toughening effect probably resulted from increased chain slippage.

In this study, the PIs derived from H-BTA with a variety of diamines were also systematically investigated to evaluate the potential of H-BTA-derived systems properly. The results demonstrated that H-BTA could lead to very tough PI film ($\epsilon_{b \text{ max}} > 100\%$) by combination with ether-containing diamines, in contrast to the results of earlier studies. A comparison of the film toughness between the PIs derived from H-BTA and three isomers of H-PMDA showed that H-BTA and H-PMDA are especially effective for enhancing the film toughness. Considering the structural similarity between H-BTA and H-PMDA, it is possible that their unique molecular shape (steric structure) plays a great role in generating high toughness. Our interests also extend to solution processability, and the H-BTA/BAPS(70);1,4,4-APB(30) copolymer achieved very high optical transparency ($T_{400} = 86.8\%$), a very high T_g (313°C), and good ductility ($\epsilon_{b \text{ max}} = 51\%$) while maintaining solution processability. Thus, the approaches proposed in this work enabled us to dramatically improve the ductility of cycloaliphatic PI films that have been believed to be essentially brittle.

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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