Solution-processable Colorless Polyimides with Ultralow CTE

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1. Importance of heat-resistant optically transparent polymeric materials with low CTE.

High-temperaturecolorless polymers are veryimportant materialsfor potential applicationsas plastic substrates, which can be alternatives to current fragile inorganic glass substrates,in image display devices, because they could contribute to weight saving and improvement of mechanical flexibility of the display devices.Evenpoly(ether sulfone) (PES), which has the highest level of T_g (225°C) among current colorless super engineering plastics, is not always sufficient in terms of short-term heat resistance for overcoming high-temperature device fabrication processes (*e.g.*, thin-film transistor deposition processes). Optically transparent polyimides (PI with very high T_gs exceeding 300°Chave been studied as the promising candidate materials. The effective strategy for completely erasing PI film coloration is to use aliphatic (usually cycloaliphatic) monomers either in diamines or tetracarboxylic dianhydrides or both[1–10].

Fig. 1. Progress in research into low-CTE transparent PIs.

However, the use of cycloaliphatic monomers often deteriorates their dimensional stability against heating–cooling cycles in the device fabrication processes, thereby the plastic substrates suffer repetitive significant thermal expansion/contraction, which can be responsible for serious problems (*e.g.*, misalignment and adhesion failure of micro-components, laminate warpage, and transparent electrode breakdown).

The dimensional stability of plastic substrate materials can be enhanced by lowering the linear coefficients of thermal expansion (CTE) along the *X–Y* direction. Low-CTE aromatic PI films are commercialized (*e.g.*, Uplilex-S, Kapton-EN, and Apical-NPI, *etc.*). However, their inherently intensive coloration, which is attributed to intra- and intermolecular charge-transfer interactions [11], disturbs the optical application mentioned above, except the use as plastic substrates in
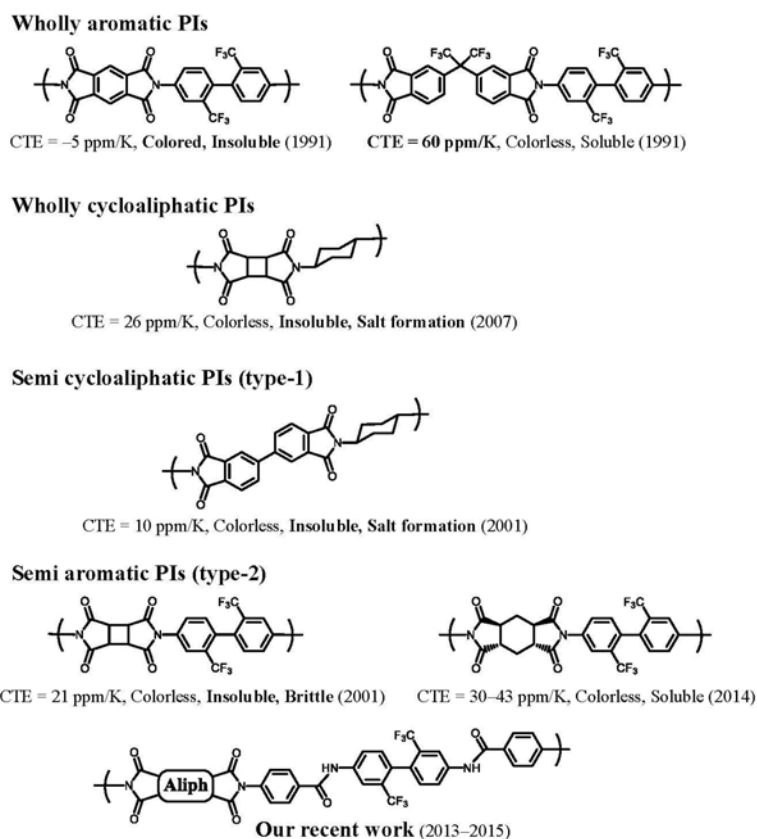
top-emission-mode organic light emitting diode displays [**12**]. Therefore, much attention has been given to optically transparent PI systems simultaneously achieving low CTE, high transparency, high T_g, and sufficient film ductility.In addition to these desired properties, the importance of solution-processability of PIs themselves has been increasing recently as described later. Examples of low-CTE transparent PIs reported in the literature are shown in **Fig.1**.

2. Progress in researchand problems inlow-CTE transparent PI systems.

The PMDA/TFMB system with a rod like chain structure is known to offer a considerably low CTE (often, a negative value) by thermal imidization of its precursor film [poly(amic acid) (PAA)] formed on substrates via its solution casting, which is attributed to prominent chain alignment along to the *X–Y*direction during thermal imidization. We have previously studied the chemical and physical factors influencing the degree of such "imidization-induced in-plane chain orientation" and proposed a mechanism for this phenomenon [**13**]. This PI system is, however, significantly colored and poorly solution-processable due to its insolubility in common solvents. In contrast, the 6FDA/TFMB system is highly soluble in various common solvents at room temperature and leads to an almost colorless PI film by solution casting.However, this system shows no low CTE characteristics [**14**], owing to its non-coplanar/distorted structure at the 6FDA-based diimide moiety [**15,16**], which reduces the overall backbone linearity/stiffness, as a result, disturbs the imidization-induced in-plane chain orientation.
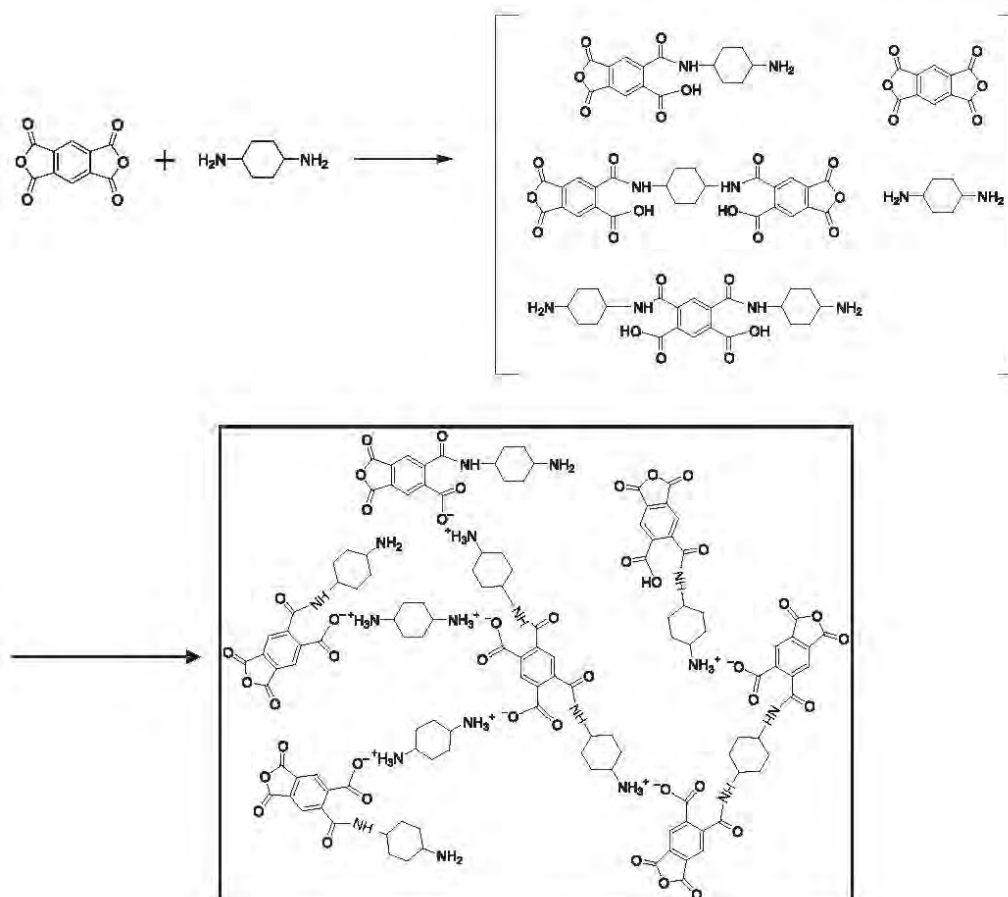

Fig. 2. Schematic illustration of salt formation in PMDA/t-CHDA system.

The strategies byusing cycloaliphatic monomers involve another serious problem; i.e., polymerizability, which is discussed by comparing the inherent viscosities(η_{inh}) of the resultant PAAs or PIs, because it is practically more useful and convenient than the second-order rate constants. When

cycloaliphatic diamines were used, salt is formed in the initial stage of PAA polymerization as poorly soluble precipitate in anhydrous amide solvents. Insystems using cycloaliphatic diamines with distorted structures[*e.g.*, 4,4′-methylenebis(cyclohexylamine), MBCHA], the salt formed is relatively "soft", so that it can be gradually dissolved just by stirring at room temperature for prolong periodsand finally leads to a homogeneous/viscous solution, as observed typically in the PMDA/MBCHA system. In contrast, the use of*trans*-1,4-cyclohexanediamine (t-CHDA) with a relatively high structural planarity/linearity, which is effective in reducing the CTE of the resultant PI films [**17,18**], gives rise to much "tighter" salt than that based on MBCHA. For example, the combination of t-CHDA and PMDA produces quite insoluble salt in anhydrous amide solvents owing to a predictable crosslinked structure of the salt as depicted **Fig. 2**. In this case, once the salt was formed in common amide solvents such as DMAc and NMP at room temperature, the PAA polymerization no longer proceedsno matter how the reaction mixture was stirred for prolong periods or heated at elevated temperatures [**18**].The PAA polymerization for PMDA/t-CHDA can be allowed only under a very limited condition. Acolorlessand low-CTE PI film (10 ppm K^{-1})was obtained with great difficulty by the combination of solvent extraction and thermal imidization of the PAA cast film [**18**]. Thus, the PMDA/t-CHDA system is not compatible to industrial processes, although it must have the makings as low-CTE transparent materials. There are also similar serious problems in the CBDA/t-CHDA system.

On the other hand, the s-BPDA/t-CHDA system gives salt with a medium degree of tightness between PMDA/MBCHA and PMDA/t-CHDA. The salt formed in DMAc can be dissolved in association with an exothermic reactionby heating 100–120°Cfor a shot period and successively stirring without external heating. Solution casting of the homogeneous PAA solution obtained and thermal imidization leads to an almost colorless PI film with a very low CTE value (10 ppm K^{-1}) [**17**]. Thus, the s-BPDA/t-CHDA system seems to be the only practically valuable system achieving both low CTE and high transparency among PI systems derived from cycloaliphatic diamines. However, there is room for further improvement into its mechanical ductility; this PI film was somewhat brittle (elongation at break, ε_b = 10% or lower), although this situation might be inevitable frompredicted poor chain entanglement based on its linear/stiff chain structure. In the s-BPDA/t-CHDA system, the use of NMP instead of DMAc allows the progress of PAA polymerization without heating by simply stirring for prolong periods at room temperature, probably owing toslightly increased solubility of the salt in NMP. However, the use of NMP with a much higher boiling point than DMAc is not always desirable, because it tends to cause appreciable coloration of the resultant PI films probably by the generation of a trace amount of a colored residual impurity from NMP. A*trans/cis* mixture of CHDA leads to "softer" salt than t-CHDA, as a result, the reaction mixtures become more easily homogeneous. However, this approach is not favorable for obtaining highly flexible and low-CTE PI films. These results emphasize how important it is to control the steric structures, when cycloaliphatic units are incorporated in the PI backbones as described later again.
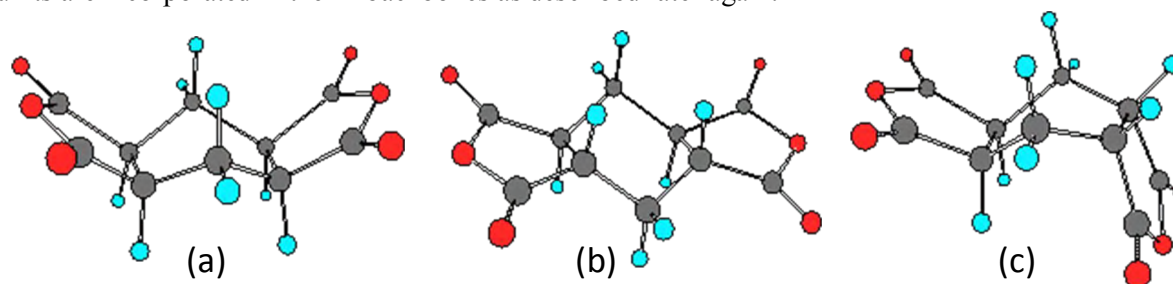

Fig.3. Steric structures of hydrogenated PMDA: (a) H′-PMDA, (b) H′-PMDA, (c) H″-PMDA.

In contrast to these systems using aliphatic diamines, the combinations between cycloaliphatic tetracarboxylic dianhydrides and aromatic diamines are capable of avoiding the salt formation in the initial PAA polymerization process. However, cycloaliphatic tetracarboxylic dianhydrides often have not enough polymerizability to obtain sufficiently high molecular weights of PAAs [7,19]. 1,2,3,4-Cyclobutanetetracarboxylic dianhydride (CBDA) [1], as well as 1,3-dimethyl substituted derivative (DM-CBDA) [9], is a limited case as being highly reactive cycloaliphatic tetracarboxylic dianhydrides. For example, the reaction between CBDA and 2,2′-bis(trifluoromethyl)benzidine (TFMB) easily leads to a homogeneous/viscous solution of PAA with a very high molecular weight ($\eta_{inh} > 2$ dL g^{-1} for the PAA) in common amide solvents. The considerably high reactivity of CBDA can be explained by "strain" in the acid anhydride ring connected to the central cyclobutane ring [9]. The CBDA/TFMB system gives a high quality of colorless PI film via thermal imidization of the PAA cast film, and it shows a low CTE of 21 ppm K^{-1} [17], which is attributed to a relatively high degree of in-plane orientation on the basis of a relatively high overall chain linearity [**Fig. 4 (d)**], although this PI film is somewhat brittle (ε_b= 8% or lower). The high (ring opening) reactivity of CBDA coming from its strained functional groups means that there exists an obstacle against the ring closure (i.e., imidization). Indeed, we experienced that heating at higher temperatures is required to complete imidization for CBDA-based systems than for other systems [*e.g.*, systems from a conventional type of hydrogenated pyromellitic dianhydride (H-PMDA)]. This situation in CBDA is unfavorable in terms of suppressing the film coloration by thermal imidization as much as possible. This problem can be solved if CBDA-based systems are compatible to chemical imidization process, because PI films can be formed by simply drying PI solutions at much lower temperatures than thermal imidization. Unfortunately, chemical imidization of the CBDA/TFMB system is unsuccessful because of gelation by addition of a cyclodehydration reagent into the PAA solution, which is due to the insufficient solubility of the imidized form. These negative trends for the solubility and film ductility are commonly observed in CBDA-derived systems irrespective of diamines [20].

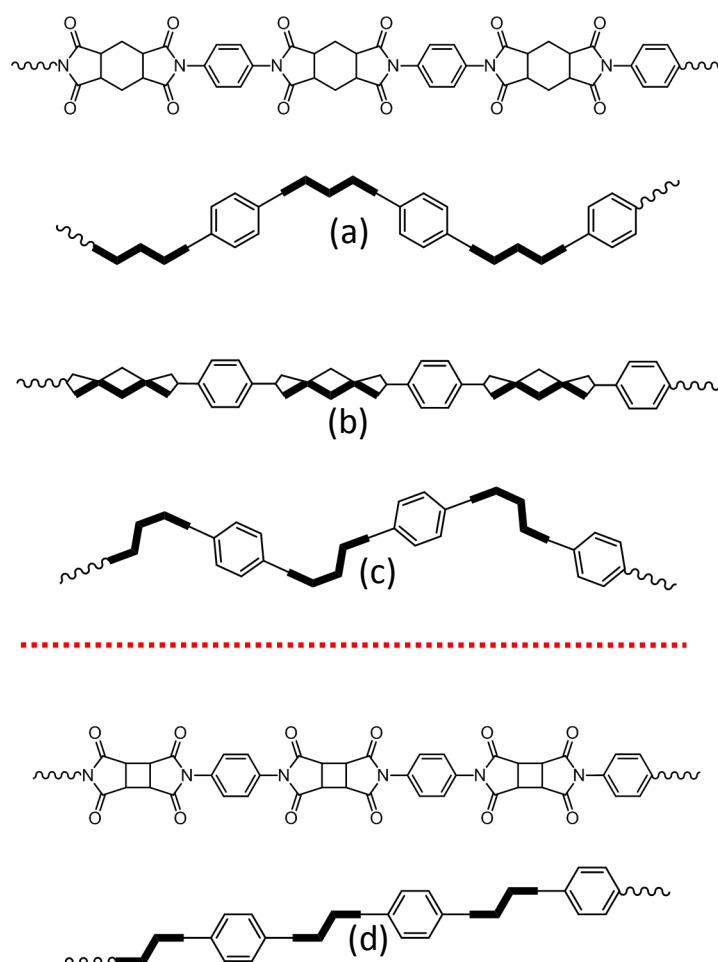CBDA is synthesized by photodimerization of maleic anhydride in solution by UV-irradiation in the

Fig. 4. Schematic illustration of extended PI chains (edge-views of diimide moieties) for systems derived from *p*-PDA and H-PMDA isomers：(a) H-PMDA, (b) H′-PMDA, (c) H″-PMDA, and (d) CBDA.

presence of a photosensitizer such as benzophenone [1]. This manufacturing process is not always suitable for mass production in contrast to common thermal reaction systems without UV-irradiation. Thus, CBDA also involves a cost-saving problem. On the other hand, H-PMDA is a very limited case as a practically useful cycloaliphatic tetracarboxylic dianhydride, which is mass-producible with a lower manufacturing cost via hydrogenation of PMDA as the cheapest aromatic tetracarboxylic dianhydride. However, H-PMDA often leads to brittle PI films on the basis of theirinsufficient molecular weights, whicharise from the insufficient polymerizability of H-PMDAwith common aromatic diamines[8,18];for example, even when highly reactive 4,4′-ODA was used, the η_{inh} value of the resultant PAA remains rather low (~0.5 dL g^{-1}). We proposed a possible mechanism for the lower polymerizability of H-PMDA [8].Another problem arising from the use of H-PMDAis the difficulty of achieving low CTE characteristics [8,18]. Thistrend results from a non-planar/non-linear local steric structure at the H-PMDA-based diimide moieties, as suggested from the steric structure of H-PMDA monomer [**Fig. 3(a)**], which significantly reduces the overall chain linearity [**Fig. 3(a)**], as a result, disturbs the imidization-induced in-plane orientation.To compensate for these shortcomings of H-PMDA, we designed novel highly reactive diamines with very rigid structures to combine with H-MPDA and attempted to simultaneously achieve low CTE, high transparency, high T_g, and sufficient film ductility in combination with a sophisticated polymerization process [21].

We have also investigated anisomer effect on the polymerizability, solubility, and film properties [8,10]. H″-PMDA possessed much higher polymerizability than H-MPDA. A mechanism is proposed for the higher polymerizability of the former; the functional groups of H″-PMDAorientpractically opposite directions each other as shown in **Fig. 3(c)**, thereby a sort of "self-steric hindrance" by a growing chain can be reduced [8]. Another feature of H″-PMDA-based systems is their outstanding solubility and concomitant good chemical imidization process compatibility, which are attributed to loose chain stacking as predicted from their highly distorted chain structures as
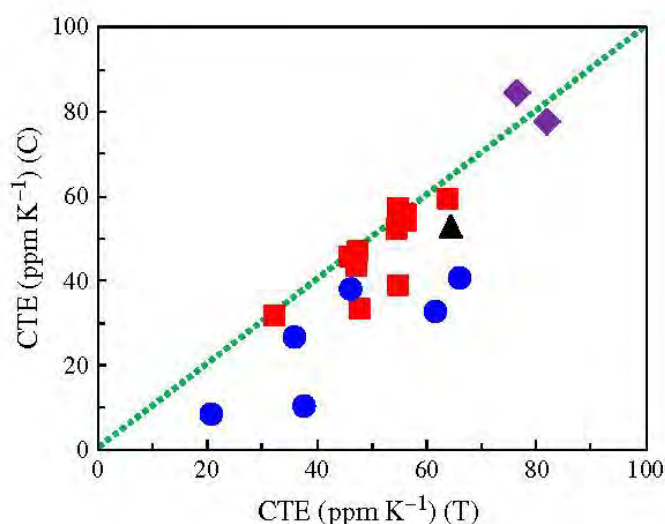

Fig. 5.Effect of imidization method (chemical (C) and thermal (T) imidization processes) on CTE. (▲) 6FDA/TFMB, (♦) HTA-HQ-based systems, (■) H″-PMDA-based systems, and (●) TA-TFMB-based systems. A straight line denoes the relation of Y=X.

shown in **Fig. 4(c)**. However, the use of H″-PMDA was unfavorable for lowering the CTE on the basis of the resultant poor chain linearity.

An additional isomer of H-PMDA, i.e., H′-PMDA [**Fig. 3(b)**] also shows much higher polymerizability than conventional H-PMDA, probably owing to a strain effect at the five-membered anhydride ring [10]. It is expected that the predicted strain in H′-PMDAshould be reflected to its thermodynamic stability.Then we estimated the standard enthalpy of formation for the H-PMDA family at 25°C($\Delta H_f°_{298}$) on the basis of the heat of combustion (Q_c), which was measured on an advanced adiabatic bomb calorimeter and obtained that $\Delta H_f°_{298} = -8.88 \times 10^2$ kJ mol^{-1} for

H′-PMDAand $\Delta H_f°_{298}$ =−1.00×10^3 kJ mol^{-1} H-PMDA.The results suggest that,when compared at 25°C, H′-PMDA is somewhat thermodynamically less stable than H-PMDA, probably relating to thestrained structure of the former [10].

We have previously proposed for poly(ester imide)s (PEsI) systems that the degree of the backbone linearity in the extended chain forms can be a major indicator representinghow some focused PEsI systems are favorable for lowering the CTE [22]. According toa similar criterion, as shown in **Fig. 4(a)** and **(c)**, the significantly meandering chain forms in the PI systems derived from H-PMDA and H″-PMDA suggest that these systems are almost difficult to lead to low CTE, which is in accordance with the actual experimental results. On the other hand, when H′-PMDAwas combined with rigid/linear structures of diamines, there would be a great chance of obtaining lower CTE as suggested from its linear/rigid main chain form in **Fig. 4(b)**. Indeed, solution casting under a controlled drying condition for the chemically imidized H′-PMDA/TFMB system with a very high molecular weight allowed to form a colorlessand ductile PI film with a significantly decreased CTE of 29.8 ppm K^{-1} [10].

On the basis of this concept, we havepreviously synthesized novel ester-incorporating cycloaliphatic tetracarboxylic dianhydrides using a *trans*-type hydrogenated trimellitic anhydride (H′-TMA)[23], which is an isomer of the conventional *cis*-type H-TMA [7]. These systems showed a positive effect of the steric structure control on low CTE property [23].

CBDA is also advantageous for lowering the CTE of PI films as expected from its edge-view with a crank-shaft-like steric structure [**Fig. 4(d)**], because its overall chain linearity can be almost maintained when CBDA was combined with diamines with rigid/linear structures.

Fig. 6. CTE–transparency–solubility diagram. Open and closed symbols denote soluble (C) and insoluble (T) systems, respectively.

Thus, it is very importantto control the steric structures of cycloaliphatic unites in order to accomplish low CTE and high transparency. In addition, we describe that chemical imidization process compatibility can be also the key factor for aiming at the present goal. **Fig. 5** shows an impact of imidization methodon CTE, where the ordinate and abscissa represent the CTE values of PI films prepared via chemical (C) and thermal (T) imidization processes, respectively [24]. In our work, when the imidized forms were highly soluble, chemical imidization method was applied; the chemically imidized PI power samples were dissolved in amide solvents (*e.g.*, DMAc) or less hygroscopic solvents (*e,g.*, *γ*-butyrolactone and cyclopentanone) to obtain homogeneous solutions with a high solid content (> 10 wt%), and the PI solution was coated on a glass substrate and dried at established temperatures. As shown in **Fig. 5**, when compared between the same compositions of PI films prepared by different imidization routes, all the data points were essentially plotted in the area below
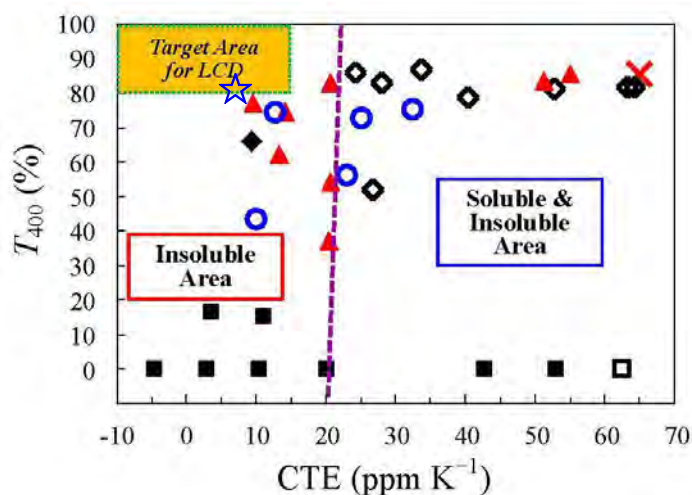
the $Y = X$ line. This result indicates that the film preparation process via chemical imidization is superior to the conventional thermal imidization process in obtaining lower CTE.The superiority of the film preparation process via chemical imidization is also observed in the transparency of PI films. This is due to the situation that PI films can be easily formed by solution casting at a much lower (drying) temperature than by thermal imidization. A similar trend was also observed in transparent aromatic PEsI systems that we previously investigated [25]. The low CTE property is attributed to high extents of in-plane chain orientation occurring in the solution casting (solvent evaporation) process, although there seems to be no prominent driving forces for dramatically enhancing the in-plane orientation just by solution casting without mechanical stretching and any external fields (electric and magnetic fields). A possible mechanism is proposed for this phenomenon [10].

3. Ultralow-CTE colorless PI film obtained by solution casting.

4,4′-Diaminobenzanilide (DABA) is known as the most effective diamine in obtaining lower-CTE PI films through thermal imidization. In some cases, DABA is superior to TFMB from this point of view. This trend is probably true even when PI films are prepared via the chemical imidization process mentioned above. Our initial attempt was to further decrease the CTE of H′-PMDA/TFMB by copolymerization with DABA while keeping chemical imidization process compatibility. However, the use of DABA as a comonomer caused gelation by addition of a chemical imidization reagent into the PAA solution even at a minor DABA content of 30 mol%, owing to thesignificantly decreased solubility of the resultant copolyimide. Thus, the structural modification with DABA for lowering the CTE was unsuccessful. On the other hand,the use of a novel diamine (AB-TFMB), which involves both structural features of TFMB and DABA as shown at the bottom in **Fig. 1**, led to a PI system compatible to chemical imidization process due to its excellent solubility, when it was combined with H′-PMDA.The dramatically enhanced solubility of H′-PMDA/AB-TFMB can be explained by effectively disturbed interchain amide–amide hydrogen bondsby 2,2′-CF$_3$-assisted highly twisted biphenylene units, which werepositioned adjacent to the amide linkages. The H′-PMDA/AB-TFMB film prepared via chemical imidization also led to a colorless and flexible PI film with a relatively lowCTE of 25.4 ppm K^{-1}.An alternative combination of CBDA and AB-TFMB was effective in further decreasing the CTE. However, this approach caused a significant decrease in the solubility, as a result, disturbed the application of chemical imidization process.

The combination of structural optimization of CBDA/AB-TFMB (shown at the bottom of **Fig. 1**) using a proper comonomer and the application of the film preparation process via chemical imidization led to a sufficiently ductile (ε_b^{max}>30%) and colorless PI film(T_{400}>80%) with an ultralow CTE of 7.3 ppm K^{-1} [20]. **Fig. 6** displays CTE–transparency–solubility diagram.A target area (temporally, CTE ≤ 15 ppm K^{-1}, T_{400}≥ 80%) is also established in this figure for the optical applications mentioned above. Transparent PI systems that we have previously examined (◊) showed significantly improved heat resistance (T_g) in comparison with engineering plastics such as PES (×) while keeping good transparency, however, the formers did not show low CTE characteristics. In contrast, the s-BPDA/t-CHDA systemgives an almost colorless PI film with a very low CTE (10 ppm K^{-1}) by thermal imidization of the corresponding PAA cast film on a substrate, however, does not allow the formation of a stable PI solution because of its essential insolubility. A trend is observed in **Fig. 6**; conventional PI systems tend to abruptly lose both of thetransparency and solubility below CTE~20 ppm K^{-1}. On the other hand, our optimized system mentioned above (☆) overcame the

difficulty of simultaneously achieving low CTE, high transparency, and solution-processability as indicated from the data point positioned within the target area. Thus, our optimized system, which achieved an ultralow CTE of 7.3 ppm K^{-1}, high transparency (T_{400}= 80.6%, YI = 2.5), a very high $T_g$of 329 °C, sufficient ductility (ε_b^{max}>30%), and good solution-processability, is practically useful as novel coating-type plastic substratematerials with excellent dimensional stability [**20**].

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