

Crosslinkable polyimides obtained from a reactive diamine and the effect of crosslinking on the thermal properties



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ABSTRACT

This study presents novel thermally crosslinkable polyimides (PIs) obtained using a diamine (3,5-DABA) containing an amide (CONH₂) group. This diamine was highly reactive with pyromellitic dianhydride (PMDA), and the equimolar polyaddition in *N*-methyl-2-pyrrolidone at room temperature led to a high molecular weight poly(amic acid) (PAA) without causing gelation or precipitation. The results suggest that the amide side group of 3,5-DABA does not participate in PAA polymerization at room temperature. A PI system derived from PMDA and 2,2'-bis(trifluoromethyl)benzidine (TFMB), which has an ultralow coefficient of thermal expansion in the *X*-*Y* direction, was modified by copolymerization with 3,5-DABA. The FT-IR spectra suggested that the amide side groups in the 3,5-DABA-modified PIs can react with adjacent imide C=O groups to form crosslinks on heating above 350 °C, even in the absence of sufficient molecular fluidity. This behavior is attributed to the presence of a very high concentration of imide C=O groups distributed in the vicinity of the amide reactive groups. A crosslinking mechanism is proposed in this paper. An effect of crosslinking on the volumetric coefficient of thermal expansion (β) was investigated by comparing the 3,5-DABA-modified PIs with their crosslinker-free counterparts, i.e., a PI derived from PMDA with TFMB and *m*-phenylenediamine (*m*-PDA). At a 3,5-DABA content of 20 mol%, the 3,5-DABA-modified copolymer film showed a lower β value than that of the corresponding *m*-PDA-containing copolymer. The difference in the β values of these copolymers increased with increasing comonomer (3,5-DABA or *m*-PDA) content. Thus, the use of 3,5-DABA is effective in reducing the β values through crosslinking. Dynamic mechanical analysis showed that crosslinking also contributed to enhancing the storage modulus and broadening the glass transition. 3,5-DABA was also applied to modify the properties of a thermoplastic poly(ester imide) (PEsI). The thermal crosslinking of the 3,5-DABA-modified PEsI caused a T_g enhancement of about 30 °C and an appreciable decrease in the thermoplasticity. Thus, the present approach is also effective in improving the low- T_g character of thermoplastic PIs.

1. Introduction

Aromatic polyimides (PIs) are the most reliable high-temperature polymers resistant to the solder-reflowing process at 260 °C. Therefore, they have been applied as electrical insulating layers in a variety of electrical and electronic devices [1–9]. Because of recent rapid developments in these devices, demand for further property improvement and the addition of new functionalities to conventional PI systems has increased. There are various approaches for improving the properties of PIs: (1) chemical modifications using well-designed monomers [10], combinations of conventional monomers (copolymerization), and molecular weight controls [11] and (2) physical modifications including controls of chain orientation [12–14], aggregated structures [15], and crystallization [13,16–18].

Chemical crosslinking reactions are another important means to improve the properties of PIs, although their current application targets are mostly confined to addition-type imide oligomer systems that are end-capped with mono-functional amines or dicarboxylic anhydrides containing crosslinkable groups [19]. In addition-type systems, the role of the curing reactions is primarily to enhance the molecular weights to obtain sufficient mechanical strength in the cured resins after the melt-processing of the initial oligomers. A variety of terminal reactive groups have been applied, including maleimide [20], nadiimide (NI) [21], 4-ethynylphthalimide [22], 4-phenylethynylphthalimide [23,24], benzoxazine (BOZ) [25–27], and benzocyclobutene groups [28]. These terminal groups can react only in the molten state through intermolecular collisions.

In contrast, photo-crosslinking reactions can occur in principle

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without molecular fluidity. For example, PIs derived from benzophenonetetracarboxylic dianhydride (BTDA) and alkyl-substituted aromatic diamines produce crosslinks upon ultraviolet-visible irradiation via interchain hydrogen abstraction of the excited triplet-state BTDA-based diimide unit from the adjacent alkyl groups [29]. However, the hydrogen donors and acceptors must be very close (in other words, there must be a very high content of these reactive units) for effective hydrogen abstraction.

Takeichi et al. [30] synthesized ethynyl (acetylene)-containing diamines and obtained high-molecular weight crosslinkable PIs using these diamines, where the crosslinkable ethynyl groups were introduced into the main chains. An ethynyl-containing tetracarboxylic dianhydride [4,4'-(ethyne-1,2-diyl)diphthalic anhydride], which has only recently become commercially available, can also be used to obtain analogous crosslinkable PIs [31]. These crosslinkable PIs contain a rather high content of ethynyl groups in the main chains to ensure effective intermolecular encountering/collision between the reactive groups during the curing reactions. Thus, when the content of ethynyl groups is low, the crosslinking reaction does not occur easily in the non-molten states. If a new type of monomer that can exert crosslinking functionality even when present in low concentrations were to become available, a focused PI system could be modified significantly by copolymerization with a minor content of such a functional monomer while maintaining the chain structures and the inherent properties of the original PI.

PI systems with linear/rigid backbone structures have been accepted to provide PI films with low CTE values in the *X*–*Y* direction (in-plane CTE) [32,33]. This is attributed to the high degree of PI chain alignment in the *X*–*Y* direction (in-plane orientation), which is induced during the thermal imidization of the PI precursor films formed on substrates [12,13] or the simple casting process (coating and drying) of PI solutions [34,35]. If these PIs could be chemically crosslinked while maintaining a low in-plane CTE property, the thermal expansion behavior in the thickness (*Z*) direction or three-dimensions could also be controlled. However, crosslinking in the molten states, which is usually indispensable for ensuring sufficient diffusional motions of the reactive groups, causes orientational relaxation of the main chains; consequently, the original low in-plane CTE property disappears. Therefore, a key strategy to solve this issue is to create novel PI systems where crosslinking reactions can occur effectively even in non-molten states with low content of crosslinkable groups. Thus, the potential applications of PIs with three-dimensionally controlled CTEs can be considered; e.g., their use as interlayer dielectrics in multi-layered circuit boards having a dramatically increased number of layers.

In this study, we present a new diamine and report the effects of the crosslinking reaction on the thermal properties of the resultant crosslinkable PIs.

2. Experimental

2.1. Materials

2.1.1. Monomer synthesis

2.1.1.1. 3,5-Diaminobenzamide (3,5-DABA). This amide-pendant diamine was synthesized according to the reaction scheme shown in Fig. 1. In detail, in a 500 mL-flask, 3,5-dinitrobenzoylchloride (3,5-DNBC, 13.86 g, 60 mmol) was dissolved in toluene (144 mL). To this solution, a 28% ammonia aqueous solution (100 mL) was added, and

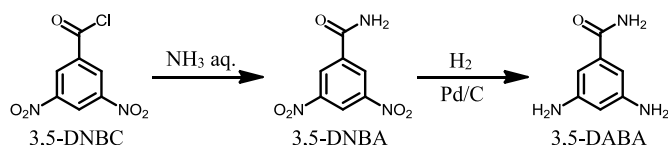


Fig. 1. Reaction scheme for the synthesis of 3,5-DABA.

the solution was vigorously stirred at room temperature for 1 h. A white precipitate formed, and this was collected by filtration, repeatedly washed with water, and dried at 100 °C for 12 h under vacuum (yield: 77%). FT-IR (KBr plate method, cm⁻¹): 3350/3168 (amide, N-H stretching), 1676 (amide-I, C=O stretching), 1631 (NH₂, deformation), 1550 (amide-II, C=O + NO₂ asymmetric stretching), 1345 (NO₂ symmetric stretching). ¹H NMR [400 MHz, DMSO-*d*₆, δ, ppm]: 9.07 (sd, 2H, *J* = 2.0 Hz, 2,6-protons of 3,5-dinitrobenzamide (3,5-DNBA)), 8.96 (st, 1H, *J* = 2.0 Hz, 4-proton of 3,5-DNBA), 8.67 (s, 1H, CONH_aH_b), 8.03 (s, 1H, CONH_aH_b). The melting point was determined from the endothermic peak by differential scanning calorimetry (DSC) and found to be 183 °C. These data confirm that the product is the desired dinitro compound (3,5-DNBA).

The nitro groups of 3,5-DNBA were reduced as follows. In a three-necked flask, 3,5-DNBA (3.05 g, 14.43 mmol) was dissolved in ethanol (60 mL), and Pd/C (0.33 g) was added as a catalyst. The reaction mixture was refluxed at 80 °C for 8 h in a hydrogen atmosphere, and the reaction progress was monitored by thin layer chromatography. After the reaction, the catalyst residue was filtered out, and the filtrate was concentrated with an evaporator. The precipitate was collected by filtration, and dried at 100 °C for 12 h under vacuum. A reddish-brown product was obtained with a yield of 60%. FT-IR (KBr plate method, cm⁻¹): 3409/3213 (NH₂), 1648 (amide, C=O). ¹H NMR [400 MHz, DMSO-*d*₆, δ, ppm]: 7.44 (s, 1H, CONH_aH_b), 6.90 (s, 1H, CONH_aH_b), 6.23 (sd, 2H, *J* = 2.0 Hz, 2,6-protons of 3,5-DABA), 5.93 (st, 1H, *J* = 2.0 Hz, 4-proton of 3,5-DABA), 4.81 (s, 4H, 3,5-NH₂). Elemental analysis: Calcd. (%) for C₇H₉O₁N₃ (151.17 g mol⁻¹): C, 55.62; H, 6.00; N, 27.80. Found: C, 55.67; H, 5.97; N, 27.73. Melting point (DSC): 151 °C. These data confirm that the product is the desired diamine (3,5-DABA).

2.1.1.2. Resorcinol bis(trimellitate). An ester-linked tetracarboxylic dianhydride (TA-RC) was synthesized from trimellitic anhydride chloride and resorcinol (RC) in anhydrous tetrahydrofuran in the presence of pyridine in a similar manner to the procedures described in our previous paper [34]. The product was purified by recrystallization from a mixed solvent (acetic anhydride/toluene, 11/50, v/v). FT-IR (KBr plate method, cm⁻¹): 3110/3064 (C_{Ar}-H), 1855/1772 (dicarboxylic anhydride, C=O), 1740 (ester, C=O), 1479 (phenyl), 1224 (Ar-O). ¹H NMR [400 MHz, DMSO-*d*₆, δ, ppm]: 8.67–8.63 [m, 4H (3.98H), 3,3'- + 5,5'-protons of the phthalic anhydride (PAN) unit], 8.29 [d, 2H (2.00H), *J* = 7.8 Hz, 6,6'-protons of PAN], 7.65 [t, 1H (1.00H), *J* = 8.3 Hz, 5-proton of the RC unit], 7.56 (st, 1H (0.97H), *J* = 2.2 Hz, 2-proton of RC), 7.42 [dd, 2H (2.00H), *J* = 8.2, 2.2 Hz, 4,6-protons of RC]. Elemental analysis: Calcd. (%) for C₂₄H₁₀O₁₀ (458.34 g mol⁻¹): C, 62.89; H, 2.20. Found: C, 62.51; H, 2.47. Melting point (DSC): 210 °C. These data confirm that the product is the desired compound (TA-RC).

2.1.2. Other monomers and raw materials

The abbreviations, commercial sources, pre-treatment conditions, and melting points for the other monomers and raw materials used in this study are listed in Supporting Data 1. The structures of the monomers are shown in Fig. 2.

2.1.3. Polymerization and thermal imidization for PI film preparation

The PI precursors [poly(amic acid)s (PAAs)] were prepared by the equimolar polyaddition of tetracarboxylic dianhydrides and diamines according to the scheme shown in Fig. 2. A typical polymerization procedure was carried out as follows. The diamine (2 mmol) was dissolved in anhydrous *N*-methyl-2-pyrrolidone (NMP). Then, tetracarboxylic dianhydride powder (2 mmol) was added to the diamine solution at room temperature with continuous stirring. The initial total solid content was 30 wt%. The reaction mixture was stirred at room temperature in a sealed bottle until it became homogeneous and had the maximum solution viscosity (typically after 72 h). If necessary, the

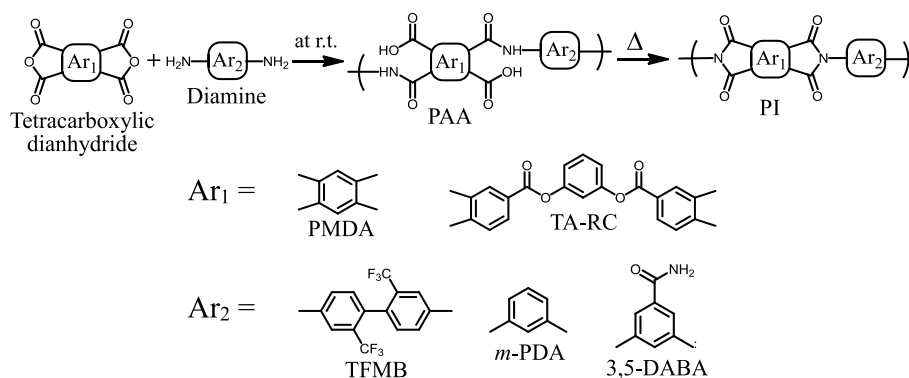


Fig. 2. Reaction schemes for the polyaddition and thermal imidization of PAAs, and the structures of the monomers used in this study.

reaction mixture was gradually diluted with the minimal quantity of the same solvent to ensure effective magnetic stirring. The PI films were prepared via thermal imidization. The PAA solution was bar-coated on a glass substrate and dried at 80 °C for 3 h in an air-convection oven. For non-thermoplastic systems, the PAA cast films were imidized at 250 °C for 1 h, then heated at 350 °C for 1 h on the substrate under vacuum, and finally, annealed at 340 or 350 °C for 1 h under vacuum without the substrate to remove residual stress. For the thermoplastic systems, the PAA cast films were imidized at 150 + 300 °C for 1 h on the substrate under vacuum. The films were additionally heated at 350 °C for 1 h under vacuum to promote crosslinking. These thermal conditions were adjusted to obtain better-quality PI films in some cases.

In this paper, the chemical compositions of the PAA and PI systems are denoted using the abbreviations of the monomer components used, i.e., tetracarboxylic dianhydride (A) and diamine (B) as A/B for homopolymers and A/B₁B₂ for copolymers.

2.2. Measurements

2.2.1. Inherent viscosities

The reduced viscosities (η_{red}) of PAAs were measured in NMP at a solid content of 0.5 wt% at 30 °C using an Ostwald viscometer. The polyelectrolyte effect of the PAAs prevents the determination of the inherent viscosities (η_{inh}) by extrapolation to zero concentration. Therefore, the η_{red} values of PAAs are often treated as the η_{inh} values.

2.2.2. Dynamic mechanical properties and thermal stability

The storage (E') and the loss modulus (E'') of PI specimens [10 mm wide, 45 mm long (chuck-to-chuck distance: $L_0 = 25$ mm), typically 20 μ m thick] were measured by dynamic mechanical analysis (DMA) in the temperature range of 30–450 °C at a heating rate of 5 °C min⁻¹ in a nitrogen atmosphere on a dynamic mechanical analyzer (TA Instruments, DMA-Q800). The measurements were conducted at a frequency of 0.1 Hz and an amplitude of 0.1% elongation to determine the glass transition temperature (T_g) from the peak temperatures in the E'' curve. The specimens mounted on the sample holder were surrounded by a wire-mesh basket to minimize the temperature distribution.

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

2.2.3. Optical properties

The XY-direction (n_{xy}) and Z-direction (n_z) refractive indices of the PI films were measured at a wavelength of 633 nm using an Abbe

refractometer (Atago, 4T, n_D range: 1.47–1.87) equipped with a polarizer by using a contact liquid (sulfur-saturated methylene iodide with $n_D = 1.78$ –1.80). A monochromated light beam was introduced to the refractometer through an optical fiber cable connected to a fluorescence spectrometer (Hitachi, F-2000) equipped with a Xe lamp (bandpass: 10 nm), as shown in Supporting Data 2. The color compensation dial of the refractometer was set at 30 when measuring at wavelengths different from the D-line (589 nm) of the sodium lamp. The raw refractive index data were corrected using a formula supplied by Atago Co., Ltd.

The thickness-direction birefringence (Δn_{th}) of the PI films, which represents the relative extent of chain alignment in the film plane (X–Y) direction, was calculated using Eq. (1).

$$\Delta n_{th} = n_{xy} - n_z \quad (1)$$

2.2.4. Linear coefficients of thermal expansion (CTE) in the XY-direction

The average XY-direction CTEs (α_{xy}) for PI specimens (15 mm long, 5 mm wide, and typically 20 μ m thick) in the glassy region were measured using thermomechanical analysis (TMA) between 100 and 200 °C at a heating rate of 5 °C min⁻¹ on a thermomechanical analyzer (Netzsch, TMA 4000) with a fixed static load (0.5 g per unit film thickness in μ m, i.e., 10 g load for 20 μ m-thick films) in a dry nitrogen atmosphere. In these measurements, after the preliminary heating run to 120 °C and successive cooling to room temperature in the TMA chamber, the data were collected from the second heating run to remove the influence of adsorbed water.

2.2.5. Z-direction CTE and volumetric coefficients of thermal expansion

The Z-direction CTEs (α_z) of the PI films in the glassy region were estimated by combining a light interferometric thickness meter (Filmetrics, F-20, measuring range: 15 nm–70 μ m) and a hot stage (Mettler Toledo, FP82HT) controlled by a central processor (Mettler Toledo, FP 90). The setup of the apparatus is shown in Fig. 3. Film specimens with good flatness were placed on a silicon wafer in a sample holder on the hot stage. The film thickness was measured in the range from 100 to 200 °C in intervals of 10 or 20 °C while holding at each temperature step for 10 min for the thickness measurements. The α_z values were determined from the slope of the thickness–temperature plots.

The thickness was determined using accessory software through curve-fitting of the measured reflectance spectra with fringe patterns to the theoretically simulated ones by inputting a surface roughness parameter and the n_{xy} values at each temperature step. The latter was estimated from the n_{xy} value measured at room temperature and the thermo-optic coefficient (dn_{xy}/dT), which was assumed to be approximately -100 ppm K⁻¹ based on previous reports that the films of some rigid PI systems formed on Si substrates have dn_{xy}/dT values ranging from -90 to -100 ppm K⁻¹ in the glassy regions [36,37]. In some cases, these input parameters were finely adjusted at each temperature step to maximize the fitting parameter (the goodness of fit).

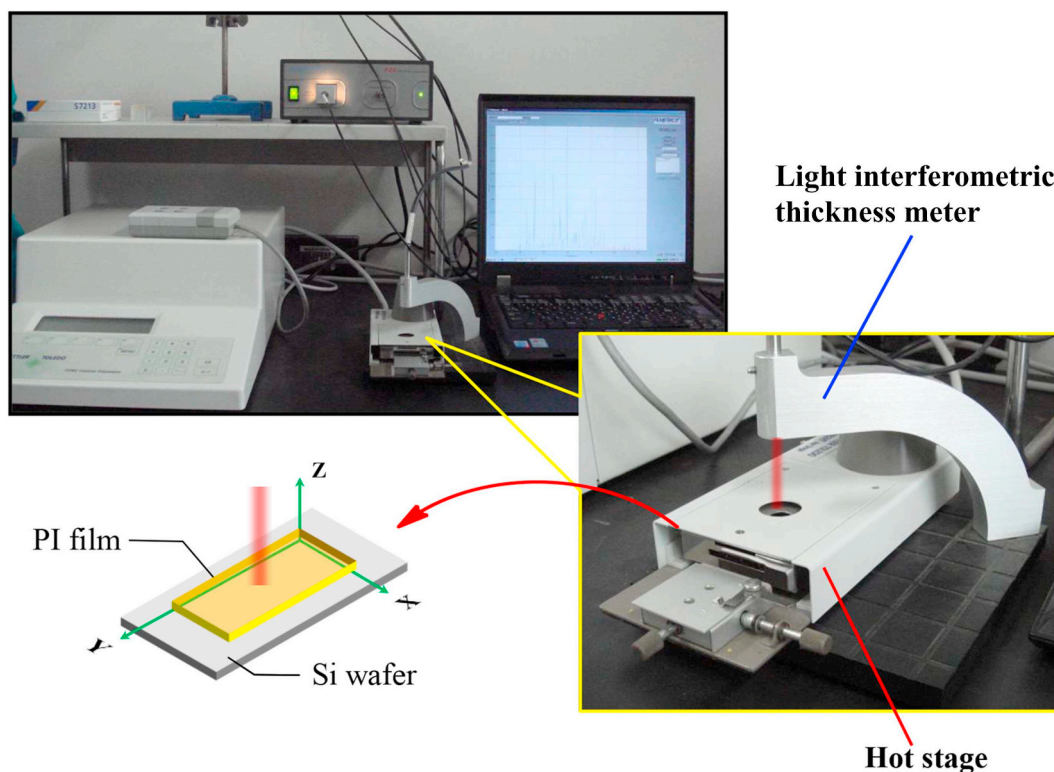


Fig. 3. Apparatus used for the measurement of film thickness as a function of temperature.

The volumetric coefficients of thermal expansion (β) for non-stretched PI films were calculated using the measured values of α_{xy} and α_z using Eq. (2).

$$\beta = \alpha_x + \alpha_y + \alpha_z = 2\alpha_{xy} + \alpha_z \quad (2)$$

3. Results and discussion

3.1. Polymerizability of 3,5-DABA and reactivity of the amide side group at elevated temperatures

The amide (CONH_2) group of 3,5-DABA is not expected to participate in PAA polymerization because of its reduced nucleophilic reactivity induced by the electron-withdrawing C=O group. Indeed, 3,5-DABA behaved as a common bifunctional diamine monomer because the equimolar polyaddition of 3,5-DABA and PMDA in NMP at room temperature caused neither gelation nor precipitation and led to a viscous and homogeneous PAA solution with a very high η_{inh} (2.18 dL g^{-1}). Thus, no crosslinking occurred during the polymerization. The resultant very high η_{inh} value also shows that the 3,5-diamino groups of 3,5-DABA have sufficient reactivity comparable to those of common diamines such as 4,4'-oxydianiline (4,4'-ODA).

On the other hand, when heated at elevated temperatures in the solid state, the amide (CONH_2) side groups introduced in the PIs can be activated. The expected crosslinking reaction mechanism in the amide-pendant PIs is shown in Fig. 4(a). This reaction probably occurs even in the glassy state without sufficient molecular fluidity because of the presence of the imide C=O groups in the different chains, which are distributed with a very high concentration in the vicinity of the amide side groups. This idea was inspired by the intramolecular reaction in the polyimide-isoindoloquinazolinone (PIQ) system [Fig. 4(b)], which was prepared by using partially 3-amide-substituted 4,4'-ODA, where the amide group is located at the *ortho*-position of the amino group [38,39]. In contrast, the use of 3,5-DABA having a *meta*-substituted amide group makes such an intramolecular reaction difficult because of

the intramolecular distance restriction between the CONH_2 and adjacent imide C=O groups; instead, a crosslinking reaction is expected to occur, as shown in Fig. 4(a).

The crosslinking reaction can be observed by FT-IR spectroscopy. Fig. 5 shows the spectral change with increasing heat treatment temperature for the PMDA/TFMB(80);3,5-DABA(20) system. The PAA-inherent infrared bands (broad O-H stretching band of the hydrogen-bonded COOH groups around 2600 cm^{-1} and the amide C=O stretching band around 1530 cm^{-1}) significantly reduced on heating the PAA film at 250°C , indicating the significant progress of the imidization reaction. The spectrum recorded after heating at 250°C also showed an N-H stretching band from the CONH_2 side group at 3370 cm^{-1} , as also observed in low-molecular weight benzamide [40] and 3,5-DNBA (dinitro compound). As observed in Fig. 5, the CONH_2 band was significantly reduced when heated at 350°C , probably indicating that the crosslinking reaction was effective, despite the absence of sufficient molecular fluidity below the T_g (406°C). The extent of decrease ($R\%$) in the CONH_2 band was estimated to be 80% when heated at 350°C using an internal standard (the 1,4-phenylene stretching band at 1500 cm^{-1}) on the assumption that $R = 0\%$ and 100% for the samples heated at 200 and 450°C , respectively.

In the infrared spectrum of the PAA film, the CONH_2 band is not observed at 3370 cm^{-1} . This is probably attributed to a significant low-frequency shift of the CONH_2 band, which can occur by hydrogen-bonding between the CONH_2 side groups and the residual NMP molecules. This assumption is supported by the fact that NMP-cast PAA films retain a large amount of the solvent (20–30 wt%), and the residual NMP molecules form hydrogen-bonds with the NHCO groups in the PAA main chains [41,42].

3.2. Effect of crosslinking on the volumetric thermal expansion behavior

The crosslinkable PIs have a better chance of controlling their volumetric thermal expansion behavior while maintaining a low X–Y direction CTE. Thus, the ultralow-CTE PMDA/TFMB system [43], which

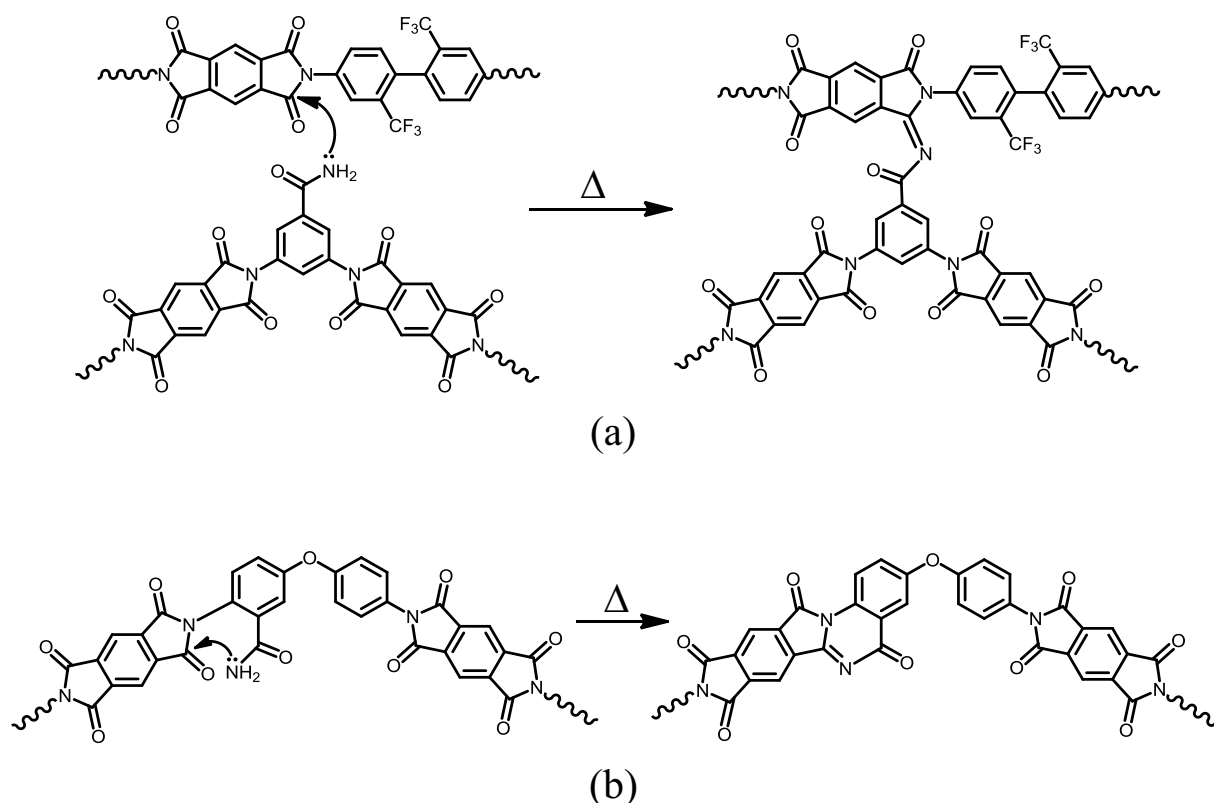


Fig. 4. Expected reaction mechanisms between the CONH₂ groups and imide groups: (a) thermal crosslinking in 3,5-DABA-derived PIs and (b) intramolecular reaction in PIQ.

has CTEs empirically ranging from -5 to 1 ppm K⁻¹ depending on the processing conditions (e.g., thermal history for imidization, PAA molecular weight, and film thickness), was modified with 3,5-DABA, and the β values of the PMDA/TFMB-based copolymers were estimated as a function of the 3,5-DABA content. Finally, these PIs were heated at 350 °C to promote crosslinking while avoiding local ordering, which occurs when the samples are heated at higher temperatures, i.e., 400 °C, as observed in the PMDA/TFMB system [44]; the local ordering probably disturbs to observe effects of crosslinking on the properties. The estimated thermal expansion coefficients (α_{xy} , α_z , and β) are summarized in Table 1 together with the other thermal properties, except for those of the PMDA/3,5-DABA homo PI film, which was significantly cracked after thermal imidization on the substrate.

The β values of the PI films have so far been evaluated directly by dilatometry [45] and indirectly from a combination of the α_{xy} (by TMA) and α_z values, which were determined from the capacitance measurements [46] and optical interferometry [31,47–49]. In the present work, the α_z values of the free-standing PI films were estimated from the slope of the linear thickness–temperature plot, as shown in Supporting Data 3.

As listed in Table 1, the PMDA/TFMB PI film (sample #1) showed very high α_z and β values. The value of the latter is approximately consistent with the data reported in the literature [49]. The very high α_z value probably results from the combined effect of the considerably high degree of in-plane chain orientation and the less crystalline structure [44]. Increasing the 3,5-DABA content in the PMDA/TFMB-based copolymers resulted in both an increase in α_{xy} and a decrease in α_z , as shown in Table 1. This is attributed to a gradual decrease in the degree of in-plane chain orientation, which arises from the reduced overall main chain linearity induced by 3,5-DABA. This corresponds to the fact the Δn_{th} value reduced from 0.129 (for the 3,5-DABA-free system) to 0.071 (for the system with 3,5-DABA = 20 mol%). Thus, the effect of crosslinking on α_z is not always distinct from its dependence on

the 3,5-DABA content. Instead, the effect of crosslinking likely appears in the change in β with increasing 3,5-DABA content rather than α_z . To clarify the effect of crosslinking further, we compared the β values for the 3,5-DABA-modified copolymers with those for the crosslinker-free counterpart, i.e., the copolymers prepared using *m*-PDA. As shown in Fig. 6, at a comonomer (3,5-DABA or *m*-PDA) content of 20 mol%, the 3,5-DABA-modified copolymer showed a lower β value than that of the corresponding crosslinker-free copolymer. The difference in the β values of these copolymers increased with increasing comonomer content. The prominent β decrease observed in the 3,5-DABA-modified system most likely results from crosslinking.

The comparison between the samples heated at 250 and 350 °C may be useful for observing the effects of crosslinking. However, we did not carry out this approach in this study; in the 3,5-DABA-modified PMDA/TFMB-based systems, heating at 250 °C leads to a “half-backed” PI film with incomplete imidization (as suggested by the presence of the residual NHCO band as a shoulder of the 1720 cm⁻¹ band in Fig. 5) and loosely stacked/less ordered structures. On the other hand, heating at 350 °C causes practical full imidization, local ordering, and crosslinking. Thus, the effects of crosslinking are masked by the other significant changes (progress of imidization and local ordering).

The effects of crosslinking were also observed in the dynamic mechanical properties. Typical E' curves of the copolymers with and without 3,5-DABA, which were both heated at 350 °C in the final step, are shown in Fig. 7. A distinct T_g was observed around 400 °C in the 3,5-DABA-free copolymer film. On the other hand, for the corresponding 3,5-DABA-modified system, the glass transition became almost undetectable in the E' curve. A similar change in the E' curves has also been observed in crosslinked NI-terminated imide oligomer systems [50]. The flattening of the E' curve is preferable for various electronic and optoelectronic applications in terms of the significantly enhanced thermal dimensional stability over a broad temperature range. The 3,5-DABA-modified copolymer film also showed a much higher E' value (ca.

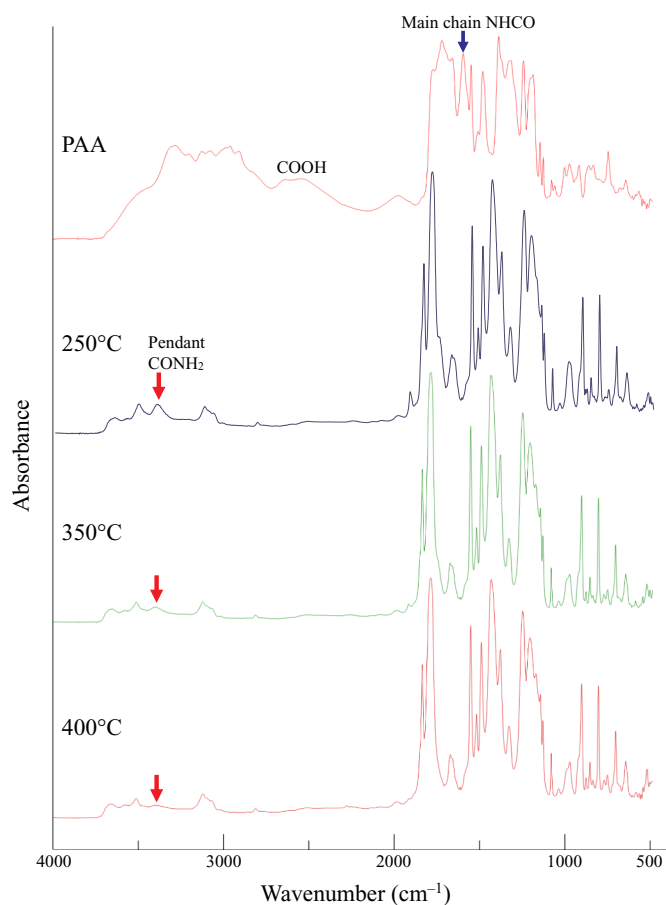


Fig. 5. Changes in FT-IR spectra with increasing imidization temperature for PMDA/TFMB(80);3,5-DABA(20) films.

4 GPa) at room temperature than that of the 3,5-DABA-free counterpart (ca. 2 GPa). These features of the DMA curves are most likely attributed to the effect of crosslinking. The increased E' value of the former also suggests that the crosslinking reaction occurred in the X – Y direction because the E' data were measured in tensile mode. However, considering that the β values decreased significantly in the 3,5-DABA-modified system, it is reasonable to assume that crosslinking occurred three-dimensionally rather than only in the X – Y direction.

On the other hand, a negative effect of crosslinking was also observed; there was a significant reduction in the thermal stability ($T_d^{5\%}$) with increasing 3,5-DABA content. Moreover, the 3,5-DABA-containing

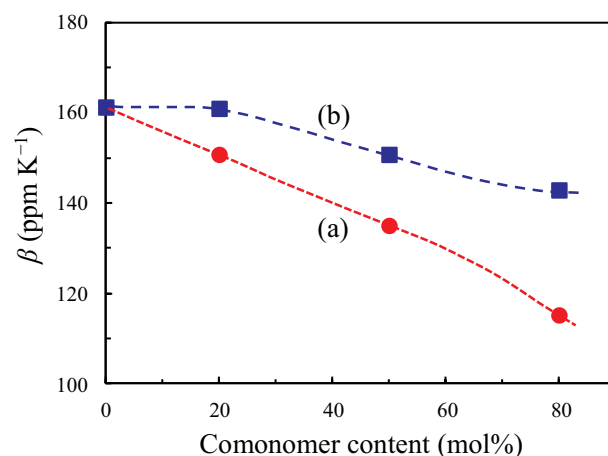


Fig. 6. Changes in the β value with varying comonomer (3,5-DABA or m -PDA) content in the PMDA/TFMB-based copolymers for PI films heated at 350 °C: (a) comonomer: 3,5-DABA and (b) m -PDA.

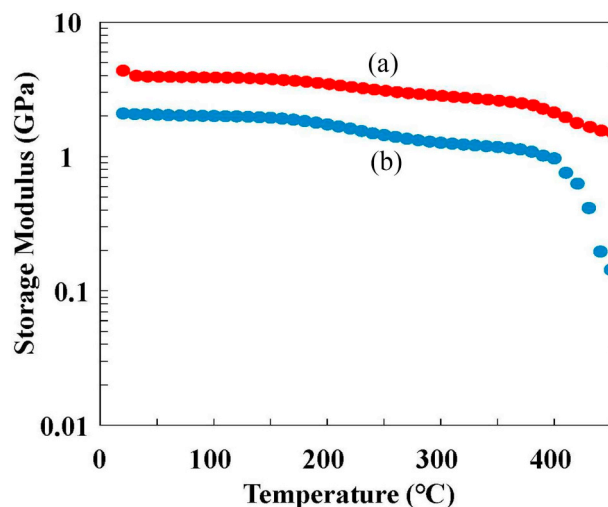


Fig. 7. The E' curves of the PI films heated at 350 °C: (a) PMDA/TFMB(20);3,5-DABA(80) and (b) PMDA/TFMB(20); m -PDA(80).

system also had lower $T_d^{5\%}$ values than those of the 3,5-DABA-free counterparts when compared at the same TFMB contents in these copolymers. The results probably reflect the lower thermal stability of the $N=C$ linkages generated by crosslinking than that of the PI main chain,

Table 1

The thermal properties of crosslinked PI films for PMDA/3,5-DABA;TFMB and the corresponding crosslinker-free PMDA/ m -PDA;TFMB systems.

| System No. | Diamine (mol%) | η_{inh} (PAA) (dL g ⁻¹) | T_g (°C) | α_{xy} (ppm K ⁻¹) | α_z (ppm K ⁻¹) | β (ppm K ⁻¹) | $T_d^{5\%}$ (N ₂) (°C) | $T_d^{5\%}$ (air) (°C) |
|------------|----------------------------|--|------------|--------------------------------------|-----------------------------------|--------------------------------|------------------------------------|------------------------|
| 1 | TFMB | 1.13 | 386 | −0.7 | 162.8 | 161.4 | 537 | 514 |
| 2 | 3,5-DABA (20) TFMB (80) | 1.20 | 406 | 14.0 | 122.8 | 150.8 | 520 | 505 |
| 3 | 3,5-DABA (50) TFMB (50) | 0.76 | 411 | 23.9 | 82.9 | 135.0 | 489 | 485 |
| 4 | 3,5-DABA (80) TFMB (20) | 1.49 | 433 | 29.8 | 55.5 | 115.1 | 467 | 454 |
| 5 | m -PDA (20) TFMB (80) | 1.02 | 406 | 12.4 | 136.3 | 161.0 | 527 | 515 |
| 6 | m -PDA (50) TFMB (50) | 0.97 | 399 | 30.2 | 90.3 | 150.7 | 536 | 522 |
| 7 | m -PDA (80) TFMB (20) | 0.86 | 423 | 34.8 | 73.4 | 143.0 | 532 | 507 |

Cure conditions: 250 °C for 1 h + 350 °C for 1 h on substrates under vacuum.

as suggested by the fact that the incorporation of an azomethine unit into the PMDA/TFMB main chains significantly reduced the T_d^{50} values [51]. A similar decrease in T_d^{50} by crosslinking was also observed in the NI-terminated imide oligomer system [50].

3.3. Effect of crosslinking on T_g enhancement in thermoplastic PI systems

In this study, 3,5-DABA was also used to improve the properties of thermoplastic PI (TPI) systems. TPis are indispensable materials as heat adhesion layers in flexible circuit boards and molding compounds. However, in practice, highly processable TPis with low processing temperatures and low melt viscosities usually have significantly decreased T_g 's because they inevitably have reduced main chain linearity, high rotational flexibility, and disturbed close chain stacking. The relationship between the thermoplasticity and T_g is plotted in Supporting Data 4. We have proposed that the thermoplasticity of PI systems is closely related to the sharpness of the glass transition, which can be expressed by a maximum slope of the logarithmic storage modulus curve measured at a frequency of 0.1 Hz just above the T_g , i.e., $-d \log E'/dT$. Previously, we also revealed that there is the trade-off between high thermoplasticity and low CTE for a variety of PIs [52].

Another trade-off is also conceivable between high T_g and high thermoplasticity. Indeed, such a trend has been observed in various PI systems (except for additive-type imide oligomers) and some super engineering plastics, as plotted in Supporting Data 4. For example, a typical TPI derived from bisphenol A-type tetracarboxylic dianhydride and *m*-PDA (ULTEM1000®, SABIC) shows a very high thermoplasticity index ($-d \log E'/dT = 0.65$) that is comparable with that of poly(ether sulfone) ($-d \log E'/dT = 0.69$). However, this TPI has the lowest T_g (215 °C) of the PI systems.

In this study, a thermoplastic poly(ester imide) (PEsI) was modified with 3,5-DABA to improve the properties “after processing”. Fig. 8(a) shows the DMA curves of the PEsI film obtained from TA-RC with *m*-PDA (20 mol%) and 3,5-DABA (80 mol%) without heat treatment at 350 °C. This PEsI film had a distinct T_g at 247 °C and excellent thermoplasticity, i.e., an abrupt decrease in the E' values just above the T_g with a very high $-d \log E'/dT$ value of 0.48. On the other hand, heat treatment at 350 °C caused a significant T_g enhancement of about 30 °C with a significant decrease in the $-d \log E'/dT$ value (0.15), as shown in Fig. 8(b). In addition, signs of a rubbery plateau were also observed above 300 °C in the E' curve. These features are most likely attributed to crosslinking. This interpretation was confirmed by comparison with the 3,5-DABA-free counterpart (TA-RC/*m*-PDA) film prepared under the same thermal conditions (with final heating at 350 °C); this non-crosslinkable PEsI film had a T_g 12 °C lower than that of the 3,5-DABA-modified system but also with a much higher thermoplasticity index ($-d \log E'/dT = 0.34$) and without a rubbery plateau, as shown in Fig. 8(c).

The DMA data for the TA-RC-based PEsIs can be found in Supporting Data 4. Fig. 9 shows the combined plots of the T_g –thermoplasticity relationship. An “upper boundary”, beyond which it is not easy to achieve simultaneously high T_g and excellent thermoplasticity, can be seen. The arrow in this figure shows the prominent effect of crosslinking on the T_g enhancement for the TA-RC/*m*-PDA(20);3,5-DABA(80) system. The results suggest that the present approach using 3,5-DABA is effective for improving the low- T_g character of TPis.

4. Conclusions

A novel diamine monomer containing an amide (CONH₂) group, 3,5-DABA, was synthesized. An ultralow-CTE PI system, PMDA/TFMB, was modified by copolymerization with 3,5-DABA. The equimolar polyaddition of 3,5-DABA and PMDA in NMP at room temperature led to a high-molecular weight PAA without causing gelation or precipitation. The results suggest that the amide group of 3,5-DABA does

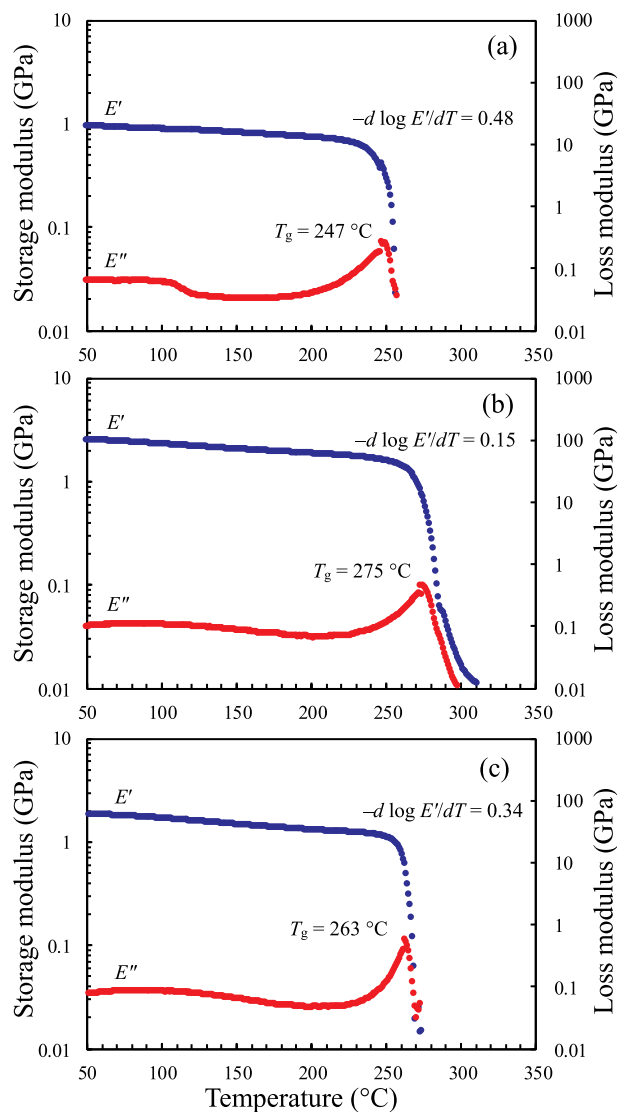


Fig. 8. DMA curves of PI films: (a) TA-RC/*m*-PDA(20);3,5-DABA(80) imidized at 150 + 300, (b) after heating at 350 °C, and (c) TA-RC/*m*-PDA heated at 350 °C.

not participate in the PAA polymerization. The FT-IR spectra suggest that the amide side groups in the 3,5-DABA-modified PIs can react with the adjacent imide C=O groups to form crosslinks upon heating at 350 °C or higher temperatures, even in the absence of sufficient molecular fluidity. This is attributed to the presence of a very high concentration of the imide C=O groups distributed in the vicinity of the amide reactive groups. A crosslinking mechanism has been proposed.

The effect of crosslinking on the β value was investigated by comparing the PMDA/TFMB;3,5-DABA copolymer system with the crosslinker-free counterparts (PMDA/TFMB;*m*-PDA). At a 3,5-DABA content of 20 mol%, the 3,5-DABA-modified copolymer had an appreciably lower β value than that of the corresponding *m*-PDA-containing copolymer. The difference in the β values of these copolymers increased with increasing comonomer (3,5-DABA or *m*-PDA) content. Thus, the use of 3,5-DABA was effective in reducing the β value via crosslinking. DMA revealed that the crosslinking reaction also contributed significantly to enhancing the storage modulus and broadening the glass transition in the PMDA/TFMB;3,5-DABA system.

3,5-DABA was also applied to modify the properties of a thermoplastic PEsI. The PEsI copolymer derived from TA-RC with *m*-PDA (20 mol%) and 3,5-DABA (80 mol%) without heat treatment at 350 °C

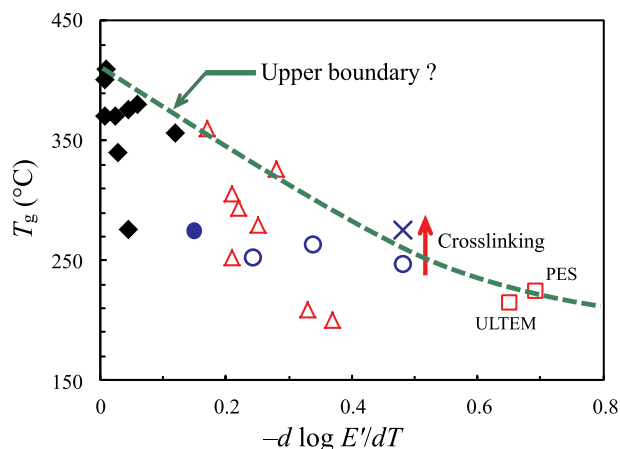


Fig. 9. Relationship between T_g and thermoplasticity in conventional PI systems ($\blacklozenge, \blacktriangle$), super-engineering plastics or thermoplastic poly(ether imide)s (\square), and thermoplastic TA-RC-based PEIs (\circ, \bullet). The closed and open symbols denote the systems with and without rubbery plateau regions in the E' curves, respectively. An arrow represents the effect of crosslinking on the T_g : (\times) TA-RC/*m*-PDA(20);3,5-DABA(80) film heated at 350 °C.

had a distinct T_g at 247 °C with excellent thermoplasticity ($-d \log E'/dT = 0.48$). On the other hand, heat treatment at 350 °C caused a significant T_g enhancement of about 30 °C with a significant decrease in the $-d \log E'/dT$ value (0.15) and signs of a rubbery plateau above 300 °C. Thus, the present approach using 3,5-DABA was also effective in improving the low- T_g character of TPIs.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.reactfunctpolym.2019.04.005>.

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