Structure and Properties of Novel Asymmetric Biphenyl Type Polyimides

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Asymmetric biphenyl type polyimides (PI) were prepared by thermal imidization of polyamic acids (PAA) derived from 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) and p-phenylenediamine (PDA) or 4,4'-oxydianiline (ODA). The degrees of molecular orientation, film densities, and dynamic mechanical properties of these PIs were compared with those of familiar PIs based on symmetric 3,4,3',4'-biphenyltetracarboxylic dianhydride (s-BPDA). PI(a-BPDA/PDA) cured at 350°C showed a Tg close to that of PI(s-BPDA/PDA) prepared under the same condition in spite of the bent chain structure of the former. Comparison of the PIs cured at 400°C manifested that PI(a-BPDA/PDA) has a Tg at 410°C (abrupt decrease in E') whereas PI(s-BPDA/PDA) show no distinct Tg. Similar result was also observed for the ODA systems. The unexpectedly high Tgs of a-BPDA-based PIs were explained in terms of the restricted conformational change around the phenyl-phenyl bond in the a-BPDA unit. The difference of the E' decrement at the Tg for both type of PIs are probably attributed to the difference of the intensity of intermolecular interactions. In PI(a-BPDA/PDA) thin film cured on a substrate, the segments unexpectedly align slightly to the film plane.

1. Introduction

Polyimides have been utilized as electrical insulators, flexible printed circuits, passivation layers, intrinsic photo-patternable materials, and alignment film for liquid crystal, owing to their outstanding thermal, mechanical, and dielectric properties. To understand how the PI physical properties are influenced by manufacturing conditions is indispensable to control precisely the properties necessary for practical applications. So far, we have studied local ordered structure[1-5] and spontaneous molecular orientation behavior induced by thermal imidization[6-10] especially for PI(s-BPDA/PDA) which possesses some excellent physical properties (e.g., lower thermal expansion coefficient (TEC) and higher modulus) better than the most familiar polyimide, Kapton® and concluded that the higher order structure strongly affects the physical properties. The present paper describes the chemical and physical structures-properties relationships for symmetric and asymmetric biphenyl type polyimides.[11,12]

A large number of systematic studies revealed that the chain structure of PI is one of the most

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important factors associated with the physical properties. For example, Bessonov et al. [18] discussed the PI chain structure-Tg relationship, i.e., the influence of the position (whether in dianhydride or in diamine moieties) and the fraction of flexible groups (-O-, -S-, -CH2-, -SO2-, -CO-) as a "hinge" on the Tg. In the present paper, polyimides composed of a new type of monomer with an inflection point, a-BPDA, which may not belong to the category of "flexible" groups mentioned above, is focused. Inoue et al. [12] reported first the thermal properties of an a-BPDA type polyimide (a-BPDA/ODA) film. We describe here the difference of the intensity of intermolecular interactions responsible for the difference between the dynamic mechanical properties of a-BPDA- and s-BPDA polyimides.

Fig. 1 Chemical structures of polyimides and their model compounds used.
2. Experimental Section

Materials. PAAs were prepared by adding the equimolar amount of s-BPDA (Woko Pure Chemical Industry) or a-BPDA powder into the DMAc solution of PDA (recrystallized from ethyl acetate) or ODA (recrystallized from toluene/DMF (10/1)) with continuous stirring at room temperature for 2 h. a-BPDA monomer[19] was supplied from the institute of space and astronautical Science. s-BPDA (without purification) and a-BPDA recrystallized from toluene/acetic anhydride (24/1) were vacuum-dried at 200°C for 24 h before polymerization. The reduced viscosities of PAAs (0.5 wt% in DMAc at 25°C) were 2.6 dl g⁻¹ for a-BPDA/PDA and 1.6 dl g⁻¹ for a-BPDA/ODA. PAA films (20-30 µm thick) prepared by bar-coating the DMAc solution on a glass plate at 60°C for 2 h were thermally imidized in free-standing state upon a given thermal program.

The model compounds of PIs were prepared by reflux of the DMAc solution of BPDA and the stoichiometric amount of aniline (AN) or 3-ethylaniline (3-EA) for 1 h. The crude products were recrystallized twice from suitable solvents and then vacuum-dried at 150°C for 24 h. Fig.1 shows the chemical structures of PIs and model compounds.

Measurements. TECs of PI specimens (15 mm length, 5 mm width, 10-20 µm thickness) were measured on a thermomechanical analyzer (Mac Science TMA-4010) with a load (0.5 g per thickness of 1 µm) in a nitrogen flow. The viscoelastic properties were measured using the same apparatus with a heating rate of 5°C min⁻¹ and a load frequency of 0.1 Hz in N₂. The thermogravimetric analysis (TGA) (Mac Science TG-DTA 2000) of fully cured PI films and PAA cast films was conducted to estimate the chemical heat resistance and the amount of residual solvent in PAA films with 10°C min⁻¹ in a N₂ flow. Differential scanning calorimetry (DSC) were carried out using Mac Science DSC-3100 with 10°C min⁻¹ for PAA films and with 2°C min⁻¹ for the PI model compounds. The second runs for the DSC and TGA thermograms were taken after preheating up to 100°C to remove the adsorbed water.

The densities of PI films prepared upon various cure program were measured at 25°C using a density gradient column composed of xylene-CCl₄ mixtures.

The corrected intermolecular charge-transfer (CT) fluorescence spectra of PI films[2-4] were recorded at room temperature in a front-face reflection geometry (excitation: 350 nm, sharp-cut filter: L-39, bandpass: 10 nm (excitation side) and 20 nm (emission side)) on Hitachi F-2000 fluorescence spectrometer. Uv-vis absorption spectra of the model compounds in dichloromethane were taken using Jasco V-520 spectrophotometer.

Polarized infrared absorption spectra (transmission mode) for PI films cast on a silicon wafer were recorded at a constant incidence angle of 60° on Jasco FT-IR 5300 spectrometer equipped with a KRS-5 polarizer (Jasco PL-81) to estimate the degree of in-plane orientation of PI chains.[10]

The anhydride groups formed in PAA films in the course of stepwise annealing were conventionally followed by the absorbance ratio of the 1850 cm⁻¹ to 1515 cm⁻¹ (1,4-phenylene...
stretching) bands.

3. Results and Discussion

Cure Conditions. PAA(a-BPDA/PDA) did not provide good PI films upon common thermal cure processes: (1) Solution cast of high molecular weight PAA(a-BPDA/PDA) gave highly tough films. However, a stepwise cure process (150°C; 1 h + 200°C; 1 h + 250°C; 2 h), which provides flexible PI films for most of high molecular weight PAAs except for PMDA/PDA system, makes very brittle PI(a-BPDA/PDA) films. (2) The thick PAA films are broken or cracked through cure in a metal frame (bifix-cure) and cure on a substrate. (3) One-step cure of the PAA films above 300°C tends to generate bubbles in the films. Then, first of all, we searched cure conditions to obtain good PI(a-BPDA/PDA) films. There was no significant difference of the amount of residual DMAc (ca. 20 wt%) in PAA films of a- and s-BPDA/PDA (17 µm thick for both). An endothermic peak due to imidization in the DSC thermograms was observed at 154°C for the former and 171°C for the latter.

In stepwise thermal imidization processes, a back reaction of acylation occurs partially to form the amino and anhydride terminal groups, and by additional higher temperature annealing the formed reactive groups recombines, so that finally imidization completes. Fig.2 illustrates the changes in the relative amount of anhydride group as a function of cure temperature upon stepwise cure (annealed at each temperature for ten min). Roughly speaking, the film brittleness results from the formation of the terminal anhydride and amino groups (molecular weight decrease). In fact, PI(a-BPDA/PDA) film became tough upon annealing at temperature higher than 350°C where the anhydride groups disappeared.

![Diagram](image)

Fig.2 The changes in the relative amount of anhydride group as a function of cure temperature in the course of stepwise annealing. (●) s-BPDA/PDA and (□) a-BPDA/PDA.
Figs. 3 (a) and (b) show the TGA thermograms of the fully cured s-BPDA-based PI and a-BPDA-based PI films. The latter have thermal stability a little lower than those of the former for both PDA and ODA systems, however, no appreciable weight loss was observed up to 420°C. Accordingly, we prepared PI films upon a stepwise cure process in free-standing state: additional annealing at 350°C for 1 h or at 400°C for 1 h after precuring at 200°C for 3 h for the dynamic mechanical measurements. However, brittleness of PI(a-BPDA/PDA) films can not explain in terms of only the concentration of anhydride group: although [anhydride group] in PI(a-BPDA/PDA) film cured at 300°C is lower than that in PI(s-BPDA/PDA) film cured at 250°C, the former is very brittle, and the latter is tough. For another example, PI(PMDA/PDA) film cured at 350°C has no anhydride group, but it is very brittle. A kind of molecular strain stored in polymer chains such as a bond angle distortion may be related to film brittleness.

![Weight loss curves of fully cured PI films with 10°C min⁻¹ in a nitrogen flow.](image)

(s-BPDA/PDA(1) and a-BPDA/PDA(2) films)
(b) s-BPDA/ODA(3) and a-BPDA/ODA(4) films

**Dynamic mechanical properties of a- and s-BPDA/PDA polyimide films.**

s-BPDA/PDA shows a character that the polymer chains spontaneously align parallel to the film plane during thermal imidization, and the degree of in-plane orientation depends strongly on film thickness and constraint of the films (cure in free-standing state, in a frame, or on a substrate). [7,8,10] The degree of in-plane orientation significantly influences the dynamic mechanical properties. As mentioned in the experimental section, both a- and s-BPDA-based PI films were prepared on the free-standing cure. Figs. 4 (a) and (b) display the dynamic storage modulus ($E'$) and loss energy ($E''$) as a function of temperature for PI(s-BPDA/PDA) and PI(a-BPDA/PDA) films cured at 350°C. The semi-rigid PI(s-BPDA/PDA) shows a glass transition at 390°C. It is widely known that the introduce of inflection points into rigid PI main chains lowers considerably the $T_g$.[18] But for PI(a-BPDA/PDA), in spite of sharp bending of the polymer chains, an unexpectedly high $T_g$ at
380°C was observed.

Let us consider the cause of the unexpectedly high $T_g$ of PI(a-BPDA/PDA). The factors influencing $T_g$ are in general as follows: (1) intramolecular interactions (chain rigidity) and (2) intermolecular interaction (interchain cohesive force). The glass transition in amorphous polymer solids is generally explained in terms of the equal configurational entropy ($S_c$) theory. The scission of interchain physical bonds (hydrogen bonding, dipole-dipole, and CT interactions etc.) is required for free conformational changes as a result of thermal energy higher than the rotational barriers to attain to the $S_c$ at glass transition. There is a significant difference between the flexible units (e.g., -O-) described by Bessonov et al. [18] and a-BPDA moiety, although both units indeed introduce inflection points into PI chains, consequently the chains take random coil form: the former have comparatively low rotational barrier (a few kcal mol$^{-1}$ in solution), whereas the internal rotation about the phenyl-phenyl bond in a-BPDA unit is most likely forbidden due to the steric hindrance. Therefore, in PI(a-BPDA/PDA), only the unit $>\text{N-phenylene-N}<$ is probably allowed to rotate[20], but this rotation provides no significant change in the chain form. Thus, the high $T_g$ observed for PI(a-BPDA/PDA) is attributed to the
suppressed internal rotation around the phenyl-phenyl bond, that is, very low configurational entropy (factor 1).

However, the bent structure in a-BPDA/PDA chains makes the interchain packing loose, consequently it weakens the intermolecular interactions (factor 2). As demonstrated in Fig.5, comparatively low densities of PI(a-BPDA/PDA) films manifest the low degree of molecular packing. The loose molecular packing caused by the bent structure prevents the formation of low enthalpy glass, so that it also contributes to a decrease in $T_g$.

For semi-rigid PI(s-BPDA/PDA), the $T_g$ increases with increasing annealing temperature, corresponding to the increase in the film density (see Fig.5 (1)) and to an increase in the intermolecular CT fluorescence intensity.[10] This demonstrates that for the semi-rigid PI the intensity of intermolecular interactions (factor 2) plays an important role to elevate the $T_g$.

The consideration mentioned above leads us to conclude that the entropy effect (inhibited internal rotation) is predominant to raise the $T_g$ of PI(a-BPDA/PDA) compared with the enthalpy effect.

For a class of PIs containing the flexible ether linkages, a good empirical relationship, $T_m \approx 1.3T_g$, is observed.[18] Since it is generally difficult to measure experimentally $T_ms$ of rigid PIs, relative values of $T_g$s for a series of polymers is roughly estimated on the basis of $T_m (= \Delta H_m / \Delta S_m)$ of their model compounds.[21,22] The values of $T_m$, $\Delta H_m$, and $\Delta S_m$ of the model compounds are listed in Table 1. In contrast to our expectation, the model compound, M(a-BPDA/AN), showed $\Delta S_m$ higher than that of M(s-BPDA/AN). In addition, the value of $\Delta H_m$ for the former was a little higher than that for the latter. Accordingly, the inconsistency between the consideration of $T_g$ for both PIs and that of $T_m$ for both model compounds on the basis of the thermodynamic parameters means probably that both conformation and intermolecular interactions in PI(a-BPDA/PDA) in glassy state differs significantly from those in the model compounds in crystalline state.

Table 1  $T_m$ and the changes in enthalpy and entropy of melting for models.

<table>
<thead>
<tr>
<th>Model Compounds</th>
<th>$T_m$ / °C</th>
<th>$\Delta H_m$ / kcal mol$^{-1}$</th>
<th>$\Delta S_m$ / cal mol$^{-1}$K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(s-BPDA/AN)</td>
<td>390</td>
<td>12.6</td>
<td>19.0</td>
</tr>
<tr>
<td>M(a-BPDA/AN)</td>
<td>308</td>
<td>13.4</td>
<td>23.0</td>
</tr>
<tr>
<td>M(s-BPDA/CHA)</td>
<td>270</td>
<td>12.1</td>
<td>22.3</td>
</tr>
</tbody>
</table>

Figs.6 (a) and (b) exhibit that the $E'$ and $E''$ curves for PI(s-BPDA/PDA) and PI(a-BPDA/PDA) films cure at 400°C. Note that the decrement in $E'$ at $T_g$ for PI(s-BPDA/PDA) film became moderate.
by the increase in annealing temperature from 350 to 400°C, whereas PI(a-BPDA/PDA) showed an abrupt decrease in $E'$ at $T_g=410^\circ$C. For both systems, the significant difference of the effect of annealing at 400°C on the $E'$ decrement at the $T_g$ is probably attributed to the difference of the intensity of intermolecular interactions as physical crosslinking points. In general, the introduction of chemical crosslinks, and an increase in crystallinity (a kind of physical crosslink) or a decrease in the amorphous fraction make the $E'$ decrement at $T_g$ moderate, and they expand the rubbery plateau region.[23] In our system, since the molecular weights of all the polymers used are high enough, an effect of the difference of the extent of entanglement on the $E'$ decrease can be neglected.

If a strong intermolecular interaction in our PI systems acts as physical crosslinks still above the $T_g$, the decrement in $E'$ at $T_g$ should be significantly influenced by the fraction of such a physical bond. We observed a considerable enhancement in the fluorescence from intermolecular CT complexes[2-4] by additional annealing at 400°C for s-BPDA/PDA system, corresponding to the significant change in the $E'$ curve as shown in comparison of Figs.4 (a) and 6 (a). In addition, PI(s-BPDA/CHDA) (CHDA:trans-1,4-cyclohexanediamine) which has no CT interaction showed a more sudden decrease in $E'$ at $T_g$ compared with the case of PI(s-BPDA/PDA).[8] If intermolecular interaction influencing the $E'$ decrement is only the diimide-diimide interaction, no difference of the $E'$ decrease behavior could be observed.

Fig.6 Dynamic storage modulus and loss energy as a function of temperature. (a) PI(s-BPDA/PDA) and (b) PI(a-BPDA/PDA) films cured at 400°C.

Fig.7 Uv-vis absorption spectra of PI model compounds in dichloromethane (1.00 x 10^{-4} M). (1) s-BPDA/3-EA, (2) a-BPDA/3-EA, and (3) PA/AN (x 2).
Hence, these results suggest that not only the interaction between the biphenyl diimide fragments, but also the intermolecular molecular CT interaction contributes somewhat to inhibition of the abrupt $E'$ decrease for semi-rigid s-BPDA/PDA system.

The bent structure of PI(a-BPDA/PDA) prevents both types of interchain interactions as physical crosslinks (see the abrupt decrease in $E'$ at $T_g$ in Fig.6 (b)). Therefore, it is very important to get information on the most stable steric structure (dihedral angle) in glassy state, together with the rotational barrier for conformational change as described above. Unfortunately, we have in the present stage no experimentally determined dihedral angles around the phenyl-phenyl bond in a-BPDA unit.

To estimate qualitatively the degree of phenyl-phenyl conjugation as a function of the dihedral angle, we measured the uv-vis absorption spectra of the model compounds in solution (Fig.7). If for biphenyl derivatives the phenyl-phenyl dihedral angle is close to right angle, the absorption spectrum similar to the simple twofold of the spectrum of the corresponding monomeric unit (phenyl derivatives) is observed, but a spectral red-shift and enhancement of the band intensity become marked as it approaches coplanar structure [24,25]. As we reported previously[26], the model compound, M(s-BPDA/3-EA), showed the intensification and red-shift of the benzimide ($\pi,\pi^*$) absorption band in comparison with the corresponding N-phenylphthalimide (M(PA/AN)), indicating that the dihedral angle is between 0 and 90°. As an example, Kaneda et al.[27] estimated it to be about 60° by a crystallographic calculation based on the WAXD pattern of the heat-treated highly drawn PI(s-BPDA/PDA) fiber. On the other hand, M(a-BPDA/3-EA) provided a weaker and blue-shifted band compared with that of s-BPDA model as illustrated in Fig.7. This indicates that the phenyl-phenyl conjugation for a-BPDA model is much weaker than that for s-BPDA model, and suggests that the dihedral angle of the former is not right angle but close to it, since the spectrum is stronger and red-shifted than the twofold of the M(PA/AN) spectrum. 9-phenylphenanthrene (see Fig.1 for its structure) as a steric structure model of the a-BPDA unit represents an absorption spectrum similar to that of phenanthrene[24,28]; this suggests that the phenyl-phenyl dihedral angle in the a-BPDA unit is most likely close to normal and supports the conclusion from the absorption spectra.

Figs.8 (a) and (b) show the $E'$ and $E''$ curves for PI(s-BPDA/ODA) and PI(a-BPDA/ODA) films. We first searched a cure condition common to both PIs; since PI(s-BPDA/ODA) film cured at 250°C in free-standing state is flexible and has a distinct $T_g$ at 290°C (abrupt $E'$ decrease)[29], the film deforms considerably upon annealing at temperatures higher than 300°C. PI(a-BPDA/ODA) film cured at 250°C is, however, very brittle. Then, both PI films were annealed at 350°C for 1 h in a frame after free-standing precure at 200°C for 3 h to obtain flat films suitable for the dynamic mechanical measurements. For the bifix-cure PI(s-BPDA/ODA) film (Fig.8 (a)), a glass transition was observed still at 280°C although the decrement of $E'$ at $T_g$ became moderate (broadened $E''$.
peak). On the other hand, surprisingly, PI(a-BPDA/ODA) possessing more bent chain structure provided a distinct T_g = 320°C higher than that of PI(s-BPDA/ODA). One possible explanation about this abnormal result is that the conformational changes in the former is more suppressed than that in the latter, as described for the PDA systems.

The behavior of the E' decrement for the ODA systems was essentially consistent with that of the PDA systems; the abrupt decrease in E' for PI(a-BPDA/ODA) can be explained in terms of weaker intermolecular interactions. PAA(s-BPDA/ODA) has a sharp exothermic peak at 300°C due to precrystallization in the DSC thermogram, whereas PAA(a-BPDA/ODA) does not. In addition, the film densities of the latter much lower than those of the former (see Fig.4) indicate the lower degree of molecular packing of PI(a-BPDA/ODA). Thus, the significant difference of the E' decrement at T_g is probably attributed to the difference of the intensity of intermolecular interactions (crystal-like order and CT complex formation) as physical crosslinks, as well as the PDA systems described above.

In-plane Molecular Orientation of a- and s-BPDA/PDA Polyimides.

We found that s-BPDA/PDA chains highly align spontaneously parallel to the film plane through on-substrate cure or bifix cure and that the degree of in-plane orientation depends strongly on film thickness in the case of free-standing cure [7,8,10] PI(a-BPDA/PDA) film (18 µm thick) showed TEC = 9.7 ppm K^{-1} close to that (8.8 ppm K^{-1}) of PI(s-BPDA/PDA) film (17 µm thick) when both were cured in free-standing state upon 200°C for 3 h + 350°C for 1 h.

Unfortunately, bifix and on-substrate cure of a-BPDA/PDA thick films generates cracks, but it is possible to form good films in the case of on-substrate cure of thin film. We measured the infrared absorption dichroic ratios of the imide carbonyl symmetric stretching band peaking at 1774 cm^{-1}, which has a transition dipole along the chain axis, at a constant incidence angle of 60°. In this measurements, the dichroic ratio takes unity if polymer segments orient three-dimensionally random and decreases as the in-plane orientation proceeds. PI(s-BPDA/PDA) showed the value of 0.738, indicating that the segments highly align parallel to the film plane. On the other hand, in spite of its
bent chain structure, PI(a-BPDA/PDA) provided the value of 0.815, in contrast to our initial anticipation that the value should be close to unity.

More detailed studies on the microstructures of a-BPDA-based homopolyimides and the properties of a-BPDA PI-containing composite systems are in progress and will be reported elsewhere.

4. Conclusion
1. Annealing at temperature above 350°C is required to obtain highly flexible PI(a-BPDA/PDA) films, relating to the anhydride group disappearance in the film.
2. a-BPDA-based polyimides show an unexpectedly high T_g. This is explained in terms of the restricted conformational change in a-BPDA unit.
3. The abrupt decrease in E' at T_g observed for a-BPDA-based polyimides is associated with the weaker intermolecular interactions caused by the bent chain structure.
4. PI(a-BPDA/PDA) chains slightly align to the film plane upon on-substrate cure of the thin film.

References