

# Molecular Aggregation and Property of High Performance Polyimide Films

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## Introduction

Aromatic polyimides (PI) exhibit high thermal stability, and excellent chemical, physical, and mechanical properties owing to the thermally stable phenyl and imide moieties of the backbone. For these advantageous properties, they have been highly considered for the advanced technological applications in the microelectronics and aerospace industries. The history of aromatic polyimides has been governed by the opposing requirements of thermal stability and processability. An insoluble rodlike polyimide exhibits high thermomechanical stability, high modulus, and low thermal expansion, whereas a soluble flexible polymers shows good adhesion, high elongation, and lower  $T_g$ .

Polyimides are usually applied by casting or spin-coating their soluble precursor, e.g. poly(amic acid) (PAA) solutions onto the desired substrate, followed by thermal or chemical imidization. The molecular order and in-plane orientation have some remarkable effects on the film properties. Especially in electronic packaging applications, such properties as high glass transition temperatures, high planarization, high processability, low dielectric constants and low thermal expansion coefficients are crucial to device fabrication, performance, and reliability.

The aim of this article is to review briefly some factors in the molecular aggregation of polyimide films and to present our findings on the molecular aggregation and thermal, mechanical properties of rodlike/flexible biphenyltetracarboximide composite films.

## I Factors in the molecular aggregation of PI

### Chemical structure

Aromatic polyimides do not have a sufficient flexibility, as can be expressed by the equivalent Kuhn length. For example, the Kuhn length of PI(PMDA/ODA) is ca. 72 Å, and it increases to ca. 112 Å for the PI(BPDA/PDA). Therefore, their Kuhn axial ratios defined as the Kuhn length divided by the average cross-sectional diameter normally exceed the critical value of 6.4; that marks the critical flexibility beyond which a disordered random amorphous state is impossible [1]. Hence, aromatic polyimide chains in solid films are expected to assume a highly ordered state. In fact, even flexible PI(PMDA/ODA) chains adopt both the conformational order to form an extended local conformation [2] and the orientational order to align along the film surface [3]. D. Y. Yoon et al. [4] revealed the conformation-order relationship for typical polyimides. The rodlike PI(PMDA/PDA) chains show a very highly ordered smectic crystal order. The semi-rodlike PI(BPDA/PDA) provides a significant lateral interchain packing order in addition to the excellent monomer repeat

packing order along the extended chain axis. It is noteworthy that with increasing film thickness of PI(BPDA-PDA), the intermolecular packing order is enhanced, whereas the molecular in-plane orientation is degraded in spite of no significant variation of the polymer chain order due to the inherently high chain rigidity [5].

It is interesting to consider the effect of bulky side groups on the morphology of polyimide films. The precursor of photosensitive polyimide, PSPI(BPDA-PDA), with 2-(dimethylamino)ethyl methacrylate revealed typical amorphous halos in the WAXD pattern like PAA(BPDA-PDA)[6]. However, the inter-molecular packing order of the PSPI(BPDA/PDA) was more enhanced than that of PI(BPDA-PDA). This may be due to the increase in the chain mobility caused by the bulky group in the precursor of PSPI(BPDA-PDA). On the other hand, the in-plane orientation of polymer chains decreased for PSPI(BPDA-PDA). Since these mechanical properties are the properties in the film plane, the dynamic storage and loss moduli were relatively lower in the PSPI(BPDA /PDA) films than in the PI(BPDA/PDA) films.

### Precursor

The cycloimidization reaction is not limited to the acid precursor (PAA) and several derivatives of the PAA-poly(amic alkyl ester)s (PAE) were developed. Compared with the PAA precursors, the PAE precursors have improved solution properties, better resistance to hydrolytic degradation, apparent lack of exchange reactions, and a higher, broader imidization temperature regime [7]. The PAE precursors generally yield more processable formulations.

The molecular aggregation of PI(PMDA-PDA) and PI(BPDA-PDA) showed somewhat better intermolecular packing order for the ester-derived polyimide films than for the acid-derived polyimide films [8]. However, both the polyimides derived from the two sets of precursors indicate no significant influence of the precursor on the in-plane orientation in the final polyimide films.

Although the WAXD reflection pattern indicated, as mentioned above, a better lateral packing order of the molecular chains for PI(BPDA/PDA) from the poly(amic ethyl ester) precursor than from poly(amic acid), the larger CTE was exhibited by the ester-derived PI(BPDA/PDA). This may reflect the presence of some not rodlike conformational defects, because WAXD reflects solely the packing order of ordered chain segments.

### Solvent

The direct relationship between solvent and morphology of polyimide films still are unresolved. However, the effects of solvent on the imidization reaction and PAA/solvent interaction have been investigated by various authors.

The rate of imidization for PAA(PMDA/ODA) decreased in the order NMP > DMAc > DMSO [9]. The presence of solvent considerably speeds up the cyclization reaction and with increasing film thickness, more solvent is retained and thus the thicker films cure more quickly and to a higher degree of imidization at a particular temperature. This is mainly attributed to the plasticizer effect of solvent. Baise [10] noted that stepwise cures of PAA(PMDA/ODA) were less imidized than isothermal cures at higher temperatures, and suggested that all of the solvent is lost in two-step cures during the first step. FT-Raman data for PAA(PMDA/ODA) in

the absence NMP solvent indicated that both the acid and amide carbonyls were tightly bound in the form of intramolecular hydrogen bonds, leading to the decrease in imidization rate [11]. J.-H. Jou et al. [12] pointed out that polyimide molecules located near the center of the film exhibit poorer structure ordering than those near the surface. The precursor polymer chains in the center may have least restraints, since they can shrink more freely upon solidifying than those near the substrate and air.

## II Biphenyltetracarboximide blends

Since they cannot be met by a single polymer, all the properties required in the advanced applications are expected to achieve through rodlike/flexible composites with a desired level of molecular mixing. Yokota et al. [13] have previously reported the composite formation of rodlike PI(BPDA-PDA) with flexible PI(BPDA-ODA) by solution blending the respective PAAs. However, mixing of PAAs in a mutual solvent can result in transamidation reactions forming segmented blocky or random copolymers rather than molecularly mixed precursor blends [14]. Unlike PAA, poly(amic dialkyl ester) (PAE) in a solvent is not in equilibrium with its constituent monomers [15]. In this study both PAAs and PAEs were used for the resulting polyimides PI(BPDA-PDA) and PI(BPDA-ODA).

### Film preparation

The precursor polymers were blended at various compositions in 10wt% DMAc for 2 days. PI films were prepared by doctor-blading the respective precursor mixtures onto glass substrates, followed by drying at 50°C for 1h and finally thermal imidization. The thermal history of standard samples was as follows: samples were successively held in vacuum at 150°C for 1h, at 200°C for 1h, and at 250°C for 2h. The annealed samples were obtained by annealing the standard samples at 380°C for 1h. The thickness of PI films was ca. 40  $\mu$ m.

### Characterization [16]

All the ternary precursor solutions were optically clear, indicative of the miscible solutions. The resultant polyimide composite films were also optically transparent regardless of the composition and thermal history. Based on the optical transparency, the PI(BPDMe-PDA) from the methyl ester precursor seems to be molecularly well mixed with PI(BPDMe-ODA) in the composite films. However, optical microscopy is known to have a resolution of submicrometers in phase heterogeneities [17].

The composite films were further investigated by a dynamic mechanical measurement. The annealed homopolymer PI(BPDMe-PDA) showed a broad glass transition over the range of 300-400°C, whereas the annealed homopolymer PI(BPDMe-ODA) showed a relatively sharp glass transition over the range of 260-310°C. The annealed composite films but the 30/70 composite exhibited intermediate glass transition behavior between those of the homopolymers. The 30/70 composite exhibited a  $T_g$  (240°C) lower than that (260°C) of PI(BPDMe-ODA). It should be noted here that despite the better resolution of dynamic mechanical analysis, single  $T_g$  behavior is not enough to distinguish structural heterogeneities on a length scale less than 50 Å [18].

### Molecular aggregation

In the WAXD patterns for the annealed homopolymer PI(BPDMe-PDA), the multiple (001) peaks remarkably appeared in the transmission geometry in which the diffraction vector is in the film plane. This means that rodlike polyimide chains of PI(BPDMe-PDA) are preferentially oriented in the film plane. A similar molecular in-plane orientation was observed for annealed cocomposite films with PI(BPDMe-ODA), depending on the composition. In contrast to the rodlike PI(BPDMe-PDA), the flexible PI(BPDMe-ODA) homopolymer film revealed several weak diffraction peaks over  $12-27^\circ$  ( $2\theta$ ) in both the transmission and reflection geometry, indicating no significant in-plane orientation of the PI(BPDMe-ODA) chains. However, these weak peaks may reflect the existence of an inhomogeneous two-phase superstructure including molecularly ordered regions. In fact, Y. Kim et al. [24] measured the SAXS for PI(BPDMe-ODA) to observe a relatively distinct peak with a mean long period of ca. 170 Å. This two-phase superstructure of PI(BPDMe-ODA) may explain the abnormally low  $T_g$  behavior of the 30/70 composite.

### References

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45Å (1) PI

BPDA-PDA } Blend of  
BPDA-ODA } miscibility