Spontaneous Molecular Orientation of Polyimides Induced by Thermal Imidization. 3. Component Chain Orientation in Binary Polyimide Blends

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ABSTRACT: The degrees of uniaxial and in-plane molecular orientation for homopolyimides (PI) and PI/PI binary blends were estimated from the absorption dichroism of perylenetetracarboxydiimide (PEDI) bound to the main chains. Thermal cure of a slightly drawn film of poly(amic acid) (PAA) derived from 3,4,3′,4′-biphenyltetracarboxylic dianhydride (BPDA) and *p*-phenylenediamine (PDA), BPDA/PDA, showed marked spontaneous orientation toward the stretching direction. The dependence on the chain structure revealed that in addition to the chain stiffness (linearity) the molecular packing is an important factor for the spontaneous orientation behavior. In a miscible binary blend system composed of semirigid BPDA/PDA labeled with PEDI and flexible BPDA/ODA (ODA: 4,4′-oxydianiline), the extent of spontaneous orientation for the labeled BPDA/PDA chains decreased with increasing BPDA/ODA content in the blends. From the result, the marked spontaneous orientation behavior of homo-BPDA/PDA is interpreted as a kind of "cooperative phenomenon" where the neighboring chains promote the molecular orientation of each other in the cure process. Effects of film thickness, amount of residual solvent, cure method, and heating rate on the extent of spontaneous orientation were also discussed for the homo-BPDA/PDA system.

Introduction

Polyimides are utilized in the fields of microelectronics and aerospace industries because of their outstanding thermal, mechanical, dielectric, and radiation-resistant properties. For the precise control of polyimide (PI) properties, to find out the relationships between the properties and the chemical and higher order structures is indispensable. Thermal imidization processes are widely recognized as a key point to improve PI properties. We have so far investigated the local ordered structures, influenced considerably by the cure conditions, by means of the small-angle X-ray scattering,[1] the intrinsic charge-transfer fluorescence,[2−5] and FT-IR spectroscopy.[6] These results revealed that some processing conditions which increase molecular mobility, i.e., the increases in initial imidization temperature, final annealing temperature, heating rate, the amount of residual solvent, and film thickness, are favorable for the structure organization (crystallization, charge-transfer complex formation, liquid−crystal (LC)-like ordering).

Thermal imidization of uniaxially cold-drawn poly(amic acid) (PAA) films for semirigid 3,4,3′,4′-biphenyltetracarboxylic dianhydride/*p*-phenylenediamine (BPDA/PDA) gave rise to considerable enhancement of Young's modulus.[7] Combination of the semirigid PI with a flexible BPDA/4,4′-oxydianiline (ODA) led to a PI/PI molecular composite material with some improved mechanical properties.[8] On the other hand, cold stretching of the isotropic BPDA/PDA polyimide films is less effective to produce highly oriented PI films because of its low extent of elongation (DR less than ∼15% at room temperature). We showed previously that the degree of molecular orientation for BPDA/PDA markedly increases spontaneously upon thermal cure reaction from slightly stretched PAA (Hermans' orientation function $F \sim 0.2$) to the resulting PI ($F \sim 0.7$).[9] Similarly, our previous work[10] demonstrated that the in-plane orientation of BPDA/PDA is increased considerably upon thermal cure of the PAA films adhered on a substrate and described the effects of the chain stiffness, film thickness, presence of substrate, heating rate, and residual solvents in the PAA films on the spontaneous in-plane orientation. Several papers reported that PMDA/ODA (PMDA: pyromellitic dianhydride) also shows comparatively high orientation upon thermal cure of the uniaxially cold-drawn PAA films.[11−13] Thus, the chain orientation of the resultant PIs, associated closely to the properties, can be considerably varied during the imidization processes.

The present paper focuses on the spontaneous orientation behavior of the rigid PI component in the binary blends during cure processes and discusses how the blend miscibility affects the orientation behavior. The result will provide a valuable indicator to control the mechanical properties of the molecular composites. To determine the chain orientation of the PI components in the blends, we prepared PAAs labeled with a dichroic dye, perylenetetracarboxydiimide (PEDI). This technique is applicable for a wide thickness range (a few to a hundred microns) by adjusting the PEDI concentration.

Experimental Section

PAA Preparation. PAAs were polymerized by adding an equimolar amount of dianhydride powder into the *N*,*N*-dimethylacetamide (DMAc) solution of diamine with continuous stirring at room temperature for several hours. DMAc

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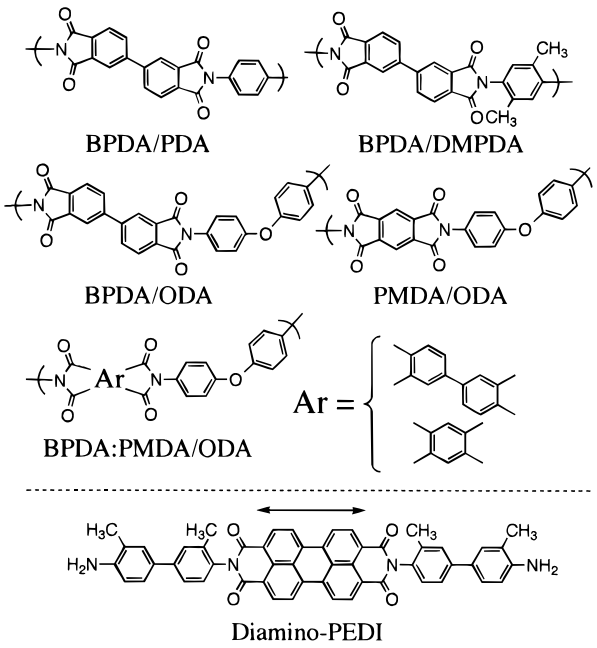

Figure 1. Chemical structures of PAAs, PIs, and dichroic dye used. The arrow represents the direction of the absorption transition moment for PEDI.

dried with molecular sieves 4A was vacuum-distilled before use. Figure 1 shows the structures and symbols of PIs represented as PI(X/Y) (X, dianhydrides; Y, diamines) and as PI(X:X′/Y) and PI(X/Y:Y′) for random copolymers. The following monomers were used: BPDA (Wako Pure Chemicals) vacuum-dried at 200 °C for 24 h, PMDA recrystallized from dioxane and then vacuum-dried at 130 °C for 48 h, PDA recrystallized from ethyl acetate, ODA recrystallized from toluene/*N*,*N*-dimethylformamide (10/1), and 2,5-dimethyl-*p*-phenylenediamine (DMPDA) recrystallized from benzene. PAA films (60 μm thick unless indicated otherwise) were prepared by bar-coating the DMAc solutions on a glass plate at 60 °C for 2 h in an air convection oven.

We prepared PAAs labeled with PEDI (Figure 1). First, diamino-PEDI as the probe molecule was synthesized from perylenetetracarboxylic dianhydride and *o*-tolidine as reported previously.[10] A small amount of diamino-PEDI was copolymerized to introduce it into the PAA main chains (PEDI/repeating unit = 1/900 or 1/600). Upon chemical imidization of the PEDI-labeled PAA thin film, no PEDI molecules extracted from the film were detected in the reaction solution, whereas for the PEDI-dispersed PAA film the dye molecules were readily extracted with the same solution. Thus, introduction of the PEDI units into the PAA main chains was confirmed.

Blend Film Preparation. In the present study, miscible and immiscible binary blend systems were established: (1) labeled (BPDA/PDA)/unlabeled BPDA/ODA and (2) labeled (BPDA/PDA)/unlabeled BPDA:PMDA/ODA. To suppress transamidation, we prepared the PAA blend films (60 μm thick unless indicated otherwise) by casting at 60 °C after immediate vigorous mixing of PAA solutions (10 wt %) for 10 min at room temperature. In the blend system (2), thinner films (20 μm) were used to reduce the turbidity (due to the phase separation) undesirable for the orientation measurements. All the thickness values indicated represent those of PAA films before stretching.

Stretching, Imidization, and Annealing. The dye-labeled PAA film specimens (machine direction (MD), 8 cm; transverse direction (TD), 1.5 cm) were uniaxially stretched at room temperature with various draw ratios [DR = $(L - L_0)/L_0 \times 100$] and then cured stepwise at 150 °C for 1 h + 200 °C for 1 h + 250 °C for 2 h (step-cure, unless indicated otherwise) in a metal frame (both edges in MD were fixed) in a nitrogen atmosphere. The oriented PI films cured at 250 °C (step-cure) were additionally annealed at 330 °C for 1 h in a free-standing state.

The 30% drawn PAA films were dipped into water to change the residual solvent concentration in the films, then vacuum-dried at 60 °C for 24 h to remove the adsorbed water, and cured under the same cure conditions as mentioned above.

Chemical imidization was carried out by dipping the drawn PAA films (~5 μm thick) fixed in a stainless steel frame into the acetic anhydride/pyridine mixture (70/30, v/v) at 100 °C for 2 h, then washing in dichloromethane, and vacuum-drying at 100 °C. Chemical imidization was practically completed through this procedure.

Measurements

Uniaxial Orientation. Diamino-PEDI possessing an absorption transition moment (530 nm band) parallel to the long molecular axis was bound into the main chains (angle θ between the polymer chain axis and the transition moment is nearly zero). The polarized absorption measurements allowed one to get the value of F for both stages of PAAs and PIs. The dichroic ratio D_u ($=A^{\parallel}/A^{\perp}$), where $A^{\parallel}$ and $A^{\perp}$ are the absorbances with respect to the incident beams linearly polarized parallel and perpendicular to the stretching direction, respectively, gives Hermans' orientation function:

$$F = (3\langle\cos^2\theta\rangle - 1)/2 = K(D_u - 1)/(D_u + 2) = (D_u - 1)/(D_u + 2) \quad (1)$$

where $K = (D_{u0} + 2)/(D_{u0} - 1)$ (D_{u0}: dichroic ratio in the case of complete uniaxial orientation) is reasonably regarded as nearly unity since the rodlike PEDI moieties are incorporated parallel to the polymer chain axis. We estimated the values of K for the PI films with varying DR from eq 1 on the basis of F determined from the infrared dichroism of the 1774 cm^{-1} band (ν_S, imide carbonyl group[14]) possessing a transition moment parallel to the chain axis[11] and confirmed that $K \approx 1$.

The polarized visible absorption spectra were recorded using a Jasco Ubest-30 spectrophotometer equipped with polarizers (both sample and reference sides) located between the sample and light source. Polarized infrared spectra for thin PI films were recorded on a Jasco FT-IR 5300 spectrometer with a KRS-5 polarizer (Jasco PL-81).

In-Plane Orientation. For the unstretched as-cast PAA and the resulting PI films cured on a glass substrate, the degree of in-plane molecular orientation was estimated by measuring the dichroic spectra at an incidence angle Θ. Details are described in ref 10. We defined an in-plane orientation parameter:

$$f = (1 - D)/(1 - D_0) \quad (2)$$

where D is the dichroic ratio A_P/A_S (subscripts P and S mean P- and S-polarized beams) at the peak wavelength of PEDI (around 535 nm) and D_0 ($=\cos^2\alpha$) is the dichroic ratio for the complete in-plane orientation distribution. The f value ranges from 0 (three dimensionally isotropic) to unity (complete in-plane orientation). To obtain the dichroic ratios at a constant refraction angle ($\alpha = 28^\circ$) for all film samples, Θ with respect to both P- and S-polarized beams were adjusted on the basis of the refractive indices (in-plane, n_{in}, and out-of-plane, n_{out}) of PAA and PI films. Θ was calculated from the following equation:

Snell's law $\sin \Theta = n \sin \alpha$
($n = n_{in}$ for S-polarized light) (3)

$$n^{-2} = n_{in}^{-2} \cos^2 \alpha + n_{out}^{-2} \sin^2 \alpha$$
(for P-polarized light) (4)

Other Measurements. Dynamic mechanical measurements were conducted on a thermomechanical analyzer (Mac Science TMA-4010) with a heating rate of 5 °C min^{-1} and a load frequency (sinusoidal) of 0.1 Hz in a nitrogen flow. The densities (ρ) of PI films were measured at 25 °C using a density gradient column (xylene−CCl_4 system).

For the uniaxially oriented PI films, the refractive indices [stretching (n_{MD}), transverse (n_{TD}), and thickness (n_{ThD}) directions] were measured by using an Abbe's refractometer (Atago-4T) equipped with a sodium lamp and a polarizer. The values of n_{MD} for the highly oriented PI(BPDA/PDA) films were calculated from the average refractive index (n_{av} = 1.7710)[10] and the measured n_{TD} and n_{ThD}).

The amounts of residual solvent in PAA films were determined on the basis of an infrared absorption of DMAc as reported previously.[10]

Results and Discussion

Effect of the Chain Structure on the Spontaneous Orientation for BPDA-Type Homopolyimide Systems. In this chapter, we discuss how the chain structures (chain stiffness or linearity, presence of side-chain substituents) influence the molecular orientation of the resultant PIs. Three kinds of BPDA-type PIs, i.e., semirigid BPDA/PDA, BPDA/ODA containing the flexible ether linkages, and BPDA/DMPDA possessing bulky methyl substituents on the same backbone as BPDA/PDA, were used here as shown in Figure 1.

First of all, we show the results of BPDA/PDA. In the present study, the uniaxial stretching was conducted at the stage of PAA films and subsequently the drawn films were thermally imidized. Therefore, one of the most important problems is an orientational change during the cure reaction. Then we examined the degree of orientation at the both stages of PAA and PI. Parts a−c of Figure 2 display the dichroic absorption spectra of the labeled PAA(BPDA/PDA) and the resulting PI films. For the undrawn PAA film, both polarized spectra were completely overlapped (Figure 2a), indicating that the film is isotropic in the Thru view. A low extent of uniaxial stretching (DR = 40%) of the PAA films led to a slightly anisotropic film. What should be noted is that heat treatment required for cure reaction did not cause orientational relaxation but considerably larger anisotropy. The orientational change during cure depended strongly on the chain structure as illustrated below.

Parts a−c of Figure 3 exhibit F as a function of DR for three kinds of BPDA-type PIs with different diamine components. For all PAAs, a low extent of stretching (DR less than ∼40%) naturally does not give high molecular orientation. The DR−F curves are, in fact, almost independent of the chain structure. However, a large dependence of F on the chain structure was observed after imidization; for the semirigid BPDA/PDA system (Figure 3a), the F values increased markedly upon thermal cure if the precursor films were drawn. On the other hand, BPDA/ODA containing flexible ether linkages showed no spontaneous orientation behavior; on the contrary, orientational relaxation took place upon

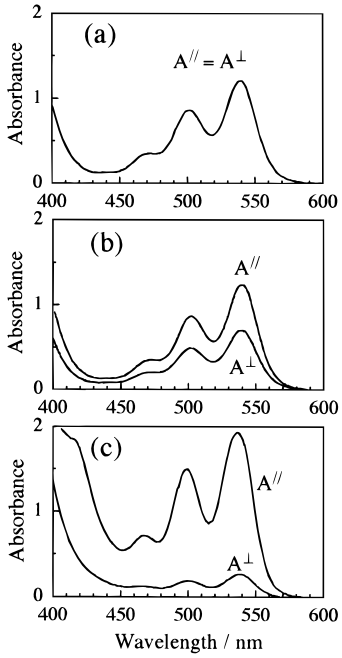

Figure 2. Dichroic absorption spectra of labeled BPDA/PDA films: (a) undrawn PAA, (b) drawn PAA (DR = 40%), and (c) PI obtained from the drawn PAA.

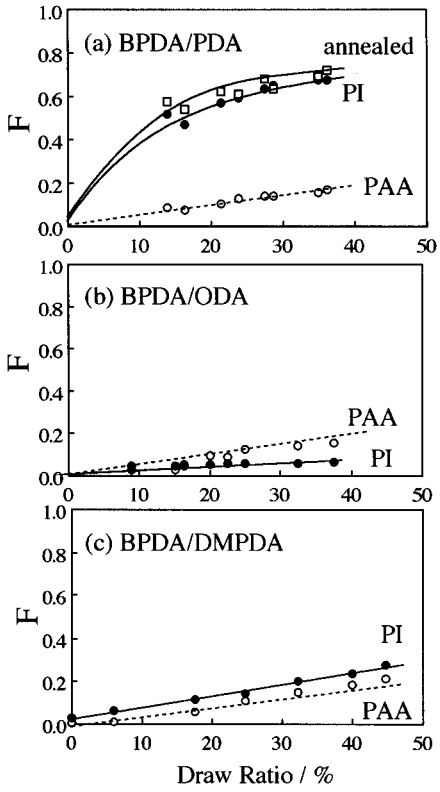

Figure 3. Orientation functions of PAA and the corresponding PIs as a function of DR for (a) BPDA/PDA, (b) BPDA/ODA, and (c) BPDA/DMPDA systems. (○) PAA, (●) PI, and (□) annealed at 330 °C after imidization at 250 °C (step-cure).

cure as shown in Figure 3b. Orientational relaxation by annealing is a common phenomenon. However, for the anomalous behavior (increase in macroscopic orientation) observed in the BPDA/PDA system, what is the driving force? The PI chain linearity (stiffness) seems to be one of the most important factors responsible for that. However, Figure 3c demonstrates that BPDA/DMPDA possessing bulky substituents shows almost no spontaneous orientation, in spite of the fact

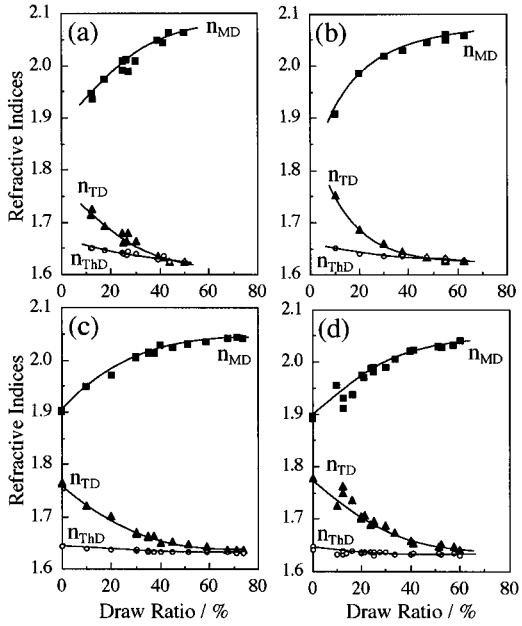

Figure 4. Refractive indices of three directions (MD, TD, ThD) for uniaxially oriented PI(BPDA/PDA) films with varying DR. Thickness of PAA films before stretching: (a) 50−60, (b) 36, (c) 10−11, and (d) 4−7 μm thick (the initial PAA). (■) n_{MD}, (▲) n_{TD}, and (○) n_{ThD}.

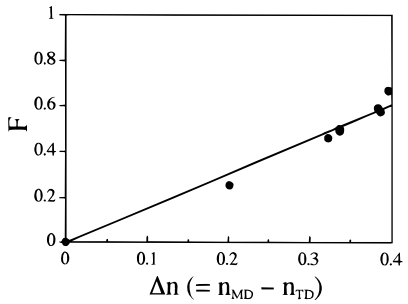

Figure 5. Relationship between Δn (=n_{MD} − n_{TD}) and the orientation function for uniaxially oriented PI(BPDA/PDA) films (50 μm thick for the initial PAA films).

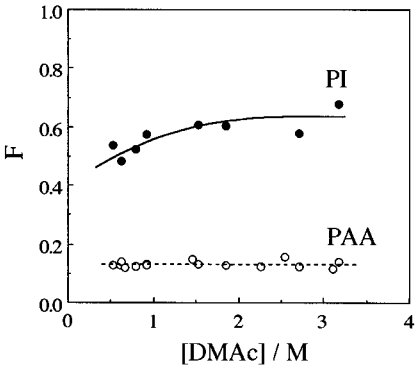

Figure 6. Orientation functions of the uniaxially drawn PAA-(BPDA/PDA) films (17 μm thick, DR = 30%) and the resulting PIs as a function of residual DMAc concentration in the initial PAA films.

that the chain backbone is really the same as BPDA/PDA. The film density of PI(BPDA/DMPDA) (ρ = 1.3097 g cm^{-3}) cured at 250 °C (step-cure) was much lower than that of BPDA/PDA (ρ = 1.4260 g cm^{-3}) prepared under the same conditions, indicating the looser molecular packing (weaker interchain interactions) of the former. These results suggest that interchain interactions probably play an important role to bring about "*F*-jump" (the extent of spontaneous orientation $\Delta F = F_{PI} - F_{PAA}$ at DR = 40%). The BPDA/PDA system showing marked spontaneous orientation is focused on below. In this system with stiff chain structure, additional annealing at higher temperatures (e.g., 330 °C) of the highly oriented PI(BPDA/PDA) films cured at 250 °C (imidization is almost completed) did not practically change the degree of orientation.[9] Accordingly, an imidization process where molecular mobility sufficient for the chain rearrangement is obtainable is only a chance of orientational enhancement for the rigid chain systems.

Orientation Behavior of BPDA/PDA Homopolyimide. (a) Trirefringence of Oriented PI(BPDA/PDA) Films. To estimate the orientational distribution of the uniaxially oriented PI films, we measured the refractive indices of three directions as shown in Figure 4. With an increase in DR, the anisotropy in the Thru view ($n_{MD} - n_{TD}$) increased, but that in the End view ($n_{TD} - n_{ThD}$) decreased on the contrary and finally became zero (isotropic in the End view). The End view anisotropy suggests the presence of a certain degree of in-plane orientation for the only slightly drawn films (DR < 20%). Figure 4 also illustrates that DR where the End view distribution becomes isotropic increased with decreasing film thickness. However, at DR ~ 50%, the values of $n_{TD} - n_{ThD}$ became nearly zero for all films (4−60 μm thick).

The *F* estimated from the PEDI dichroism was plotted as a function of $n_{MD} - n_{TD}$ for the 50 μm thick films in Figure 5. A linear relationship, $n_{MD} - n_{TD} = \Delta n_0 F$, was frequently observed for uniaxially stretched polymer systems. Although the result in Figure 5 deviates a little from a linear relation, the slope gives tentatively the intrinsic birefringence $\Delta n_0 = 0.66$ for the BPDA/PDA system.

(b) Effects of Amount of Residual Solvent, Film Thickness, and Heating Rate. A large amount of solvent ([DMAc] = 2.5−3 M) is still remaining in PAA films cast at 60 °C for 1 h owing to the complex formation of DMAc with the carboxyl and with amide groups in the PAA units[15,16] but can be readily extracted by dipping the as-cast films into water.[10] Figure 6 shows the dependence of *F* on the amount of residual solvent in the PAA films controlled by changing the dipping time. There was no effect of dipping on *F* for the drawn PAA films (DR = 30%), but the *F* values of the resulting PI films do depend on the initial DMAc concentration. Complete solvent removal is unfavorable for the spontaneous orientation. This is probably a reason why molecular motion required for the spontaneous orientation during cure was insufficient for the solvent-free films. Other results also manifest a role of residual solvent as a plasticizer; cure of the solvent-free PAA films provides lower imidization rate and less ordered structures.[6]

On the other hand, the excess amount of residual solvent probably causes relaxation of uniaxial orientation. Thus, for inducing the spontaneous orientation there should be an optimum degree of molecular motion related to the initial amount of residual solvent. In fact, we found the presence of such an optimum condition in a similar system; when undrawn PAA(BPDA/PDA) thick films (80 μm) with different *N*-methyl-2-pyrrolidone (NMP) concentrations (0.5−2.7 M) were cured in a metal frame (bifix-cure), the initial PAA films with an intermediate [NMP] (=1.8 M) gave the highest degree of in-plane orientation for the resultant PI film. Similarly, Miwa et al.[17] prepared several PI(BPDA/PDA)

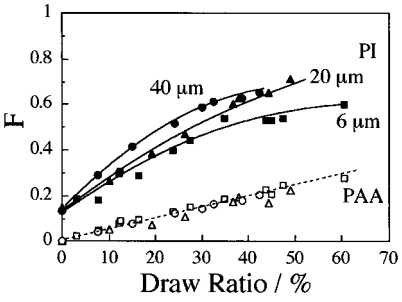

Figure 7. Effect of film thickness on DR−*F* curves for PAA-(BPDA/PDA) and the corresponding PI films: (●) 40, (▲) 20, and (■) 6 μm thick. Open marks (○, △, □) represent PAA.

films from the PAA films with different [NMP] varied with casting temperature (80−120 °C) and observed the lowest coefficient of thermal expansion at an intermediate [NMP] in the initial PAA films. An interesting point to note is that these results are essentially different from the fact that the more severe cure conditions (higher temperature ramps and higher cure temperatures) which give more intensive molecular motion are favorable for the local structure ordering (crystal-like order and intermolecular charge-transfer complex formation, etc.) for the BPDA/PDA system.[2,3,6,7]

Not only the initial solvent concentration but also the rate of evaporation of solvent and water (byproduct of imidization) from the films during cure influence the chain mobility. Accordingly, film thickness is an important parameter. Figure 7 exhibits the dependence of the DR−*F* curve on film thickness. Comparison at DR = 50%, where the End view anisotropy almost disappeared for the 4−60 μm thick films, showed that the DR−*F* curves shift only slightly toward high orientation with increasing thickness. Thus, for the rigid chain system with restricted molecular mobility an increase in film thickness was favorable for the spontaneous orientation in this thickness range.

However, for the flexible BPDA/ODA system the dependence on film thickness was significantly different from the semirigid BPDA/PDA system illustrated above: the thicker BPDA/ODA films (60 μm) were subjected to the orientational relaxation upon cure as shown in Figure 3b, whereas the thinner BPDA/ODA films (14 μm) show a slight increase in *F* upon cure (compare with Figure 13a shown later). The opposite tendencies with thickness change for the BPDA/PDA and BPDA/ODA systems are most likely attributed to the considerable difference of the intrinsic chain mobility during cure.

In addition, as will be shown later, for the blends (50/50) of semirigid BPDA/PDA (labeled) and flexible BPDA/ODA (unlabeled), the thinner blend films (11−15 μm) provided higher *F* values for the labeled BPDA/PDA chains in the blends than the thicker blend films (60 μm) (compare Figure 10b with Figure 14a shown later). As will be discussed later, this also most probably results from the increased molecular mobility of the BPDA/PDA chains in the blends in comparison with the homo-BPDA/PDA system. These results indicate that for the systems possessing higher molecular mobility a decrease in film thickness acts favorably to the spontaneous orientation.

Heating rate during cure also influences molecular mobility. As shown in Figure 8, a faster heating process for imidization up to 250 °C (6 °C min^{-1}) gave a little higher *F* than a slower ramp rate (1 °C min^{-1}). Although we could not vary the heating rate widely in our

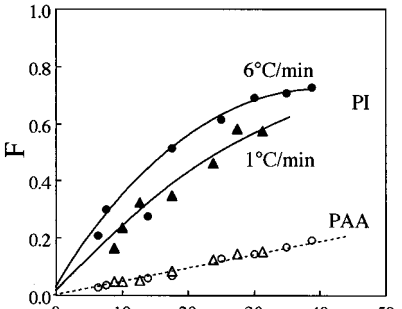

Figure 8. Effect of heating rate in the range of 100−250 °C on DR−*F* curves for PI(BPDA/PDA) films: (▲) 1, and (●) 6 °C min^{-1}. Open marks (△, ○) represent PAA. The samples were isothermally annealed for 2 h after heating up to 250 °C with different ramp rates.

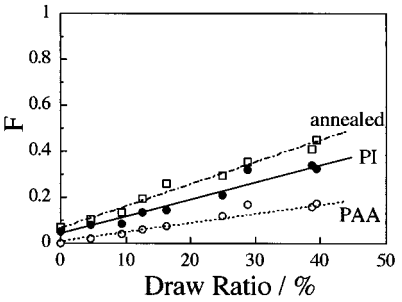

Figure 9. DR−*F* curves of PAA(BPDA/PDA) (5 μm thick), the chemically cured PIs, and PIs annealed at 330 °C for 1 h after chemical imidization.

furnace, too high ramp rate most probably brings about orientational relaxation. The optimum conditions (degree of molecular motion during cure) for the spontaneous orientation, associated with the amount of residual solvent, film thickness, and heating rate, must depend strongly on the chain (chemical) structure. In fact, for a random copolyimide BPDA:PMDA/PDA (BPDA:PMDA = 50:50), Young's moduli related closely to the degree of in-plane orientation are strongly affected by the cure program (heating rate, one-step/multistep-cure) and film thickness, whereas the influence of these conditions is not as large for homo-BPDA/PDA and homo-PMDA/PDA systems.[18]

(c) Effect of the Cure Method (Thermal and Chemical Imidization). So far, few papers have described the effect of imidization methods (thermal/chemical) on the molecular orientation of the resulting PIs.[19] Chemical imidization proceeds through swelling of the dipped PAA films by penetration of dehydrating agent (acetic anhydride) and catalyst (pyridine) molecules. Therefore, during this cure process the polymer chains can get sufficient molecular motion required for imidization in the swollen film even at room temperature. Figure 9 exhibits the DR−*F* curves for the precursor, the chemically cured PI(BPDA/PDA), and the additionally annealed PI films. Chemical imidization caused the *F*-jump much lower than thermal cure (see Figure 3a). For the reason mentioned above, it was difficult to discuss from the viewpoint of the difference of molecular mobility between two cure processes.

Additional annealing at 330 °C increased slightly the *F* values as shown in Figure 9. On the other hand, the *F* of highly oriented PI(BPDA/PDA) films cured at 250 °C did not alter practically upon the same annealing.[9] The *F*-jump upon the additional annealing was probably allowed by loose molecular packing in the chemically

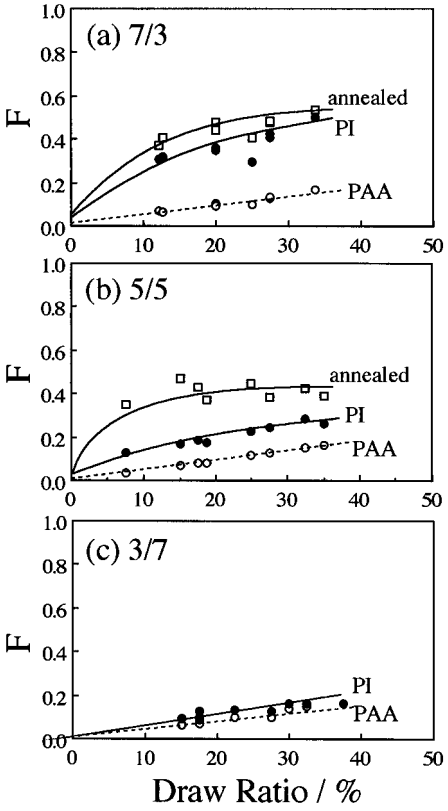

Figure 10. Orientation function vs DR for the blends of labeled BPDA/PDA and unlabeled BPDA/ODA with varying blend ratio: (BPDA/PDA)/(BPDA/ODA) = (a) 70/30, (b) 50/50, and (c) 30/70. (○) PAA, (●) PI, and (□) annealed at 330 °C after imidization at 250 °C (step-cure).

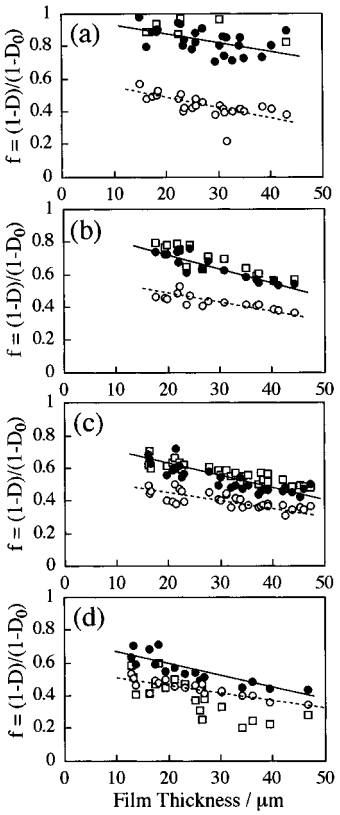

Figure 11. Degree of in-plane orientation, *f*, as a function of film thickness for the blends of labeled BPDA/PDA and unlabeled BPDA/ODA with varying blend ratio: (BPDA/PDA)/(BPDA/ODA) = (a) 100/0, (b) 70/30, (c) 50/50, (d) 30/70. (○) PAA, (●) PI, and (□) annealed at 330 °C after imidization at 250 °C (step-cure).

cured films.

Spontaneous Orientation of Component PI Chains in a Miscible Binary System. We first take up a binary system composed of BPDA/PDA (labeled) and BPDA/ODA (unlabeled). This system is known to have good miscibility.[8] In principle, one can monitor only the orientation of the labeled semirigid PI chains in the flexible PI matrix. Figure 10 displays the changes in the DR−*F* curves with varying blend composition. At the stage of PAA, there is no blend ratio dependence, and the magnitudes of *F* are quite low, as well as in the homopolyimide systems. On the other hand, the *F*-jump for the labeled BPDA/PDA chains in the blends decreased with an increase in the flexible PI content, and finally the self-orientation character of BPDA/PDA disappeared against our first expectation that the extent of *F*-jump is independent of the blend composition.

The degrees of in-plane orientation, *f*, for the labeled PI(BPDA/PDA) chains in the same blends are also plotted in Figure 11 as a function of the blend ratio. The magnitude of *f*-jump ($f_{PI} - f_{PAA}$ at a fixed thickness) decreased with increasing flexible BPDA/ODA content. This behavior is similar to that of the uniaxially oriented blend system of the same compositions. We believe that the spontaneous in-plane orientation most likely has essentially the same mechanism as the spontaneous uniaxial orientation. It should be noted that since this blend system is miscible, there exists intimate contact between different polymer chains. These results suggest that the degree of spontaneous orientation during cure is dominated by not only the chain linearity or stiffness but also interchain interactions. When a BPDA/PDA chain was surrounded by flexible BPDA/ODA chains, the spontaneous orientation of the former is hindered by the relaxation tendency of the latter. For the homo-BPDA/PDA system, the neighboring chains promote the molecular orientation of each other; consequently, considerably higher *F* values are obtained. This is interpreted as a kind of "cooperative phenomenon". Accordingly, the loose molecular packing unfavorable for the cooperative chain orientation is probably responsible for the suppressed spontaneous orientation character in the BPDA/DMPDA system (Figure 3c).

Figure 12 shows the DR−*F* curves for copolyimides BPDA/PDA:ODA as a function of the copolymer composition. The DR−*F* curves of PAAs were independent of the copolymer composition. But, the values of *F* of the resultant PI films decreased with increasing ODA content in the copolymer as well as in the corresponding blend system (Figure 10). Contrary to our first expectation that the labeled BPDA/PDA chains in the BPDA/ODA matrix (blend system (1)) would have shown the *F* values much higher than the corresponding copolymers, the difference between both systems turned out to be small.

Effect of Miscibility on the Spontaneous Orientation of the Rigid Component. We discuss here an effect of the miscibility in binary systems composed of rigid and flexible PIs on the spontaneous orientation behavior for the rigid chain component which controls the modulus and strength of the uniaxially oriented blend materials. As previously reported, the blends of BPDA/PDA with PMDA/ODA are immiscible,[4] whereas those of BPDA/PDA with BPDA/ODA are miscible. From these results it is expected that for the blends (50/50) of BPDA/PDA with BPDA:PMDA/ODA an increase

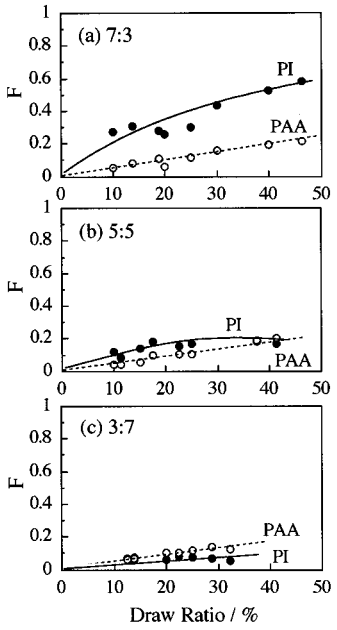

Figure 12. Orientation functions of PAA(BPDA/PDA:ODA) with different compositions and the corresponding PIs as a function of DR: PDA:ODA = (a) 70:30, (b) 50:50, and (c) 30:70. (○) PAA, (●) PI.

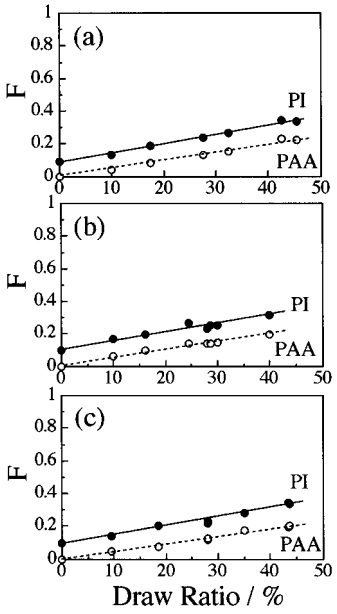

Figure 13. Orientation functions vs DR for three flexible matrix polymers, (a) BPDA/ODA, (b) PMDA/ODA, and (c) BPDA:PMDA/ODA (BPDA:PMDA = 50:50). The initial PAA film thickness is 13−15 μm.

in the BPDA content in the copolymer should result in the domain size decrease.

Parts a−c of Figure 13 confirmed that the matrix polymers containing the flexible ether linkages, i.e., PMDA/ODA and BPDA:PMDA/ODA, show no marked spontaneous orientation upon cure as well as BPDA/ODA. Figure 14 manifests the dependence of the *F*-jump for the labeled BPDA/PDA chains in the BPDA:PDA/ODA matrices on the blend miscibility controlled with the PMDA content in the matrix copolymers. In this blend system (50/50), the blends provided optically transparent films within the PMDA contents of 0−10 mol % in the copolymer. At 20 mol % PMDA, the blend film became only slightly opaque and the turbidity gradually increased with increasing PMDA content in

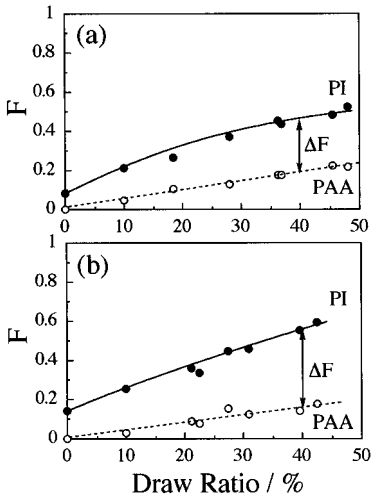

Figure 14. DR−*F* curves for the labeled BPDA/PDA for (a) a miscible blend (50/50), (BPDA/PDA)/(BPDA/ODA), and (b) an immiscible blend (50/50), (BPDA/PDA)/(BPDA:PDA/ODA) (50:50). The initial PAA film thickness is 11−15 μm.

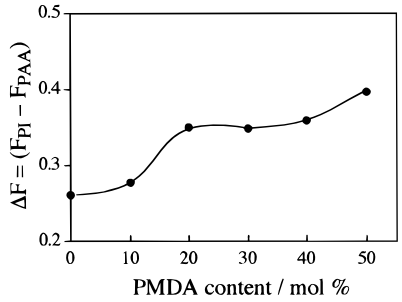

Figure 15. Change in ΔF ($=F_{PI} - F_{PAA}$) at DR = 40% for the labeled BPDA/PDA chains in the unlabeled BPDA:PDA/ODA matrices with varying PMDA content in the copolymers.

the copolymer. The magnitude of the *F*-jump at DR = 40% replotted in Figure 15 reveals that the extent of spontaneous orientation varied abruptly between 10 and 20 mol % in the PMDA content, corresponding to the change in the blend homogeneity. It should be noted that the phase-separated blends exhibited ΔF higher than the miscible blends, which are close to those observed in the homo-BPDA/PDA system.

According to the concept of molecular composites,[20,21] mixing of rigid and flexible polymer chains at the molecular level, which prevents the bundle formation between the rigid chains and consequently increases the aspect ratio, leads to marked enhancement of Young's modulus. However, the present results demonstrated that for the rigid/flexible PI binary systems produced through a two-step method (mixing at the PAA stage and thermal cure) good miscibility disturbs the spontaneous orientation character intrinsic to the rigid PI systems, related closely to the properties of the resulting PI/PI molecular composites.

Enhancement of Orientation upon Additional Annealing at Higher Temperature. The previous section concerns the spontaneous orientation taking place during the imidization process. The present section describes self-orientation behavior of fully cured PI films upon postcure at higher temperatures in a free-standing state. Let us turn to Figure 3a. Additional annealing at 330 °C for the oriented homo-PI(BPDA/PDA) films cured at 250 °C (step-cure) did not practically alter the degree of orientation. Although the homo-PI(BPDA/PDA) film cured at 250 °C shows a broad E'' peak at 320 °C corresponding to the T_g, the

annealing at 330 °C was less effective for the orientational change. On the other hand, the 70/30 and 50/50 blends showed obviously the orientation enhancement of the labeled BPDA/PDA chains by the same annealing (see Figure 10). The observed self-orientation was allowed by an increase in molecular mobility of the PI(BPDA/PDA) chains, caused by the addition of the flexible PI component. However, this behavior is curious because annealing at a temperature above T_g, commonly, tends to randomize macroscopic uniaxial orientation.

The self-orientation induced by postcure was also observed for some fluorinated homopolyimides, semirigid PI(BPDA/TFDB), and rodlike PI(PMDA/TFDB) (TFDB: 2,2-bis(trifluoromethyl)-4,4′-diaminobiphenyl).[22−24] The trifluoromethyl substituents significantly weaken the intermolecular interactions; consequently, the molecular mobility increases. The structural factor that these fluorinated PIs possess is the combination of chain stiffness or linearity and higher molecular mobility, that is, LC-like character at the annealing temperatures. Similarly, PI(BPDA/PDA) probably have essentially LC-like character at cure temperatures[6] where molecular mobility sufficient for the chain rearrangement is obtainable, but this character is covered with the suppressed molecular mobility resulting from the strong interchain interactions.

Conclusions

PEDI incorporated into the PAA main chains made it possible to estimate the orientational changes during cure reaction for the component chains in binary PI blends. Slightly uniaxially drawn PAA films of semirigid BPDA/PDA showed marked spontaneous molecular orientation toward the stretching direction upon thermal imidization, whereas flexible BPDA/ODA (60 μm thick) was subjected to the orientational relaxation. Introduction of the bulky methyl substituents onto the BPDA/PDA backbone suppressed significantly the spontaneous orientation character. These results indicate that not only chain stiffness (linearity) but also interchain interactions intensified by denser molecular packing are important factors for the occurrence of spontaneous orientation.

In the miscible blend system composed of semirigid BPDA/PDA and flexible BPDA/ODA, the extent of spontaneous orientation, ΔF, for the labeled BPDA/PDA chains decreased with an increase in the content of BPDA/ODA as the matrix component against our first expectation that it should be independent of the blend composition. A similar tendency was observed for the spontaneous in-plane orientation in the same blend system. The marked spontaneous orientation behavior of homo-BPDA/PDA is interpreted as a kind of cooperative phenomenon, where the neighboring chains promote the molecular orientation of each other in the course of the cure process. The results of the blend system composed of the labeled BPDA/PDA and unlabeled BPDA:PMDA/ODA revealed that the blend miscibility affects the extent of spontaneous orientation.

For homo-PI(BPDA/PDA) cured at 250 °C, additional annealing at 330 °C was less effective for the orientational change owing to the restricted molecular mobility based on the strong interchain interactions. On the other hand, blending with flexible BPDA/ODA led to the self-orientation of the labeled BPDA/PDA chains in the blends under the same annealing conditions. This probably results from combination of the LC-like character of BPDA/PDA and the increased molecular mobility.

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