

Spontaneous Molecular Orientation Behavior in Polyimides

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ABSTRACT

The degrees of uniaxial molecular orientation for homo polyimides (PI) and PI/PI binary blends were measured by means of the visible absorption dichroism of a dye incorporated into the main chains. A semi-rigid PI showed marked spontaneous orientation during thermal cure of the slightly drawn polyamic acid (PAA) film. The dependence of the spontaneous behavior on the chain structure revealed that in addition to the chain linearity the molecular packing is an important factor. In a miscible binary system, the degrees of spontaneous orientation induced by cure process for the component polymers depend strongly on the blend composition. The results leads to a cooperative mechanism for the orientation enhancement.

INTRODUCTION

Thermal imidization processes are recognized widely as a key point to improve PI properties. We have so far been investigated the microstructures influencing strongly by cure condition by means of small angle X-ray scattering,[1] intrinsic fluorescence,[2-4] and FTIR spectroscopy.[5] For example, the increase in initial imidization temperature, final cure temperature, and heating rate and the presence of the residual solvent as a plasticizer cause some structure organization (crystallization, charge transfer complex formation, liquid crystal-like order formation).

Thermal imidization of uniaxially cold-drawn PAA films for a semi-rigid PI system derived from 3,4,3'4'-biphenyltetracarboxylic dianhydride (BPDA) and p-phenylenediamine (PDA) provides considerable enhancement of Young's modulus.[6] We showed previously that the molecular orientation of BPDA/PDA chains enhances spontaneously upon thermal cure reaction from slightly stretched PAA (Hermans' orientation function $F = 0.2$) to the corresponding PI ($F = 0.7$).[7] Similarly, the in-plane orientation is increased considerably upon cure of PAA(BPDA/PDA) films adhered on a substrate.[8] The present paper focuses on the spontaneous orientation behavior for each component of rigid and flexible PIs in binary

molecular composites (MC) and discuss how the blend miscibility affects the orientation behavior. The result will provide a valuable indicator to control the mechanical properties of the MCs.

EXPERIMENTAL SECTION

For the purpose mentioned above, we prepared PAAs labeled with a dichroic dye, perylenetetracarboxydiimide (PEDI, see Fig.1)[8] and established two cases of binary miscible blends: (1) labeled rigid / unlabeled flexible components and (2) unlabeled rigid / labeled flexible components. The trace amount of diamino-PEDI was copolymerized to introduce into PAA main chains (one PEDI per 900 repeating unit). To suppress transamidation, we prepared the PAA blend films by casting (at 60°C for 2h) after immediately vigorous blending of PAA solutions (10 wt%) for 10 min at room temperature. The PAA blend films were stretched at room temperature with various draw ratio ($DR = \Delta L/L_0 \times 100$) and then stepwise-cured at 150°C for 1 h + 200°C for 1 h + 250°C for 2 h (step 250°C cure) in a metal frame in a nitrogen atmosphere.

PEDI has an absorption transition moment (530 nm band) parallel to the long molecular axis and additionally the diamino-PEDI units are introduced covalently along the polymer chain segments (angle θ between the polymer chain axis and the transition moment is nearly zero). This allows to get the value of F for both stages of PAAs and PIs in MCs. Measurements of the dichroic ratio $D (= A^{\parallel} / A^{\perp})$, where A^{\parallel} and A^{\perp} are the absorbances for the incident light linearly polarized parallel and perpendicular to the stretching direction respectively, provide the orientation function $F = 0.5 (3 \langle \cos^2 \theta \rangle - 1) = (D-1)/(D+2)$.

RESULTS AND DISCUSSION

BPDA Type Homopolyimide Systems.

Fig.2 exhibits the orientation functions as a function of DR for three types of BPDA-based PI systems with different diamine components, namely, semi-rigid, flexible, and semi-rigid with bulky substituents. For all the PAAs, the low extent of stretching ($DR \sim 40\%$) naturally does not give high molecular orientation. The DR-F curves are nearly independent of the chain structure. However, a large dependence of F on the chain structure was observed after imidization; for the semi-rigid BPDA/PDA system (Fig.2a), the F values enhanced markedly upon thermal cure of the drawn PAA ($DR = 40\%$) films. On the other hand, BPDA/ODA system containing flexible ether linkages showed no spontaneous orientation behavior, but slight orientational relaxation upon cure as shown in Fig.2b. The result in BPDA/ODA is regarded as a general annealing effect as observed frequently for oriented polymer films and fibers.

What is the driving force of the spontaneous orientation behavior observed in BPDA/PDA

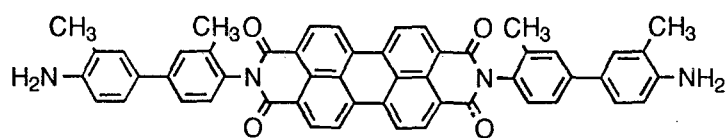


Fig.1 Structure of diamino-PEDI.

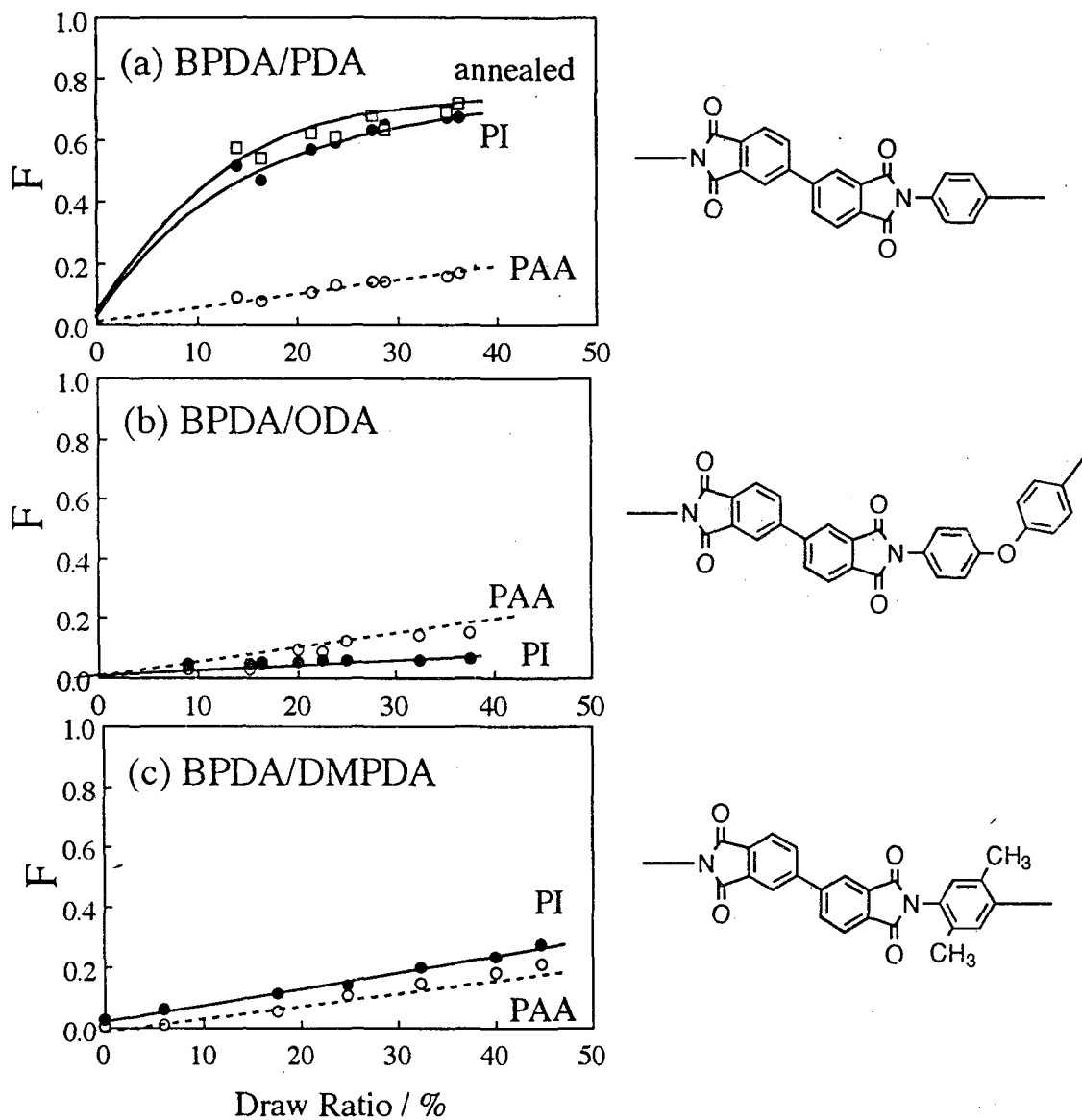


Fig.2 Orientation function of PAAs and PIs as a function of draw ratio for BPDA/PDA, BPDA/ODA, and BPDA/DMPDA systems.

system? The PI chain linearity (stiffness) seems to be one of the most important factors. However, Fig.2c demonstrated that BPDA/DMPDA (DMPDA: 2,5-dimethyl p-phenylenediamine) possessing bulky substituents causes no marked spontaneous behavior, in spite of the chain linearity the same as BPDA/PDA. The film density of PI(BPDA/DMPDA) (1.3097 g cm^{-3}) prepared on step 250°C much lower than that of BPDA/PDA (1.4260 g cm^{-3}) cured the same condition suggests the looser molecular packing (weaker interchain interactions) of the former. Thus, the results led us to conclude that the interchain interactions play an important role to cause the spontaneous orientation.

The degree of molecular mobility during cure affects somewhat. A faster heating process for imidization up to 250°C (6°C min^{-1}) gives the F values a little higher than a slower one (1°C min^{-1}). In addition, complete removal of the residual solvent in a stretched PAA film by dipping into water was subjected to a slight decrease in the F value. Moreover, chemical imidization of the drawn PAA films fixed in a frame by the mixture of acetic anhydride and pyridine at 100°C does not induce strongly the orientational enhancement.

Orientation of Component PI Chains in Miscible Binary System.

We take first a binary system composed of labeled BPDA/PDA and unlabeled BPDA/ODA. This system is known to show good compatibility.[9] In principle, one can focus only the orientation of the semi-rigid PI chains in the flexible PI matrix. Fig.3 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 degree of spontaneous orientation ($\Delta F = F_{\text{PI}} - F_{\text{PAA}}$) for the labeled BPDA/PDA chains in the MC decreased with an increase in the flexible PI content, and finally the characteristics of self-orientation for BPDA/PDA disappeared.

Fig.4 indicates the blend composition dependence in the same binary system composed of unlabeled BPDA/PDA and labeled BPDA/ODA. As shown in Fig2b, homo BPDA/ODA is preferentially subjected to the orientational relaxation through thermal cure process, whereas the degree of orientation for BPDA/ODA chains increased with increasing BPDA/PDA content in the MC.

It should be noted that this blend system is miscible; there exists intimate contact between different polymers. These results led to the following mechanism: the degree of spontaneous orientation during cure is dominated by not only the chain linearity or stiffness, but also interchain interactions. This is interpreted as a "cooperative effect" influencing between neighboring chains each other. 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 homo BPDA/PDA system, on the contrary, the neighboring chains promote each other the spontaneous orientation, consequently the PI shows considerably high F

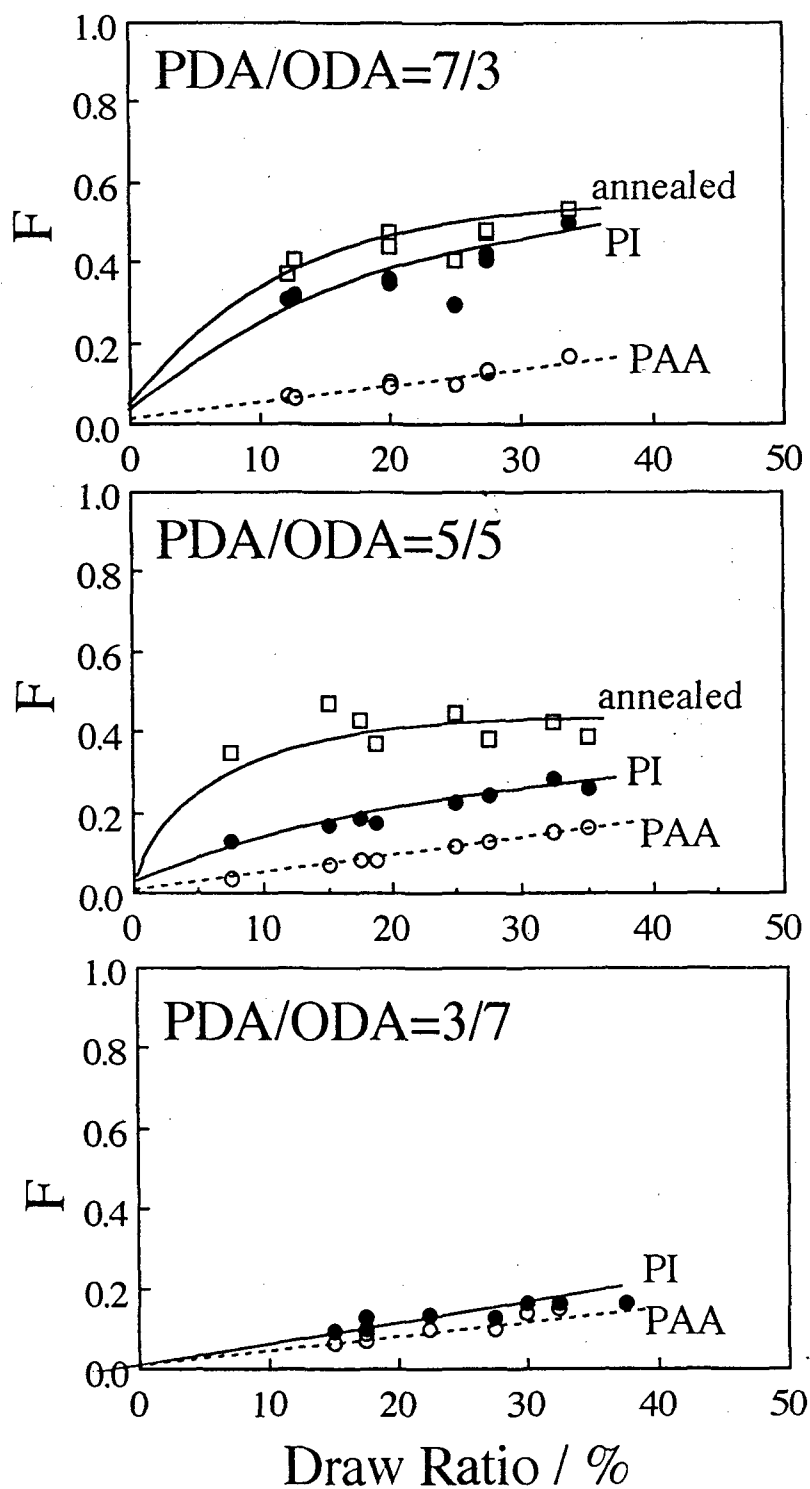


Fig.3 Orientation function of labeled BPDA/PDA chains in binary blend of BPDA/PDA with BPDA/ODA as a function of blend ratio.

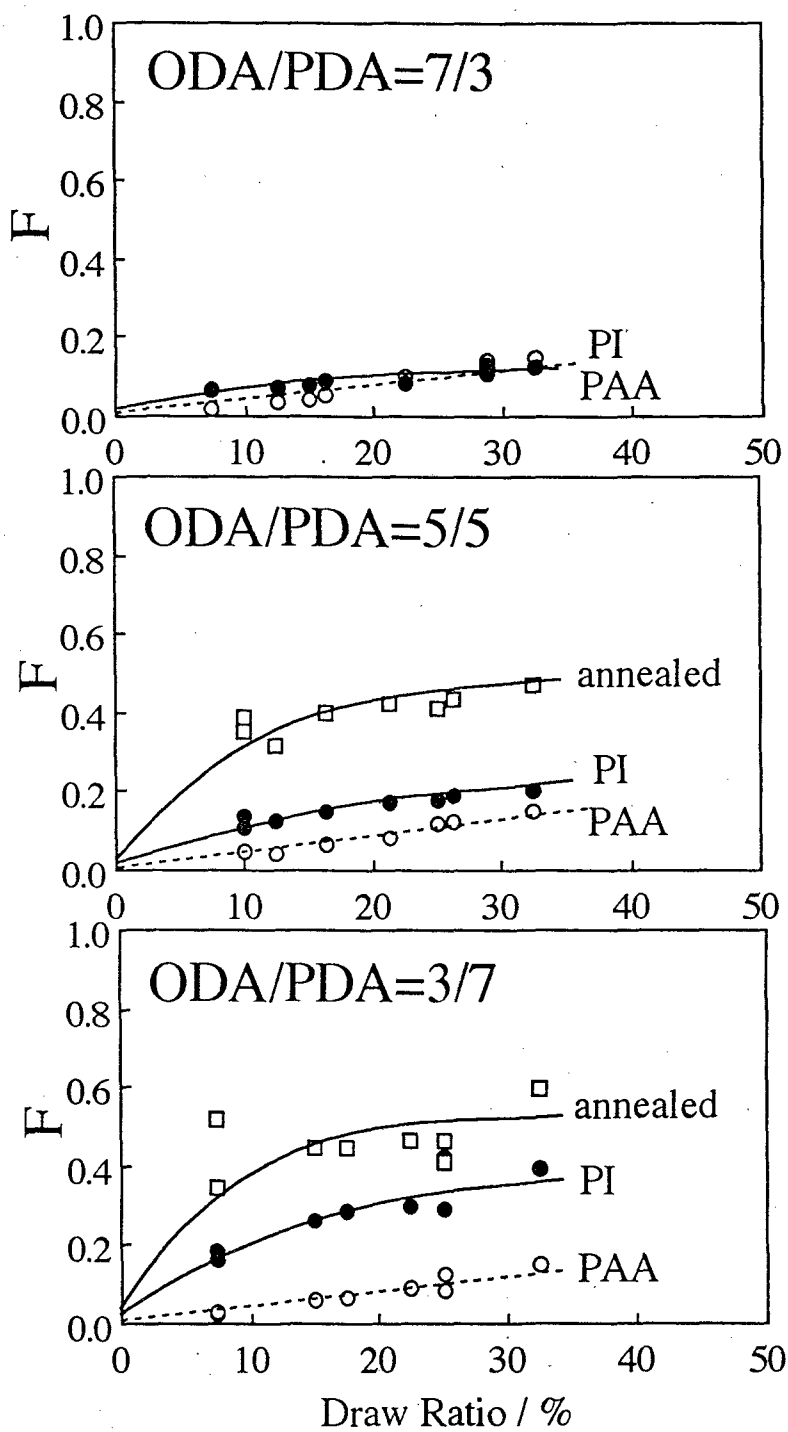


Fig.4 Orientation function of labeled BPDA/ODA chains in binary blend of BPDA/PDA with BPDA/ODA as a function of blend ratio.

values. The absence of the spontaneous orientation character in BPDA/DMPDA system (see Fig.2c) is probably attributed to the lack of intimate interchain contact between neighboring chains. The next result supports the proposed mechanism.

Immiscible Binary Blend Systems.

Fig.5 reveals an effect of the miscibility in binary systems on the orientation behavior. A previous paper[4] indicated that the blend of BPDA/PDA with PMDA/ODA (PMDA: pyromellitic dianhydride) is immiscible and forms quite opaque films. For precise measurements of F , we selected the combination of labeled BPDA/PDA and unlabeled BPDA-PMDA/ODA copolymer (BPDA : PMDA = 5 : 5), which gives a slightly cloud blend film. The flexible matrix polymer, BPDA-PMDA/ODA, were confirmed to show no spontaneous orientation upon cure as well as BPDA/ODA. The result in Fig.5 manifests that the phase separation system brings about ΔF higher than for the miscible system and the values close to those for homo BPDA/PDA system.

Thus, the degree of spontaneous orientation for the rigid PI, which affects strongly the mechanical properties of MCs, can be controlled by the blend miscibility.

Enhancement of Orientation by annealing of fully cured PIs.

Let us turn to Fig.2a. Additional annealing at 330°C of PI(BPDA/PDA) cured upon step 250°C did not alter largely the degree of orientation. However, the 7/3 and 5/5 blends showed obviously the orientation enhancement by the same annealing (see Fig.3). The self-orientation of the PI chains was probably allowed to an increase in molecular mobility of PI(BPDA/PDA) chains by the addition of the flexible PI component. The behavior may be related to a liquid crystal-like character of PI(BPDA/PDA).

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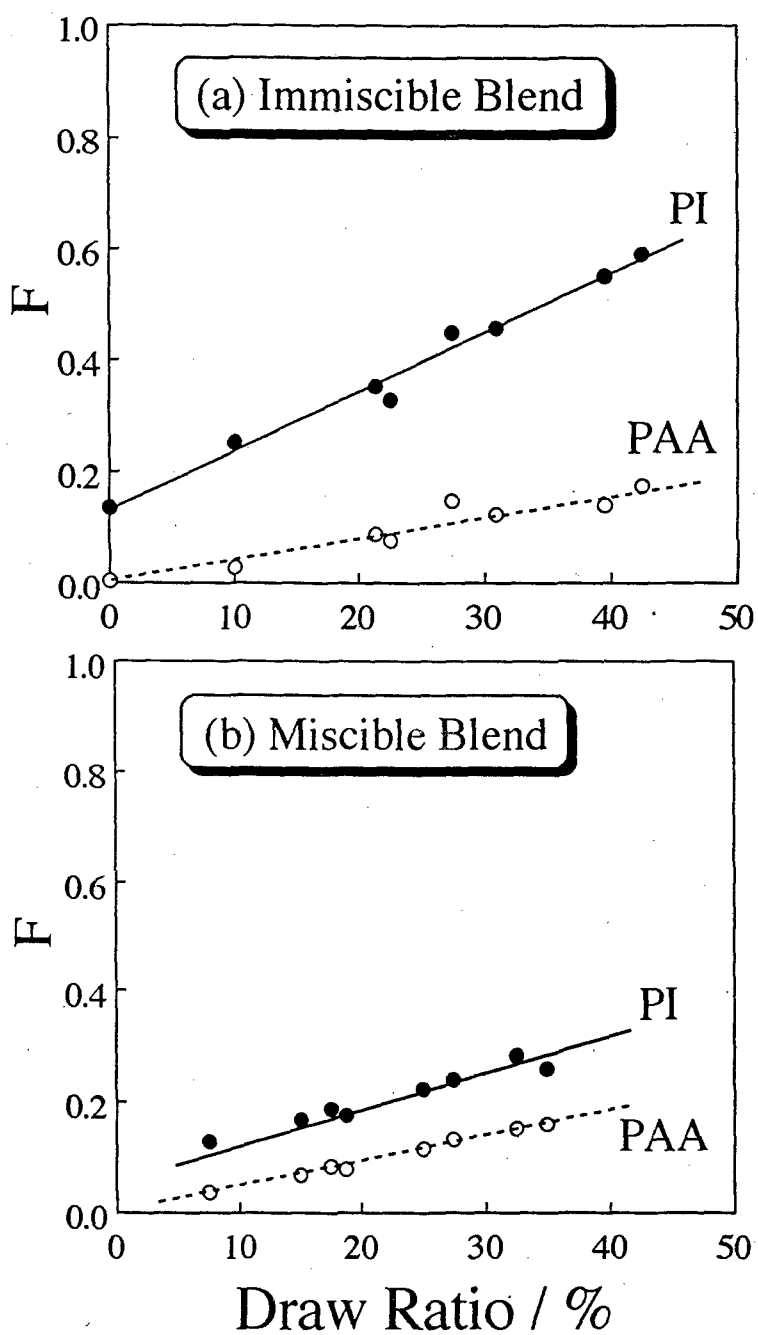


Fig.5 Orientation function of labeled BPDA/PDA chains in binary blend (5 / 5) systems: (a) BPDA/PDA / BPDA-PMDA/ODA and (b) BPDA/PDA / BPDA/ODA.