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Polyimide/Polyimide Blend Miscibility Probed by Perylenetetracarboxydiimide Fluorescence

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ABSTRACT: Perylenetetracarboxydiimide (PEDI) shows a unique fluorescence property. The dye is highly fluorescent in 3,3′4,4′-biphenyltetracarboxylic dianhydride (BPDA)-derived polyimide (PI) matrices but turns nonfluorescent in PIs from pyromellitic dianhydride (PMDA). The results can be explained in terms of a fluorescence quenching mechanism related to the charge transfer ability of the PI matrices. The miscibilities of binary blends between BPDA-derived PI and PMDA-derived PI were studied by applying this fluorescence behavior. In these blends, only BPDA-derived PIs were labeled by copolymerizing a trace amount of bifunctional PEDI. The PI/PI blend miscibilities were found to increase with an increase in drying (casting) temperature for mixed polyamic acid (PAA) solutions, a decrease in the molecular weights of PAAs, and an increase in storage temperature and its period for the mixed PAA solutions. In all cases, the fluorescence intensities decreased in accordance with an increase in the PI/PI blend miscibilities. The results reveal that the PEDI fluorescence is a powerful tool for studying the miscibility of PI/PI blends without appreciable T_g's.

Introduction

Polyimides are extensively used in microelectronics and aerospace industries for their excellent mechanical properties, low dielectric constants, low coefficients of thermal expansion, high radiation resistance, and high glass transition temperatures.[1−7] A variety of PIs have been molecular-designed on the basis of accumulated knowledge on the structure−property relationships. Owing to the simple synthetic method for PIs, random copolymerization by combining various monomers is very useful for more precise property control. Sequence-controlled copolyimides are expected to show several improved properties compared to the corresponding random copolymers.[8,9] Another approach is physical blending between different homo PIs. In general, most of polymer blends give rise to phase separation, by which property control is often disturbed. Miscible PI blends tend to exhibit properties similar to the corresponding random copolyimides as in other polymer blend systems but sometimes provide appreciably better properties.[10] Molecular composites,[11,12] where rigid and flexible components are miscible and contribute separately, for example, to mechanical reinforcement and toughening, respectively, enable to enhance simultaneously conflicting properties such as modulus and toughness. Thus, the blend method is still important for producing new PI materials.[13]

Blend miscibility is frequently assessed from the T_g shift by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). But, the chain stiffness characteristic of PIs often makes them difficult owing to the absence of distinct T_g in the blends. In this paper, we propose a fluorescence probe technique using bifunctional perylenetetracarboxydiimide (PEDI) for studying rigid PI blend miscibility. In addition, the factors influencing the PI/PI blend miscibility are also discussed.

PEDI homologies are known as functional materials for the organic photoelectric mutual conversion devices (solar cell[14,15] and electroluminescence[16]), layered organic photoconductive devices for electrophotography,[17,18] and dye for laser.[19] Recently, we demonstrated that this dichroic molecule bound to PI main chains is very useful as an indicator for monitoring the uniaxial and in-plane orientational changes of each component chain in PI/PI blends during thermal imidization.[20,21] We also found that the fluorescence yield of PEDI in PI films depends strongly on the PI chemistry, relating to the charge-transfer (CT) abilities characteristic of the aromatic PIs.[22] The present miscibility study is based on such peculiar fluorescence characteristics of PEDI introduced in aromatic PI systems.

Experimental Section

Samples Preparation. Figure 1 shows the structures of PIs and symbols: X/Y for homopolyimides and X/Y$_1$;Y$_2$ for random copolyimides (X = dianhydrides, Y$_1$, Y$_2$ = diamines). The monomers used are BPDA (vacuum-dried at 200 °C for 24 h), PMDA (recrystallized from dioxane), PDA (*p*-phenylenediamine; recrystallized from ethyl acetate), and ODA [4,4′-oxydianiline; recrystallized from toluene/DMF (10/1, v/v)]. PAAs were polymerized by adding an equimolar amount of dianhydride powder into a *N*,*N*-dimethylacetamide (DMAc) solution of diamine with continuous mechanical stirring at room temperature for several hours. An established amount of phthalic anhydride was added into the reaction solution to obtain various molecular weights of PAAs.

The fluorescent probe, bifunctional PEDI (Figure 1), was synthesized from 3,4,9,10-perylenetetracarboxylic dianhydride (Tokyo Chemical Industry) and *o*-tolidine as reported elsewhere.[20,21] Prior to polymerization, bifunctional PEDI was promptly dissolved in DMAc at 160 °C and cooled to room temperature since the solubility at room temperature is limited. A trace amount of bifunctional PEDI was copolymerized to introduce into the PAA main chains ([PEDI]/[repeating unit] = 1/700).

The DMAc solutions of homo PAA (10 wt %) were doctor-bladed on a glass plate and then dried at 60 °C for 2 h in an air convection oven. PAA binary blend films were prepared

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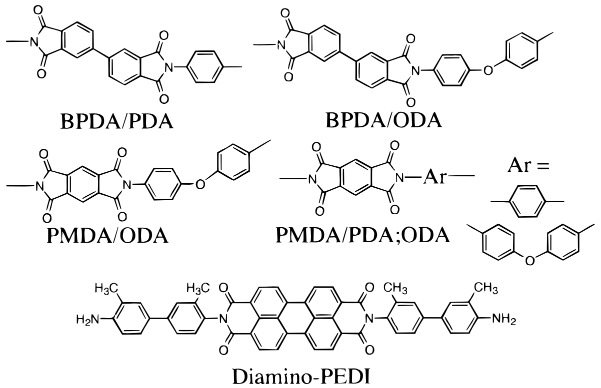

Figure 1. Chemical structures and symbols of PAAs, PIs, and fluorescent probe used.

by casting at 60 °C immediately after prompt mechanical mixing of two kinds of 10 wt % PAA solutions for 10 min at room temperature, unless stated otherwise. This procedure suppresses transamidation as demonstrated later. The casting (drying) temperature was varied within 60−120 °C to examine the effect on PAA/PAA blend morphologies. When the mixed PAA solutions were turbid, a minimum amount of DMAc was added into them to make homogeneous (optically transparent) solutions before casting.

PAA films were thermally imidized at 150 °C/0.5 h + 200 °C/0.5 h + 250 °C/1 h + 300 °C/1 h stepwise on a substrate to obtain good quality PI films (ca. 20 μm thick), unless indicated otherwise.

Measurements. Visible absorption spectra of the PEDI-containing films were recorded on Jasco Ubest-30 spectrometer at room temperature. Fluorescence spectra of the film samples, obtained by excitation at the (0−1) absorption peak near 495 nm, were measured on a Hitachi F-2000 fluorescence spectrometer (sharp-cut filter set on the emission side: O-54; the band-passes for both excitation and emission monochromators: 10 nm) at room temperature in a front-face reflection geometry. The fluorescence intensities were normalized for the absorbance (Abs) at the excitation wavelength using $I_N = I_f/[1 - \exp(-2.303\mathrm{Abs})]$, where I_f is the relative fluorescence intensity at the (0−1) emission peak near 590 nm. The fluorescence and excitation spectra were corrected on a personal computer for the intensity distribution of Xe light source and the detector sensitivity with respect to wavelength by using a rhodamine B screen solution and a light diffuser.

Storage modulus (E') and loss energy (E'') of PI films were measured as a function of temperature using a thermomechanical analyzer (Mac Science 4010) at a heating rate of 5 °C min^{-1} and a load frequency (sinusoidal) of 0.1 Hz in a nitrogen flow. For this measurement, PAA blend films were cured in a free-standing state. In this apparatus, measurements are automatically interrupted when the film elongation exceeded 3000 μm during the heating process.

PI film densities were measured at 25 °C using a xylene−CCl_4 density gradient column.

Reduced viscosities η_{red} of PAAs in DMAc at 0.5 wt % were measured at 25 °C on an Ostwald viscometer. The weight-average molecular weights (M_w) of PMDA/ODA polyamic acids were estimated from the formula[23] $[\eta] = 1.85 \times 10^{-4} M_w^{0.8}$.

Results and Discussion

PEDI Fluorescence Yield Depending on PI Chemistry and Application to PI/PI Blend Miscibility Studies. The PEDI fluorescence is not disturbed by the strong visible absorption of aromatic PI matrices due to CT interactions, since the absorption and fluorescence bands of the dye are both located in a longer wavelength region as shown in Figure 2. Our previous paper[22] demonstrated that the normalized fluorescence intensity, I_N ($\propto$ fluorescence yield, Φ_f), of a PEDI analogue molecularly dispersed in PI films is closely related to the CT ability of the PI matrices themselves. Figure 3 displays a relationship between I_N and the electron affinity, E_a, of the dianhydride monomer components[24,25] in a series of aromatic PIs with a fixed diamine component (PDA). With an increase in E_a, which means an increase in the CT ability of the PIs,[26,27] the PEDI fluorescence intensity decreased linearly. A similar relationship was also observed for the same PI systems incorporating PEDI. We proposed a PEDI fluorescence quenching mechanism,[22] which can rationalize the $I_N - E_a$ relation. Figure 4 schematically depicts the processes: first, the PEDI units are selectively excited, then the electron transfer takes place from an adjacent ground-state diamine moiety to the excited-state PEDI units, and finally the intramolecular CT ($D^+ - A^-$) state in the PI backbone and the ground-state PEDI are formed via the subsequent electron transfer from the excited-state PEDI to an adjacent ground-state diimide moiety, where the formed ($D^+ - A^-$) excited state undergoes efficient thermal deactivation. In the third process, higher intramolecular CT ability of PIs probably gives rise to more effective electron transfer and, consequently, to the higher quenching efficiency of the PEDI fluorescence.

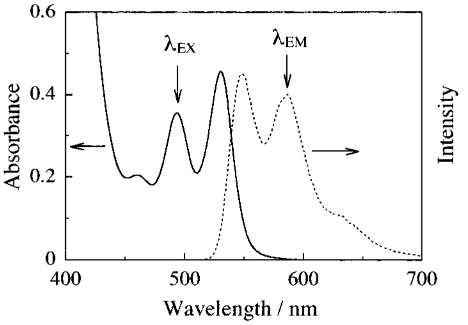

Figure 2. Visible absorption and fluorescence spectra of PEDI-bound BPDA/PDA polyimide film.

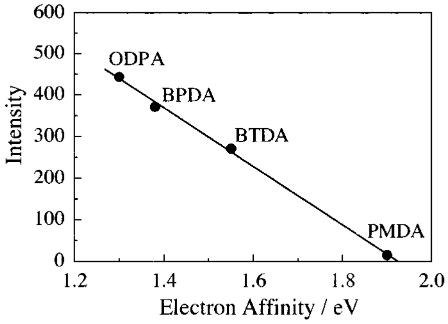

Figure 3. Relationships between I_N and E_a in a series of PIs. The PI films were cured at 150 °C + 200 °C (each 0.5 h) + 250 °C + 300 °C + 330 °C (each 1 h) stepwise.

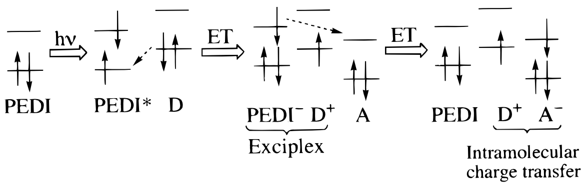

Figure 4. Schematic diagram for a mechanism of the PEDI fluorescence quenching.

As shown in Figure 3, PEDI is fluorescent in the BPDA-derived PI matrix but turns nonfluorescent in the PMDA-derived PI. The results suggest that the Φ_f of PEDI in the blends between these PIs can be a promis-

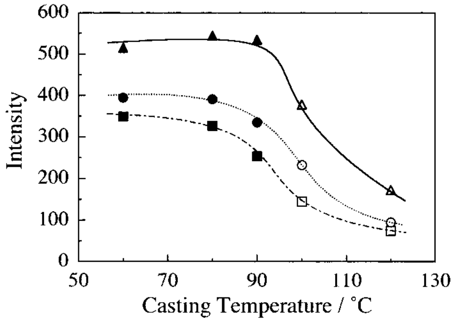

Figure 5. T_c dependence of I_N for blends of PEDI-labeled BPDA/PDA (η_{red} = 3.14 dL g^{-1}) and dye-free PMDA/ODA (M_w = 141 000) with several blend compositions: (▲, △) BPDA/PDA//PMDA/ODA = 70/30 (by weight), (●, ○) 50/50, and (■, □) 30/70. Open and closed marks represent optically transparent and opaque films, respectively.

ing miscibility indicator on the molecular level when the dye was incorporated to either PI. Then we took first a blend system composed of PEDI-labeled BPDA/PDA and dye-free PMDA/ODA. The homo-BPDA/PDA film cured on a substrate (or in a frame) is widely known to have a considerably low linear coefficient of thermal expansion (CTE),[7,20] and additionally, its highly uniaxially oriented film shows a very high Young's modulus.[28] The blend of this high-performance PI and PMDA/ODA possessing a higher T_g could be important for property control.

In principle, when the miscibility is good, the different PI chains interpenetrate; as a result, the PEDI fluorescence intensity should be significantly reduced owing to the intimate contact between the PEDI moieties connected to the BPDA/PDA chains and the PMDA/ODA segments as quencher. On the other hand, if phase-separated, the PEDI fluorescence should behave as in the homo-BPDA/PDA matrix. We describe below the PI/PI blend miscibility assessed from the PEDI fluorescence intensity change and the factors influencing the miscibility.

Effect of Casting Temperature on the Miscibility. PI/PI blend films are commonly prepared upon thermal imidization of PAA/PAA blend films obtained from solution casting, because of the limited solubilities of wholly aromatic PIs. Casting (drying) temperature, T_c, may influence significantly the resultant blend morphologies. When the component PI chains possess restricted molecular mobility even at $T > T_g$'s, the blend morphologies (domain size) do not vary significantly during thermal cure of the dried PAA blend films.[29,30] In this case, the PI/PI mixture is unable to be in a thermodynamic equilibrium state even after subsequent annealing at $T > T_g$'s. This means that the miscibility of the resultant rigid PI/PI blends, which are in a nonequilibrium state, is in advance settled at the stage of PAA/PAA blend preparation. Hasegawa et al. reported previously that an increase in T_c leads to a gradual domain size reduction in phase-separated blends of BPDA/PDA and PMDA/ODA.[29]

In the present work, we take again this blend system (system 1) where only BPDA/PDA was labeled with PEDI. Figure 5 shows the T_c dependence of I_N. The fluorescence intensity decreased as T_c is increased, corresponding well to the morphological changes mentioned above. The blend films cured after casting at $T_c \leq 90$ °C were optically opaque but turned transparent at $T_c \geq 100$ °C. At the whole blend compositions examined, the increase in T_c from 100 to 120 °C caused a discernible I_N decrease, although no morphology (transparency) varies. These PI components have no clear T_g's in the DMTA curves when cured at $T \geq 400$ °C owing to crystallization and dense molecular packing in the amorphous regions,[31,32] so that it is difficult to assess the miscibility from the T_g shift. The results indicate how the present fluorescence technique is useful for blends without distinct T_g's.

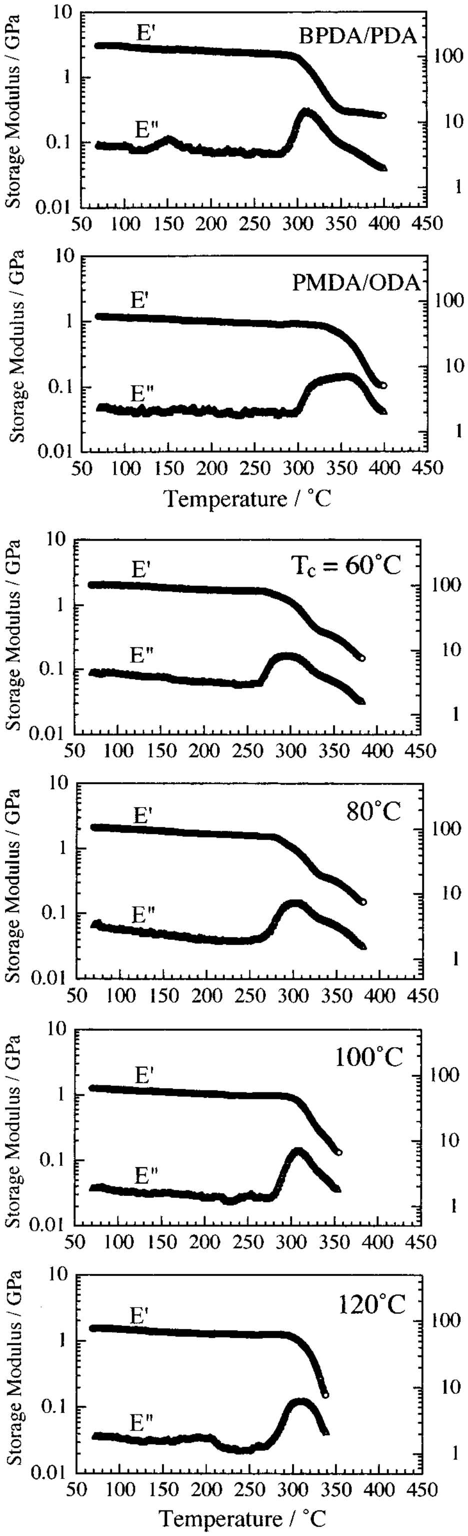

Figure 6. T_c dependence of DMTA curves for blends of labeled BPDA/PDA and dye-free PMDA/ODA (50/50, by weight). The DMTA curves of the homo-PI films were also shown for comparison.

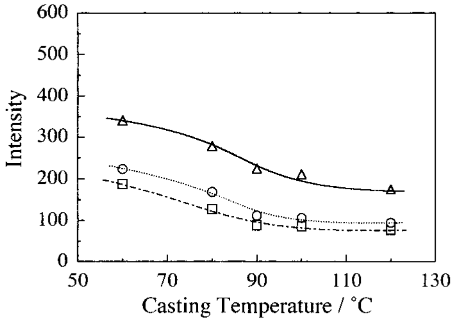

Figure 7. T_c dependence of I_N for blends of labeled BPDA/ODA (η_{red} = 2.75 dL g^{-1}) and dye-free PMDA/ODA (M_w = 141 000) with several blend compositions: (△) BPDA/ODA//PMDA/ODA = 70/30, (○) 50/50, and (□) 30/70. Open marks represent optically transparent films.

Fortunately, the PI films of BPDA/PDA and PMDA/ODA, cured at a lower temperature (e.g., 300 °C), both exhibit appreciable glass transitions in the DMTA curves. Then, we compared the T_c dependence of I_N with the DMTA curves for the 50/50 blend. As illustrated in Figure 6, the opaque PI blend films (T_c = 60 and 80 °C) clearly show very similar DMTA curves with two-step E' decrease at temperatures corresponding to the T_g's of respective homo-PIs, indicating a phase separation feature. On the other hand, the transparent blend film at T_c = 100 °C provided a single E'' peak but still with a weak shoulder, suggesting an increased miscibility. Further increase in T_c to 120 °C led to a single E'' peak without a shoulder. Thus, the T_c dependence of the DMTA profiles corresponds well to that of I_N. It should be noted that the miscibility difference between the transparent films formed at T_c = 100 and 120 °C was detected as an appreciable difference of I_N, suggesting high sensitivity and reliability of the present fluorescence technique. The I_N-T_c curves were similar to the intrinsic CT fluorescence intensity−T_c curves reported previously.[29]

BPDA/ODA was used as another component instead of BPDA/PDA. Figure 7 illustrates the T_c dependence of I_N for the blends of labeled BPDA/ODA and dye-free PMDA/ODA (system 2). In our experience, when component PIs have a common structural unit, the blends tend to show good miscibility.[33] The components in the present system commonly include the ODA unit. Whereas system 1 resulted in phase separation at $T_c \leq 90$ °C, all the blend films for system 2 were optically transparent at the whole compositions examined, independent of T_c (= 60−120 °C). Here, the average refractive indices, n^D_{av}, of the component homo-PI films cured under the same conditions were 1.7284 for BPDA/ODA and 1.6744 for PMDA/ODA, which are different enough to form an opaque blend film if phase-separated ($\Delta n^D > 0.01$).[34] This means that the blends are at least homogeneous on the visible wavelength level. As shown in Figure 7, I_N reduced gradually with increasing T_c without drastic I_N changes at a T_c as in system 1. The blends of system 2 at each composition also gave lower I_N values than those of system 1 at all T_c studied, corresponding to the miscibility difference of these blend systems.

The fluorescence results were compared with the DMTA profiles in Figure 8 since the optical transparency of the blend films does not always mean mixing on the molecular level. For the 50/50 blend prepared at T_c = 60 °C, two-step E' decrease and double E'' peak characteristic of phase separation were observed, however, accompanied by a broadening of the first E'' peak originating from BPDA/ODA and a lower temperature shift of the second E'' peak from PMDA/ODA. At T_c = 80 °C, the distinct double peak changed to a single peak with a shoulder. Further increase in T_c led to a pure single glass transition as a good miscibility feature. From the combination of the DMTA data with the film transparency, we conclude that the 50/50 blends prepared at T_c = 60 and 80 °C are partially miscible and the domain sizes are less than visible light wavelengths.

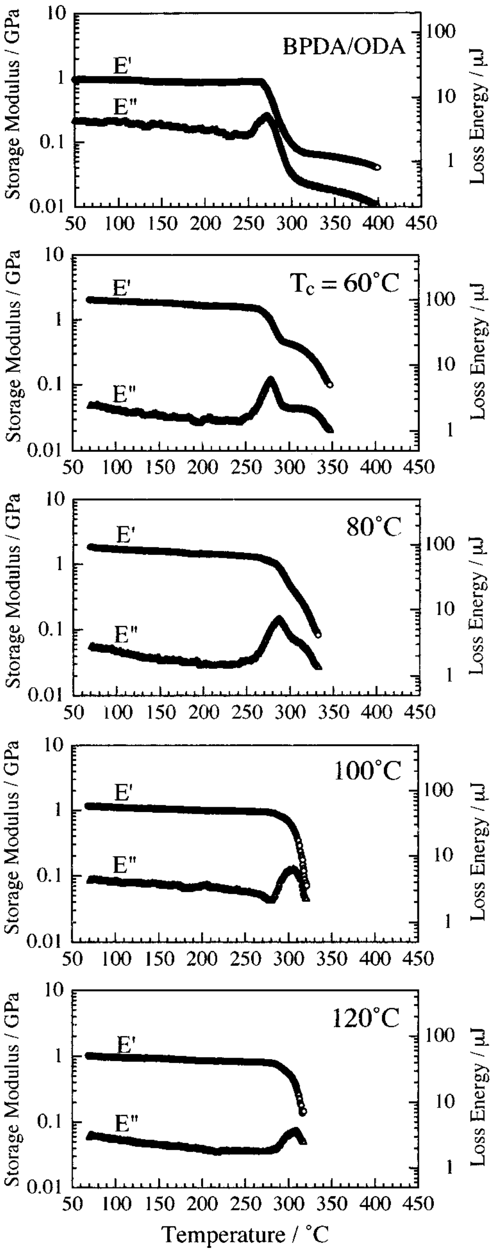

Figure 8. T_c dependence of DMTA curves for blends of labeled BPDA/ODA and dye-free PMDA/ODA (50/50). The DMTA curves of the homo-PI film were also shown for comparison.

Mechanisms of the T_c-Dependent Miscibility. We discuss the possible reasons why an increase in T_c improved the PAA/PAA blend miscibility: (1) an increase in the solvent evaporation rate and consequent rapid solidification from the homogeneous PAA/PAA solutions, (2) molecular weight decrease of the component PAAs, (3) structural changes of PAAs due to partial imidization during the drying process, (4) temperature-

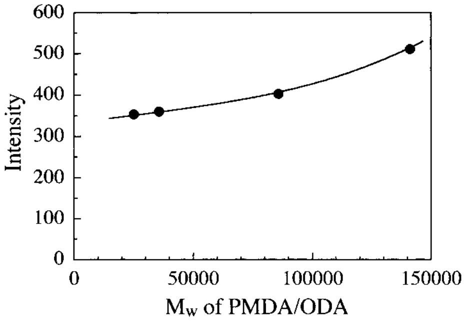

Figure 9. Change in the I_N values with varying initial M_w of PMDA/ODA for blends (60/40) of labeled BPDA/PDA (η_{red} = 4.17 dL g^{-1}) and dye-free PMDA/ODA prepared by casting at 60 °C.

dependent thermodynamic miscibility such as the upper critical solution temperature (UCST) type phase diagram, and (5) entire copolymer formation from two homo-PAAs or compatibilizer-active partial copolymer formation through transamidation. It is very difficult to assess each contribution of these competitive physical and chemical processes.

Several papers demonstrated that the solvent evaporation rate during casting process influences significantly the resulting morphologies of block copolymers and blends.[35-38] In our system, at T_c = 60 °C, drying for about 1 h was necessary for solidification of the coated solutions, whereas the dried PAA films were obtained after only ca. 10 min at T_c = 120 °C. (The time required for solidification depends on the coating thickness and oven.) Thus, factor 1 probably contributes to the increased blend miscibility.

In fact, even casting at T_c = 60 °C/2 h caused a molecular weight decrease of PAAs. For example, η_{red} of BPDA/PDA polyamic acid decreased from 2.44 dL g^{-1} for the as-polymerized solution to 1.00 dL g^{-1} for the redissolved cast film. This result corresponds to the fact that the BPDA/PDA//PMDA/PDA blend prepared at T_c = 60 °C from the mixing of as-polymerized solutions (10 wt %) is immiscible as shown later; on the other hand, the same blend via redissolution of the separately as-cast films was miscible.[29] In addition, casting at 120 °C gave a lower molecular weight (η_{red} = 0.812 dL g^{-1}), indicating that factor 2 most likely contributes to the increased miscibility.

The T_c increase also promotes imidization; for example, drying at 60 °C caused practically no imidization but 16% imidization at 120 °C (factor 3). However, it is unclear how partial imidization contributes to the miscibility.

The formation of transparent blend films at $T_c \geq 100$ °C in system 1 seems to suggest the presence of a UCST phase diagram (factor 4). However, this type of phase diagram is commonly observed in oligomer/oligomer and oligomer/polymer blends without specific intermolecular interactions.[39,40] The present systems do not belong to this category. It is difficult to confirm experimentally whether this PAA/PAA blend (system 1) indeed has a UCST phase diagram from the convenient cloud point observation on the heating process for the opaque blend films dried at T_c = 60 °C, because heating of the PAA blend films at $T > T_g$ (~150 °C[41]) promotes imidization.

PAA derived from PMDA and 4,4′-methylenedianiline can form lyotropic liquid crystal (LC) gel in *N*-methyl-2-pyrrolidone at room temperature above 14 wt %, and the gel melts at 70 °C to yield a homogeneous solution.[42]

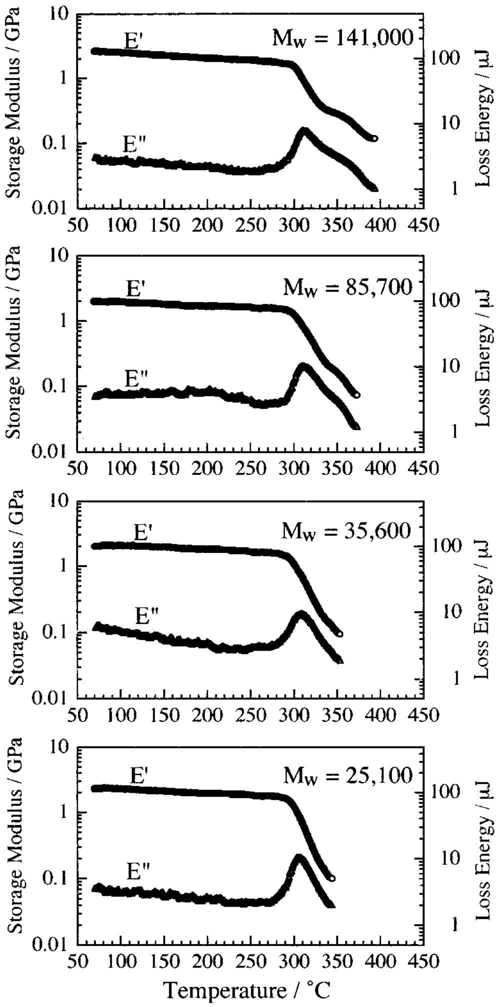

Figure 10. Changes in the DMTA curves with varying initial M_w of PMDA/ODA for blends (60/40) of labeled BPDA/PDA (η_{red} = 4.17 dL g^{-1}) and dye-free PMDA/ODA prepared by casting at 60 °C.

Factor 4 may be important, if melting of similar LC-like local aggregates also occur during the drying process at higher T_c's in our systems. However, no optical anisotropy was observed in the PAA solutions used.

Transamidation is believed to take place via the reverse reaction of acylation and successive recombination between different chains.[43] However, there are few papers describing transamidation kinetics as functions of storage temperature and PAA backbone structure, as well as the influence of the extent of the reaction on the PAA blend miscibility. The effect of factor 5 is discussed later.

From the above discussion, one should learn how the present systems are complex. A simple approach is to investigate the effect of the initial molecular weights of PAAs on the miscibility at a constant T_c (constant solvent evaporation rate). Under T_c = 60 °C, imidization and transamidation are suppressed.[44]

Effect of Initial Molecular Weight of PAAs. As discussed above, the molecular weights of PAAs in the present blend systems change from moment to moment during the casting process. This situation is significantly different from common polymer blends and makes theoretical treatments difficult. Accordingly, we show mainly Φ_f of PEDI−miscibility relationships.

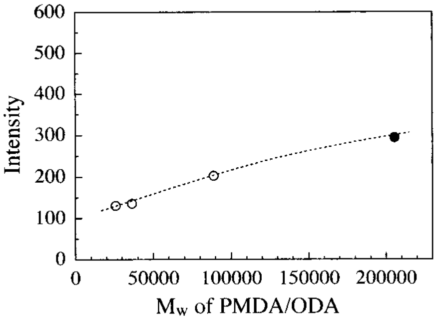

Figure 11. Change in the I_N values with varying initial M_w of PMDA/ODA for blends (60/40) of labeled BPDA/ODA (η_{red} = 2.75 dL g^{-1}) and dye-free PMDA/ODA prepared by casting at 60 °C. Open and closed marks represent transparent and opaque films, respectively.

Figure 9 exhibits the initial molecular weight dependence of I_N for system 1. According to a general thermodynamic consideration, a molecular weight decrease of component polymers in blends contributes to an increase in the combinatorial entropy (ΔS_{mix}) and, consequently, to a decrease in the free energy change for mixing (ΔG_{mix}). In fact, for the blends (60/40) between a fixed molecular weight of labeled BPDA/PDA and various M_w's of PMDA/ODA, as expected, the I_N values gradually reduced as the M_w of PMDA/ODA is decreased with a gradual decrease in the turbidity of the blend films. In addition, a molecular weight decrease of BPDA/PDA caused a downward shift of the $I_N - M_w$ curves (not shown).

The DMTA curves for the same blends (60/40) are illustrated in Figure 10. At the highest M_w of PMDA/ODA (=141 000), the dual glass transition was observed. As the M_w of PMDA/ODA is decreased, a shoulder in the E'' peak weakened gradually, similar to the T_c dependence shown in Figure 6. Thus, the change in the DMTA curves from double to single glass transition corresponds to the I_N decrease with decreasing M_w of PMDA/ODA.

Similarly, for the BPDA/ODA//PMDA/ODA blends (system 2), the dependence of I_N on the M_w of PMDA/ODA is shown in Figure 11. The blend films varied from opaque to transparent as the M_w of PMDA/ODA is decreased in accordance with the I_N decrease, whereas system 1 provided opaque films at the whole M_w studied. The higher miscibility of system 2 including a common structural unit (ODA) corresponds to the lower I_N values at the whole M_w's than those of system 1.

As illustrated in Figure 12, the DMTA curves of the opaque blend film at M_w = 205 000 have a dual glass transition typical of phase separation. On the other hand, the transparent film at M_w = 25 100 showed a sharp single E'' peak at an intermediate temperature of T_g's of each component. The sharpened glass transition, compared to that of homo-BPDA/ODA, most likely results from suppressed crystallization of the BPDA/ODA component in the blend due to good miscibility.[31] These results for two systems reveal how the initial molecular weights of PAAs influence significantly the miscibilities of PAA/PAA blends and, as a result, of PI/PI blends.

Effect of Copolymer Composition in Blends of BPDA-Derived Homo-PI and PMDA-Derived Copolyimides. The miscibilities of blends between labeled BPDA/ODA and dye-free PMDA/PDA;ODA copolyimides were studied as a function of the copolymer composition.

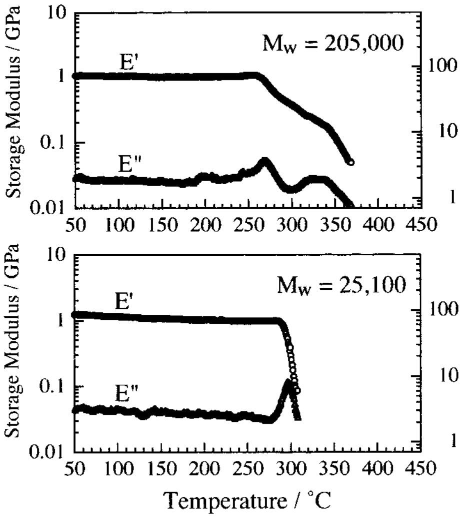

Figure 12. Changes in the DMTA curves with varying initial M_w of PMDA/ODA for blends of labeled BPDA/ODA (η_{red} = 2.75 dL g^{-1}) and dye-free PMDA/ODA prepared by casting at 60 °C.

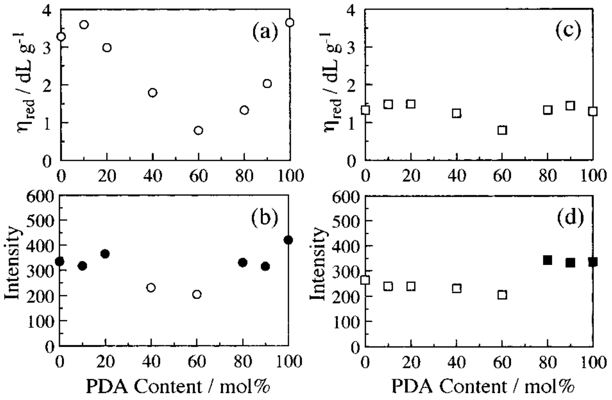

Figure 13. Reduced viscosities (a, c) of PMDA/PDA;ODA copolyamic acids and the I_N values (b, d) as a function of the copolymer composition in PI/PI blends (70/30) of labeled BPDA/ODA (η_{red} = 2.75 dL g^{-1}) and dye-free PMDA/PDA;ODA before (a, b) and after cooking (c, d). Open and closed marks in (b) and (d) represent transparent and opaque films, respectively.

Parts a and b of Figure 13 display the initial η_{red} of the copolyamic acids and the I_N values of the cured blend films as a function of the PDA content in the copolymer, respectively. From comparison between the miscibilities of systems 1 and 2, it was expected that the miscibility of the present blend system decreases with increasing PDA content (decreasing common structural unit (ODA) content). However, no clear relationship was observed in Figure 13b. The unexpected result may arise from the unfixed molecular weights of the copolyamic acids, according to the above-demonstrated results of the miscibility$-M_w$ relationship. Then, the scattered molecular weights (viscosities) of the copolyamic acids became uniform through so-called "cooking", namely, storage at 60 °C for 24 h as illustrated in Figure 13c. After that, the relationship between I_N and the copolymer composition is again plotted in Figure 13d. In a low PDA content region ([PDA] $\leq$ 60 mol %), the blends provided transparent films with almost constant and lower I_N values. At [PDA] $\geq$ 70%, the I_N increased suddenly in accordance with the turbid film formation. The results correspond to our first prediction. Thus, the blend morphologies could be readily controlled by the copolymer composition in this system.

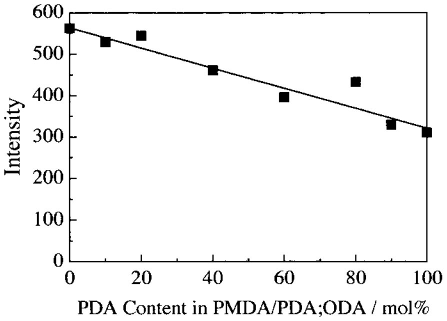

Figure 14. I_N values as a function of the copolymer composition in blends (70/30) of labeled BPDA/PDA (η_{red} = 3.14 dL g^{-1}) and dye-free PMDA/PDA;ODA which underwent cooking.

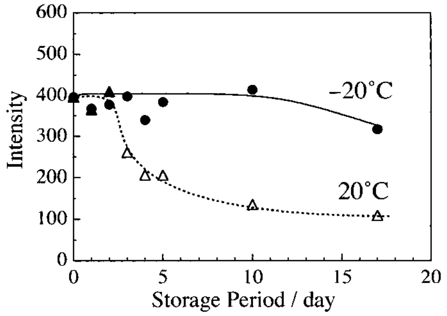

Figure 15. I_N changes of PI/PI blend (50/50) between labeled BPDA/PDA (η_{red} = 3.14 dL g^{-1}) and dye-free PMDA/ODA (M_w = 141 000) during storage of the mixed PAA solution at −20 (●) and 20 °C (▲, △). Open and closed marks represent transparent and opaque films, respectively.

Similarly, the blends of BPDA/PDA and the copolyamic acids were also studied (Figure 14). One notices that the blend films were all opaque and gave much higher I_N values than those in the BPDA/ODA// copolyimide blends. It should be noted that the I_N values of the phase separation blends decreased discernibly with an increase in the content of PDA as the common structural unit. The result manifests that the PEDI fluorescence is highly sensitive to a slight change in the degree of mixing.

In all binary blends of labeled BPDA-derived PIs and dye-free PMDA-derived PIs examined in this work, there seems to exist a critical I_N value around I_N = 200−300, where the blend morphologies vary drastically.

Effects of Storage Temperature and Its Period for Mixed PAA Solutions. It is known that a well-mixed PAA/PAA solution alters from opaque to transparent after prolonged storage.[45,46] In fact, the homogenization takes place even at a low temperature at which no significant molecular weight changes occur for the component homo-PAAs.[45] This process is believed to be based on copolymer formation via transamidation.[9,43] However, it is unclear whether PAAs in the mixture participate wholly or partially in the copolymer formation, as well as how the partially produced copolymers can act as a compatibilizer for the unreacted PAA mixture. The transamidation rates in the solutions seem to depend on the PAA chemistry.[9]

We examined the effects of storage temperature and its period for the mixed PAA solution of system 1. The solution vigorously mixed at room temperature for 10 min was stored for a given period at −20 and 20 °C in the dark and then cast at 60 °C. The PAA/PAA blend films obtained were cured for the I_N measurements. The 50/50 blend gave opaque films within our experimental storage periods at −20 °C, and the I_N values remained practically unchanged until 10 days as shown in Figure 15. Note that the initial mixed solutions before casting were all transparent. On the other hand, storage at 20 °C caused a significant morphological change from turbid to transparent with a gradual I_N decrease. Similar behavior was also observed for the 70/30 and the 30/70 blends (not shown).

Figure 16 exhibits the changes in the film densities of the 50/50 blend. The densities of PI/PI blend films remained almost constant during storage at −20 °C but

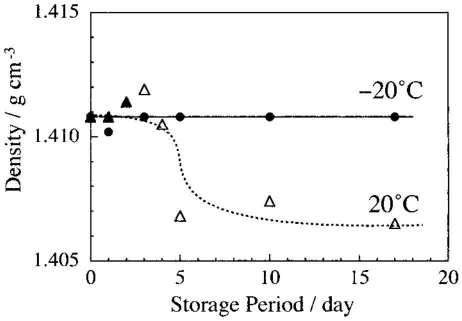

Figure 16. Changes in the film densities of PI/PI blend (50/50) between BPDA/PDA (η_{red} = 3.14 dL g^{-1}) and PMDA/ODA (M_w = 141 000) during storage of the mixed PAA solution at −20 (●) and 20 °C (▲, △). Open and closed marks represent transparent and opaque films, respectively.

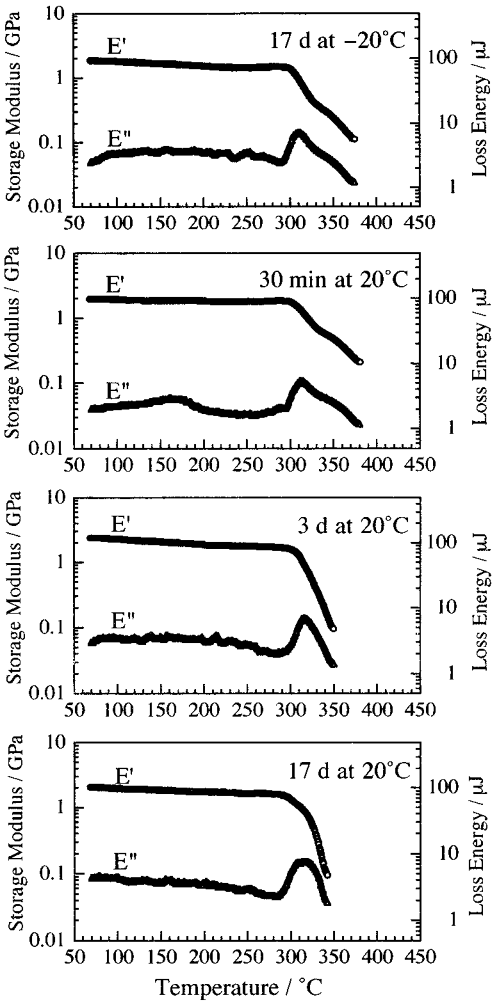

Figure 17. Changes in the DMTA curves of PI/PI blend (50/50) between BPDA/PDA and PMDA/ODA during storage of the mixed PAA solution at −20 and 20 °C.

decreased gradually at 20 °C, corresponding well to the storage temperature dependence of the I_N changes. The decreased densities with storage period probably mean that crystallization of the component PIs was disturbed by either an increase in the miscibility due to the compatibilizer-active partially formed copolymer or whole copolymer formation.

The changes in the DMTA curves with storage period at 20 °C are shown in Figure 17. The opaque blend film, prepared after storage at 20 °C for 30 min, still provided dual glass transition, very similar to those at −20 °C for 17 days. The DMTA curves varied toward single glass transition after 3 days storage at 20 °C in accordance with the I_N decrease. However, from the changes in I_N and the DMTA curves with storage period, it was difficult to specify which mechanisms mentioned above contribute mainly to the actual homogenization process.

The results shown above reveal how the PEDI fluorescence is powerful tool for investigating PI/PI blend miscibility. We reported that originally very brittle PMDA/PDA film, which has a potential low CTE, can be significantly improved by blending a small amount of a novel asymmetric biphenyl-type PI without a undesirable increase in CTE.[47] The present technique will be successfully applied to the miscibility study for this blend.

Conclusion

The miscibilities of binary blends between BPDA-derived PI and PMDA-derived PI were studied from the fluorescence intensity change of PEDI incorporated in the BPDA-derived PIs. From the changes in the DMTA curves, it was found that the miscibility is increased with an increase in casting temperature, a decrease in the molecular weights of PAAs, and an increase in storage temperature and its period. The PEDI fluorescence intensity of the blends decreased in accordance with the miscibility increase, indicating that the PEDI fluorescence is a very useful tool, especially for the miscibility studies of PI/PI blends without appreciable T_g's.

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