Miscibility of polyimide/polyimide blends and charge-transfer fluorescence spectra

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The miscibility of polyimide/polyimide (PI/PI) blends was investigated by using intermolecular charge-transfer (CT) fluorescence of aromatic PIs. Two blend systems, i.e. clear PI(BPDA/PDA)/PI(PMDA/PDA) and cloudy PI(BPDA/PDA)/PI(PMDA/ODA), were selected for fluorescence measurements (BPDA = biphenyltetracarboxylic dianhydride; PDA = *p*-phenylene diamine; PMDA = pyromellitic dianhydride; ODA = oxydianiline). For PI(BPDA/PDA)/PI(PMDA/PDA) blends, the fluorescence intensity rapidly decreased with the addition of a non-fluorescent PI(PMDA/PDA) into fluorescent PI(BPDA/PDA), while for PI(BPDA/PDA)/PI(PMDA/ODA) the fluorescence intensity first increased and then decreased with the addition of non-fluorescent PI(PMDA/ODA), showing that the miscibility of the blends strongly affects the fluorescence behaviour. In order to correlate the fluorescence data with the miscibility of PI/PI blends, dynamic mechanical analysis and phase-contrast microscopy were also carried out. Furthermore, binary blends of fluorescent PI(BPDA/PDA) with non-fluorescent PI(PMDA/PDA:ODA) random copolymer indicated that with the increase of PDA content in the copolymer the transparency of the blends (5/5) became better and the fluorescence intensity decreased. This shows that as a result the formation of intermolecular CT complexes in the homo-PI(BPDA/PDA) phase is hindered by the copolymer. The dependence of the miscibility of PI/PI blends on casting temperature (T_{cast}) at the stage of poly(amic acid) was also studied. It is clearly shown that the miscibility of PI/PI blends depends strongly on T_{cast}. As T_{cast} increases from 40 to 120 or 130°C, the domain size in the phase-separated structure is reduced, and finally at 120 or 130°C the blends become perfectly transparent. Furthermore the dynamic mechanical spectra of the blends with higher T_{cast} show that the blends are miscible. On the other hand, the CT fluorescence intensity of the blends decreases drastically with increasing T_{cast}. It was found that the decrease of CT fluorescence intensity reflects the increase of the miscibility of PI/PI blends.

(Keywords: polyimide; blend; miscibility; charge-transfer fluorescence)

INTRODUCTION

Rigid-rod molecular composites (MC) have been shown to have outstanding mechanical properties. We have investigated high-modulus and high-strength aromatic polyimide (PI)[1] and PI/PI MC[2]. For the preparation of PI/PI MC or other PI alloys, it is important to know the miscibility of the polymer mixtures[3,4]. Studies of blends of PI with other polymers and PI/PI blends using d.s.c. and d.m.a. have so far been reported[5-12]. D.s.c. and d.m.a., usually used for the evaluation of miscibility of common polymer blends, are unsuitable when the T_g values of the component polymers are very close[13] and/or the polymer chains are very rigid, as for wholly aromatic PIs.

Photoluminescence methods developed by some research groups are very sensitive to the miscibility of polymer blends[14-19]. Unfortunately the strong absorption from the u.v. to the visible range in aromatic PIs makes it difficult to introduce common luminescence probe molecules into PI systems. In the present paper, we will show that the intrinsic fluorescence of solid PIs, which is due to the intermolecular CT interaction[20], is very useful to study the miscibility of PI/PI blends.

EXPERIMENTAL

PI precursors, poly(amic acids), PAAs, were synthesized as reported previously[20]. The chemical structures and symbols of PIs used are shown in *Figure 1*. The following

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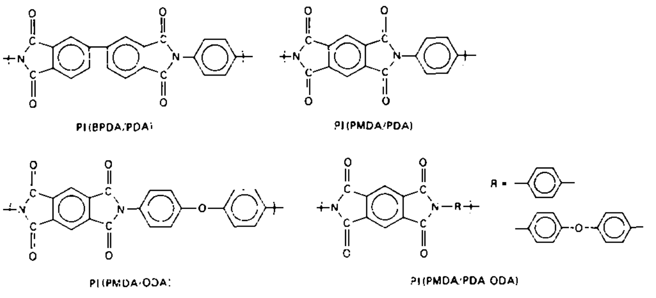

Figure 1 Chemical structures and symbols of the PIs used

abbreviations of the monomers are used: pyromellitic dianhydride (PMDA), biphenyltetracarboxylic dianhydride (BPDA), *p*-phenylene diamine (PDA) and oxydianiline (ODA). The weight-average molecular weights M_w of PAAs, which were determined by the light-scattering method (Union Giken, model LS-601), the extinction coefficients and the densities are shown in *Table 1*. Homo-PAA films were prepared by casting 10 wt% solutions in *N*,*N*-dimethylacetamide (DMAc) onto a glass plate at 50°C, followed by vacuum drying at 50°C for 24 h. Imidization practically does not occur at around 50°C. PAA/PAA binary blends were prepared by dissolving the requisite ratios of solid PAAs into dry DMAc at 7–8 wt% polymer concentration at 0–5°C away from moisture in air, and followed by vacuum drying at 50°C for 24 h. Then PAA/PAA blend films were thermally imidized stepwise at 150°C/1 h, 200°C/1 h, 250°C/2 h (step 250°C) in a vacuum oven to obtain PI/PI blend films (30–40 μm thick).

A fluorescence spectrophotometer (Hitachi, model 850) was used for measurement of the emission and excitation spectra. The spectrum was obtained at room temperature in a front-face arrangement using 5 nm bandpasses for both the excitation and emission monochromator and a sharp-cut filter (L-39) for the emission side. The reabsorption of the fluorescence is negligible in all cases.

The refractive indices of some homo-PI films were measured by using a Abbe refractometer. The morphologies of the phase-separated blends were observed using a phase-contrast microscope.

Dynamic mechanical loss measurement was carried out using a viscoelastometer (Toyo Baldwin, Rheovibron model Rheo-200) at 110 Hz at a heating rate of 3°C $\min^{-1}$.

The densities of the blend films were measured using a density gradient column (xylene/CCl_4 system). The extinction coefficients were determined from the absorbance and thickness of thin PI films using a u.v.-vis. spectrophotometer (Jasco, model Uvidec-660).

RESULTS AND DISCUSSION

Miscibility of PAA/PAA and PI/PI blends

Since PI/PI blends are generally obtained by a thermal cyclization reaction of PAA/PAA blends, the morphology of PI/PI blends formed is determined by the miscibility of the initial PAA/PAA blends, the rigidity of the polymer chains, which increases as the reaction proceeds, and the translational diffusion. The following factors should be noted with regard to the rigidity of PI chains.

(1) The miscibility of PI/PI blends in the *thermodynamic equilibrium* state. When the PI chains are flexible, phase equilibrium can be realized by sufficient thermal treatment above the T_g of the PI/PI blends. Accordingly, even if a PAA/PAA blend is immiscible, the blend morphology of the PI/PI blend can be changed from immiscible to miscible due to sufficient heat treatment if the PI/PI blend is miscible in the thermodynamic equilibrium state.

(2) The miscibility of PI/PI blends formed in *non-equilibrium conditions*. When the PI chains are very rigid, the PI/PI blend formed is in a non-equilibrium state, because the molecular mobility of the PI chains decreases rapidly as imidization proceeds. That is, the miscibility of the PI/PI blends depends strongly on the miscibility of the initial PAA/PAA blends and the imidization conditions.

Since thermal imidization of PAAs is an intramolecular cyclization reaction, so large molecular motions are not required for the reaction. This illustrates the fact that the reaction proceeds gradually even if the imidization temperature (T_i) is lower than the T_g, increasing with the conversion. On the other hand, for the change of the blend morphology, higher T_i than T_g, increasing with the conversion, is required to allow very large molecular motions of the polymer chains (translational diffusion). It is empirically expected that when imidized at step 250°C the reaction temperature will always be lower than the T_g increasing with conversion, because deformation of films and adhesion between the films and aluminium wrapping foil are not practically observed.

As an example of case (2), the PI(BPDA/PDA)/PI(PMDA/ODA) blend, selected for fluorescence studies in a later section, is cloudy due to phase separation, and both component polymer chains are very rigid[1,21]. Actually, when imidized at step 250°C, there was little difference in the phase-separated structures between the PAA/PAA and PI/PI blends (the morphology of PAA/PAA is fixed). That is, the miscibility of PI/PI blends depends on that of PAA/PAA blends. It is interpreted that the imidization at step 250°C is a kinetically controlled process and that the PI/PI blend formed is in a non-equilibrium state.

The experimental result that additional heat treatment of a PI/PI blend imidized at step 250°C above T_g of both component PIs does not change the blend morphology indicates that the PI/PI blend imidized at step 250°C is

Table 1 Weight-average molecular weights $\bar{M}_w$ of PAAs and extinction coefficients ε and densities of PI films

Symbol	$\bar{M}_w$	ε_{350}[a]	Density (g cm^{-3})
PI(BPDA/PDA)	75000	2600	1.4239
PI(PMDA/ODA)	110000	1200	1.3807
PI(PMDA/PDA)	89000	1600	1.5107
PI(PMDA/PDA:ODA)			
PDA:ODA = 10:0	89000	1600	1.5107
9:1	43000	1600	1.4944
8:2	45000	1500	1.4677
7:3	40000	1300	1.4475
5:5	30000	1300	1.4139
3:7	67000	1200	1.3990
2:8	59000	1200	1.3934
0:10	40000	1200	1.3805

[a] The values of ε depend on the cure temperature

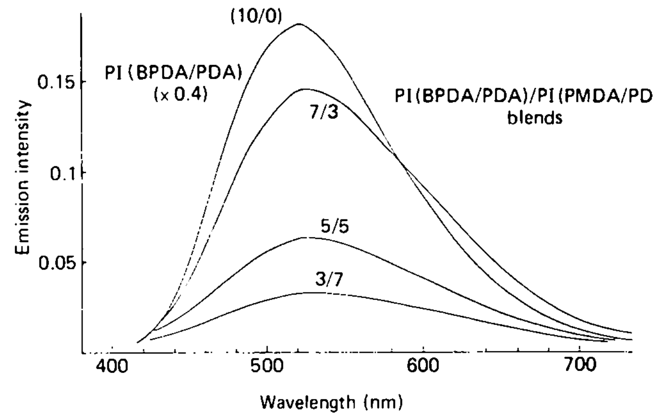

Figure 2 Fluorescence spectra of PI(BPDA/PDA)/PI(PMDA/PDA) blends as a function of blend ratio

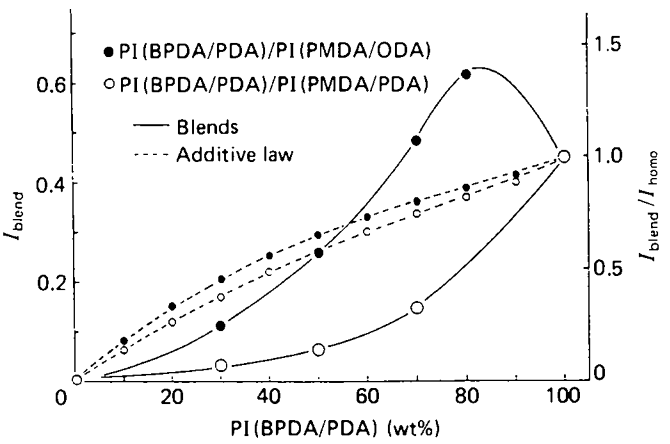

Figure 3 Change of the fluorescence intensity for (a) PI(BPDA/PDA)/PI(PMDA/PDA) and (b) PI(BPDA/PDA)/PI(PMDA/ODA) with blend ratio

perfectly frozen. Although the PI/PI is not in the thermodynamic equilibrium state, it is important to argue the degree of mixing for the perfectly frozen PI/PI blend.

As mentioned above, since the miscibility of rigid PI/PI blends depends strongly on that of the initial PAA/PAA blends, the control of the miscibility of PAA/PAA is very important. The effect of casting temperature (T_{cast}) on the miscibility of PAA/PAA blends is remarkable. This will be discussed later.

One may point out the possibility of an amide exchange reaction of PAA/PAA systems in solutions[22] or solid states[11]. But we have some reliable evidence that the exchange reaction is not predominant under our experimental conditions. The problems will be discussed in separate papers in detail.

Fluorescence spectra of PI/PI blends

In the previous paper[20], we have reported that, of the PIs used, PI(BPDA/PDA) emits strong fluorescence and PI(PMDA/PDA) and PI(PMDA/ODA) are almost non-fluorescent. Consequently the fluorescence of PI(BPDA/PDA) mixed with a non-fluorescent PI will present information on the degree of self-aggregation of PI(BPDA/PDA) chains (in other words, degree of mixing). Two blend systems, i.e. clear PI(BPDA/PDA)/PI(PMDA/PDA) and cloudy PI(BPDA/PDA)/PI(PMDA/ODA) blends, were selected for fluorescence measurements.

Figure 2 shows blend ratio dependence of the fluorescence spectra for clear PI(BPDA/PDA)/PI(PMDA/PDA). With the addition of non-fluorescent PI(PMDA/PDA) into fluorescent PI(BPDA/PDA), the fluorescence intensity decreases. As shown in *Figure 3*, the experimental data (open circles) deviate downwards from a simple additive law corresponding to a perfectly phase-separated blend. The additive law curves are calculated on the basis of the following equation:

$$I_b = \frac{\varepsilon_1 C_1}{\varepsilon_1 C_1 + \varepsilon_2 C_2} I_1 + \frac{\varepsilon_2 C_2}{\varepsilon_1 C_1 + \varepsilon_2 C_2} I_2 \qquad (1)$$

where I is fluorescence intensity; suffixes b, 1 and 2 denote the blend, pure PI(BPDA/PDA) and non-fluorescent PIs, i.e. PI(PMDA/PDA) or PI(PMDA/ODA) or PI(PMDA/PDA:ODA) copolymer respectively; ε is the extinction coefficient, summarized in *Table 1*; and I_2 is negligible. For phase-separated blends, equation (1) should be corrected for the loss of incident light due to light scattering. But since the light absorption of the PI/PI blends at 350 nm is very strong ($OD > 3$) and/or the ratio of scattering light intensity to the incident light is small for all blend ratios (within 5%), the correction of the fluorescence intensity for the light scattering can practically be neglected under our experimental conditions. Also we confirmed using a thermotropic liquid crystalline (LC) polymer in the amorphous state (clear) and LC state (cloudy) that no shift of the fluorescence spectrum due to the light scattering occurs. Accordingly the changes of the intensity and position in the fluorescence spectra for the cloudy PI/PI blends are essential phenomena. The fluorescence behaviour for the PI(BPDA/PDA)/PI(PMDA/PDA) in *Figure 3* means that the PI(PMDA/PDA) chains entered into the homo-PI(BPDA/PDA) phase and as a result the formation of intermolecular CT complexes in homo-PI(BPDA/PDA) is hindered. If no interaction exists between the component polymers, the experimental data should approach the additive law curve (broken curve), and the spectral shape of the blends and that of pure PI(BPDA/PDA) should be identical. But in *Figure 4* the spectral shapes normalized at 525 nm are not identical for PI(BPDA/PDA)/PI(PMDA/PDA) (5/5) and for pure PI(BPDA/PDA), showing the existence of some interchain interactions in this blend.

For cloudy and consequently macroscopically incompatible PI(BPDA/PDA)/PI(PMDA/ODA) blends, the blend ratio dependence of fluorescence spectra is shown

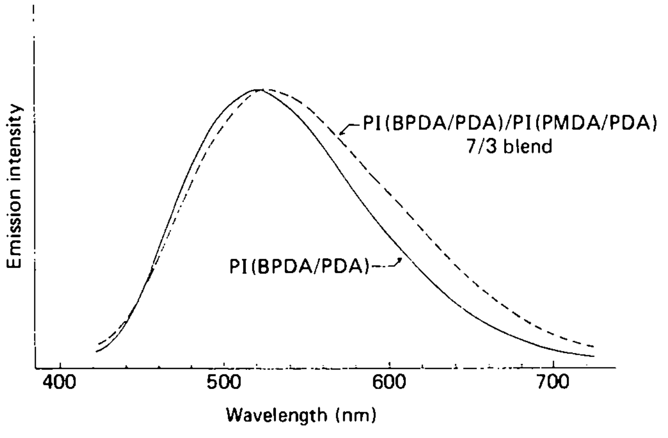

Figure 4 Fluorescence spectra of PI(BPDA/PDA)/PI(PMDA/PDA) (5/5) and homo-PI(BPDA/PDA) normalized at 525 nm

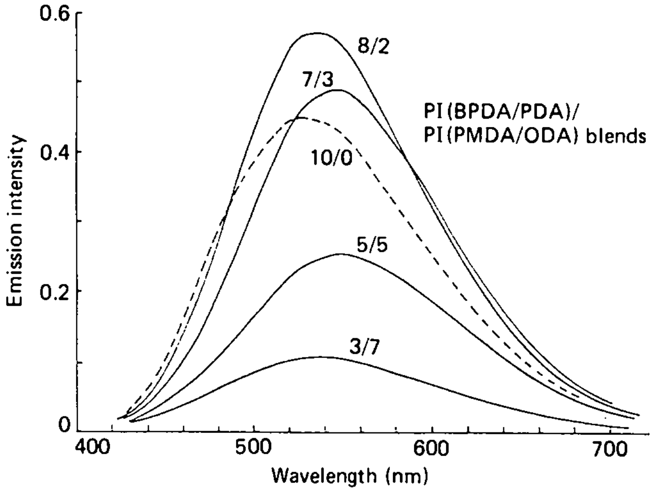

Figure 5 Fluorescence spectra of PI(BPDA/PDA)/PI(PMDA/ODA) blends as a function of the blend ratio

in *Figure 5*. With the addition of PI(PMDA/ODA) into PI(BPDA/PDA) the fluorescence of blends first increases and then decreases as shown in *Figure 3*. It is interesting to note that the fluorescence intensity is stronger at around 8/2 composition than for pure PI(BPDA/PDA), although the reason is not yet clear. The fluorescence intensity as a function of blend ratio indicates that the miscibility for PI(BPDA/PDA)/PI(PMDA/PDA) is better than for PI(BPDA/PDA)/PI(PMDA/ODA) because the intensity for the former is smaller than for the latter for the whole blend ratios.

It is reasonable to assume that for the PI(BPDA/PDA)/PI(PMDA/ODA) any electronic interaction between the distinct PIs is small except for that at the interfaces because the phase separation occurs macroscopically. Although it is not yet clear, the unusual behaviour for the PI(BPDA/PDA)/PI(PMDA/ODA), such as the fluorescence enhancement and spectral shift, may be due to internal stress generated during the thermal imidization of the macroscopically phase-separated PAA/PAA blends.

Dynamic mechanical spectra

As the refractive indices (n_D) of homo-PI(BPDA/PDA) and homo-PI(PMDA/PDA), which depend on curing conditions, are 1.544 and 1.553 respectively, if phase separation occurs in PI(BPDA/PDA)/PI(PMDA/PDA) (5/5) blend, the films should become cloudy due to the difference of the n_D (ref. 23). Practically the blend films prepared from $T_{cast} = 50°C$ were clear for all blend ratios, and domains due to phase separation were not observed by optical microscopy. This indicates that the domains in the blends are smaller than the extent of the wavelength of visible light.

In order to obtain further information on degree of mixing, the dynamic mechanical spectra for the blends and the homo-PIs were measured. Fortunately d.m.a. is applicable to PIs or PI/PI blends imidized at step 250°C, although when post-cured at more than 330°C the blends and the homo-PIs do not show a clear α loss peak. *Figures 6a* (curves (1)) and *6b* show the storage modulus E' and the loss modulus E'' curves for PI(BPDA/PDA) and PI(BPDA/PDA)/PI(PMDA/PDA) (5/5, $T_{cast} = 50°C$) respectively. Unfortunately it was impossible to measure the thermally imidized PI(PMDA/PDA) because the film

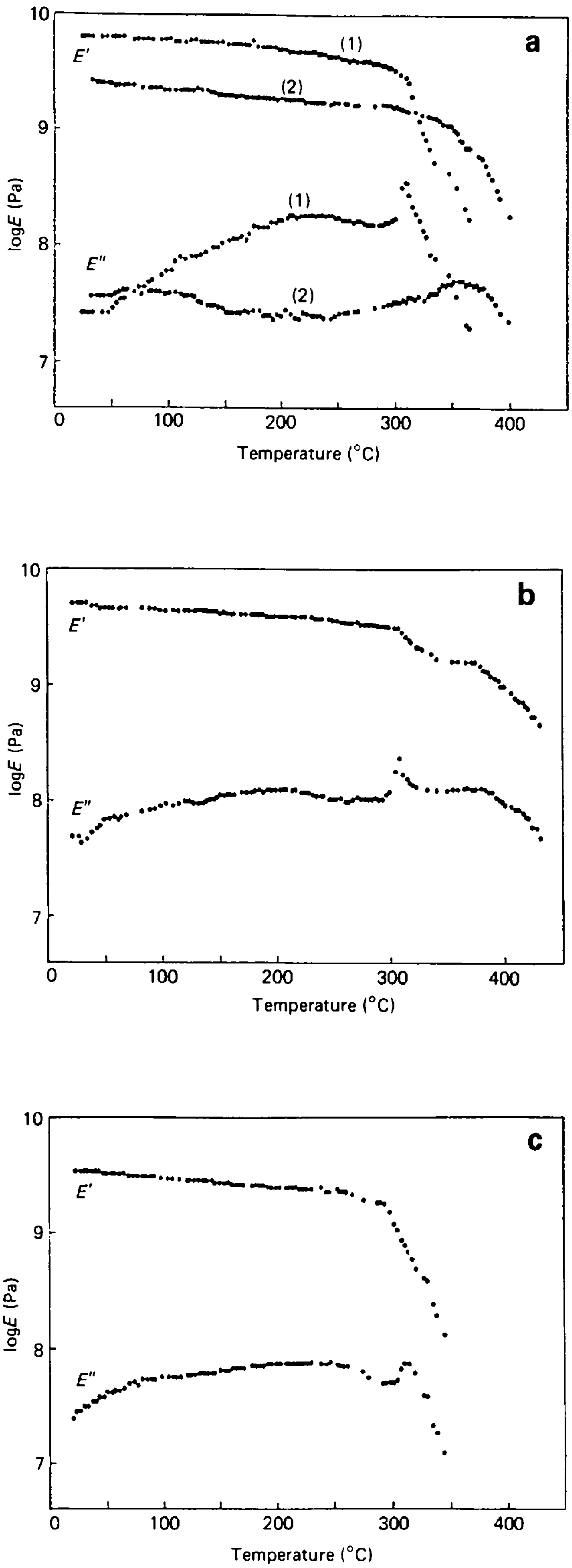

Figure 6 Dynamic mechanical spectra of (a) homo-PI(BPDA/PDA) (1) and homo-PI(PMDA/ODA) (2), (b) PI(BPDA/PDA)/PI(PMDA/PDA) (5/5) and (c) PI(BPDA/PDA)/PI(PMDA/ODA) (5/5)

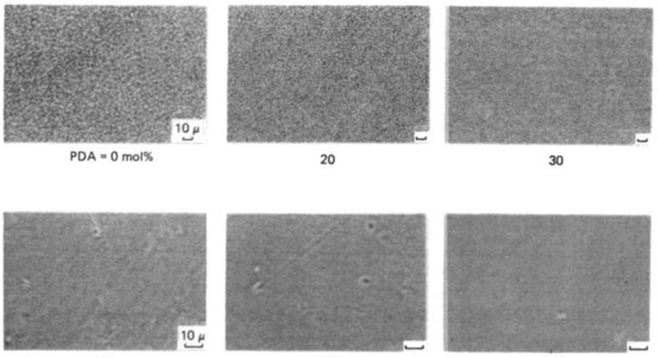

Figure 7 Phase-contrast microscope photographs of PI(BPDA/PDA)/PI(PMDA/PDA:ODA) (5/5) with various PDA contents in the copolymer

is very brittle. The homo-PI(BPDA/PDA) shows an α loss peak at about 310°C, and a broad β loss peak at around 230°C. The blend also has an α loss peak at the temperature corresponding to pure PI(BPDA/PDA), showing the PI(BPDA/PDA) phase exists partially in the blend. A broad loss peak at around 370°C for the blend is very likely different from that of homo-PI(PMDA/PDA) because it has been reported[24] that the calculated T_g is about 700°C (it is difficult to measure it experimentally because of thermal degradation) and different from the β loss peak of PI(PMDA/PDA) as described below. Accordingly it appears that the peak is due to the partial mixing phase. Although we do not have data for homo-PI(PMDA/PDA) imidized at step 250°C, from the following experimental results it is reasonable to assume that the β loss peak of PI(PMDA/PDA) appears at around 80°C. Dynamic mechanical spectra of PI(PMDA/PDA:ODA) copolymers (PDA = 0–80 mol%) imidized at step 250°C show that the β loss peak always appears around 80°C regardless of PDA content in the copolymer. As reported previously, the position of the β loss peak of PI(PMDA/ODA) is independent of the cure conditions unlike the T_g, which depends on the cure conditions[21]. Furthermore the dynamic mechanical spectra of the chemically imidized PI(PMDA/PDA) can be measured. The E'' curve of the polymer shows a β loss peak around 80°C[25]. According to the T_g criterion for miscibility of polymer blends, in PI(BPDA/PDA)/PI(PMDA/PDA) blend in which the β loss peak appears at a temperature between the β loss peaks of the two component homopolymers (80°C for PI(PMDA/PDA) and 230°C for PI(BPDA/PDA)), the effect of mixing is observed. This will become clear by comparing with the phase-separated PI(BPDA/PDA)/PI(PMDA/ODA) in *Figure 6c* where the β loss peaks of PI(PMDA/ODA) (80°C) and PI(BPDA/PDA) (230°C) appear independently.

On the other hand, as shown in *Figure 6c* the E'' curve for cloudy PI(BPDA/PDA)/PI(PMDA/ODA) (5/5, T_{cast} = 50°C) shows only an α loss peak corresponding to PI(BPDA/PDA) without a peak due to partial mixing, and the E' curve decreases rapidly over about 310°C similarly to homo-PI(BPDA/PDA). No effect of mixing in this blend was observed. From their dynamic mechanical spectra, the degree of mixing for PI(BPDA/PDA)/PI(PMDA/PDA) is better than for PI(BPDA/PDA)/PI(PMDA/ODA), coinciding qualitatively with the fluorescence data.

PI(BPDA/PDA)/PI(PMDA/PDA:ODA) blends

Since PI(BPDA/PDA)/PI(PMDA/PDA) and PI(BPDA/PDA)/PI(PMDA/ODA) are transparent and cloudy respectively, when a random copolymer PI(PMDA/PDA:ODA) (PDA = 20–90 mol%) is used as a component of blends it is expected that with increasing PDA content in the copolymer the morphology of PI(BPDA/PDA)/PI(PMDA/PDA:ODA) (5/5, T_{cast} = 50°C) changes from heterogeneous to homogeneous and that the fluorescence of the blends reduces successively. The copolyimides imidized at step 250°C were non-fluorescent. The observation of the blend films by a phase-contrast microscope shows the successive reduction of the domain size with increasing PDA content in the copolymer, as shown in *Figure 7*. The blends become perfectly transparent over 80% in PDA. *Figure 8* shows the fluorescence spectra of the blends (5/5) as a

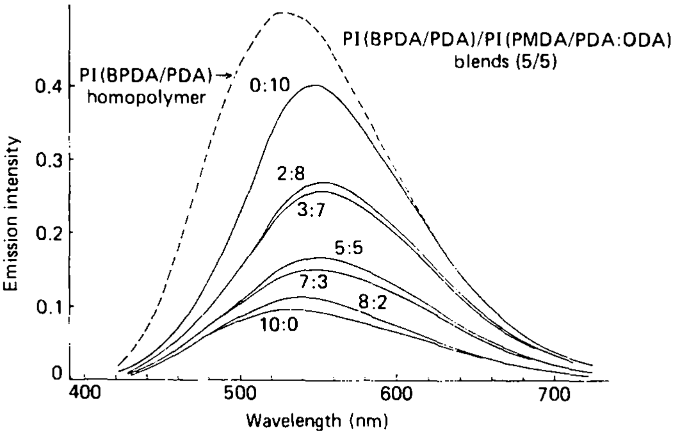

Figure 8 Fluorescence spectra of PI(BPDA/PDA)/PI(PMDA/PDA:ODA) (5/5) as a function of PDA content in the copolyimide

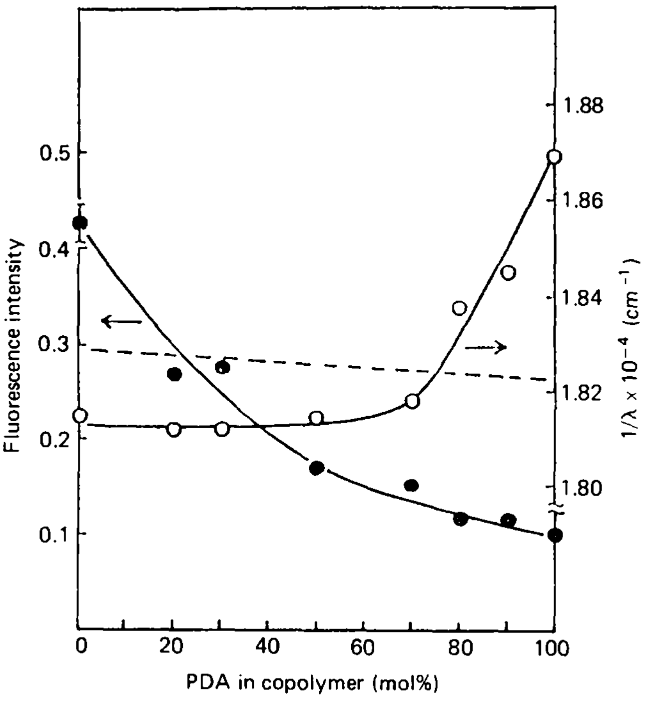

Figure 9 Change of fluorescence intensity and the peak position for PI(BPDA/PDA)/PI(PMDA/PDA:ODA) (5/5) with the PDA content in the copolyimide

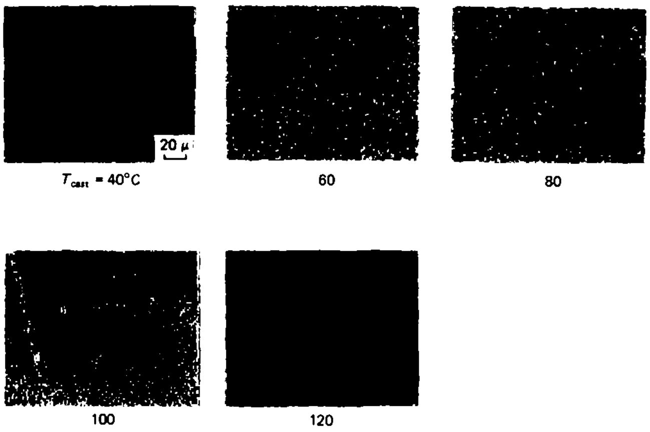

Figure 10 Phase-contrast microscope photographs of PI(BPDA/PDA)/PI(PMDA/ODA) (5/5) with various T_{cast}

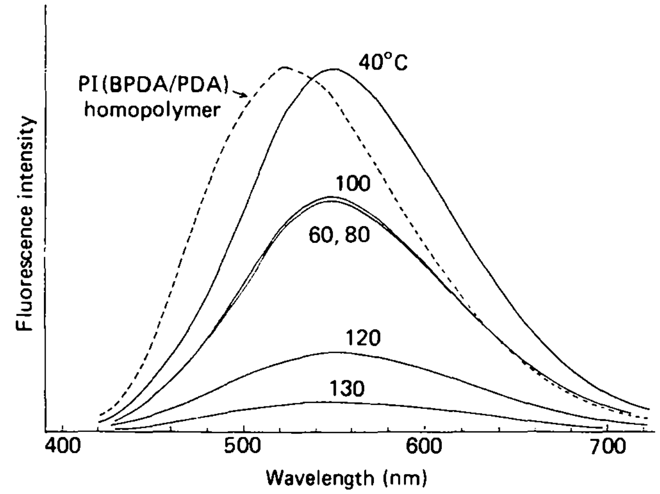

Figure 11 Fluorescence spectra of PI(BPDA/PDA)/PI(PMDA/ODA) (5/5) as a function of T_{cast}

function of PDA content in the copolymer. The fluorescence of the blends reduces with some spectral shifts as the blends become homogeneous. The changes of the intensity and the peak position are plotted in *Figure 9*. It is interesting to note that the additive law curve (broken line) is nearly independent of PDA content, while the experimental data rapidly decrease with the increase of PDA content. Further experimental evidence is necessary to explain such spectral shifts. But in any case, the reduction of the intermolecular CT fluorescence can be strongly correlated to the increase of the degree of mixing in the PI/PI blends.

Casting temperature dependence

Dependence of the miscibility of PI/PI blends on the casting temperature (T_{cast}) at the stage of the precursors was also examined. It is clearly shown that the miscibility of PI/PI blends depends strongly on T_{cast}. As shown in *Figure 10*, the observation of PI(BPDA/PDA)/PI(PMDA/ODA) by a phase-contrast microscope shows that as T_{cast} increases from 40 to 130°C the domain size in the phase-separated structure is reduced and finally the blends become perfectly transparent over 120°C.

On the other hand, the CT fluorescence spectra of the blends decrease drastically with increasing T_{cast} and finally at 130°C the fluorescence becomes very weak as

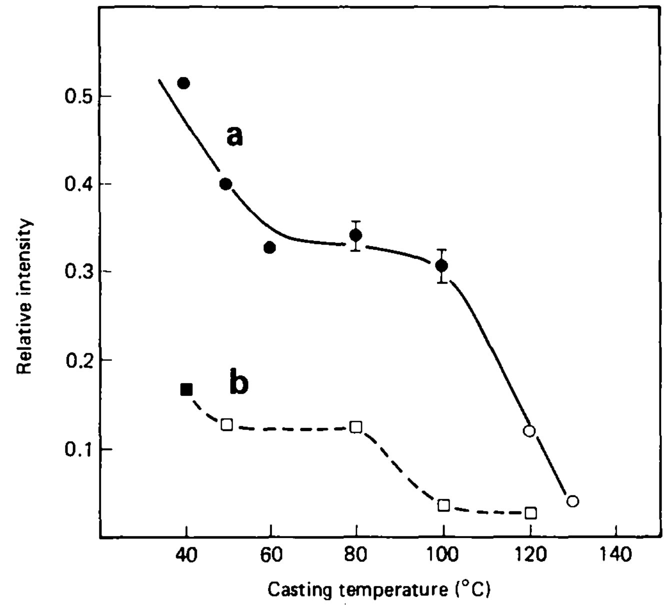

Figure 12 Change of the fluorescence intensity for (a) PI(BPDA/PDA)/PI(PMDA/ODA) (5/5) and (b) PI(BPDA/PDA)/PI(PMDA/PDA) (5/5) against T_{cast}. Open and full symbols denote optically clear and cloudy blends, respectively

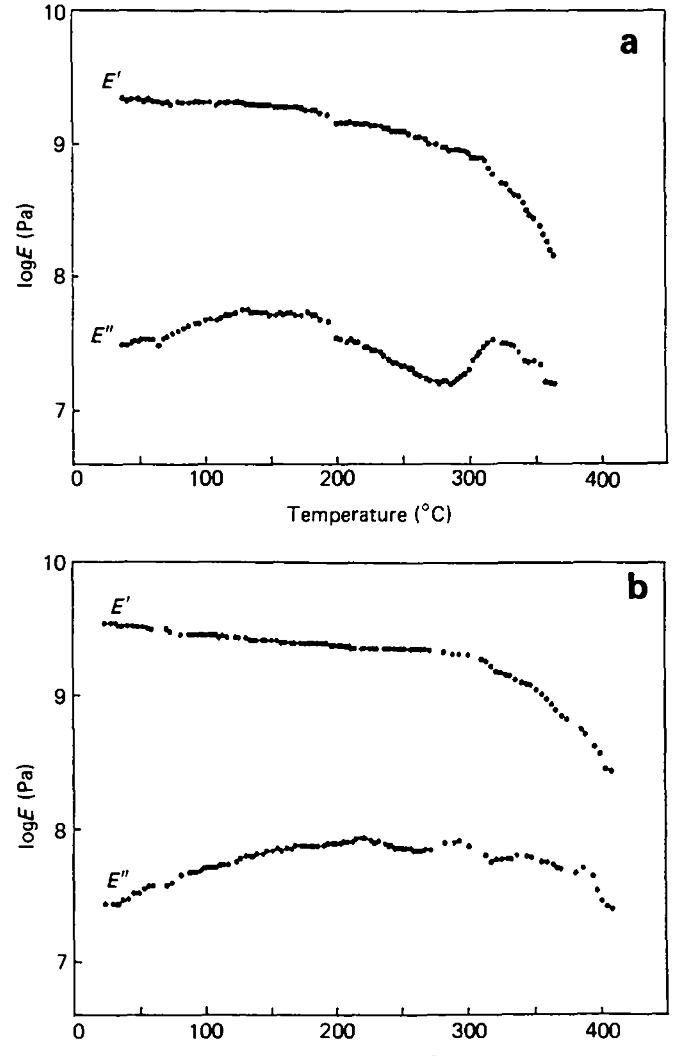

Figure 13 Dynamic mechanical spectra of (a) PI(BPDA/PDA)/PI(PMDA/ODA) (5/5, T_{cast} = 130°C) and (b) PI(BPDA/PDA)/PI(PMDA/PDA) (5/5, T_{cast} = 120°C)

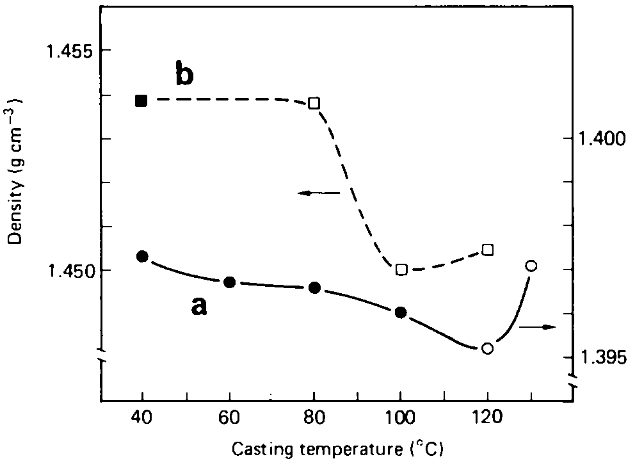

Figure 14 Change of density for (a) PI(BPDA/PDA)/PI(PMDA/ODA) (5/5) and (b) PI(BPDA/PDA)/PI(PMDA/PDA) (5/5) against T_{cast}

shown in *Figure 11*. The changes of the intensity due to T_{cast} for PI(BPDA/PDA)/PI(PMDA/ODA) and PI(BPDA/PDA)/PI(PMDA/PDA) are plotted in *Figure 12*.

The dynamic mechanical spectra for PI(BPDA/PDA)/PI(PMDA/ODA) (5/5, $T_{cast} = 130°C$) and PI(BPDA/PDA)/PI(PMDA/PDA) (5/5, $T_{cast} = 120°C$) are shown in *Figures 13a* and *13b* respectively. *Figure 13a* shows a very broad β loss peak at around 150°C, between 80°C (PI(PMDA/ODA)) and 230°C (PI(BPDA/PDA)), and a broad single α loss peak at around 330°C, between 310°C (PI(BPDA/PDA)) and 350°C (PI(PMDA/ODA)), indicating that the blend is miscible compared with *Figure 6c*. Similarly *Figure 13b* shows a very broad β relaxation and the disappearance of the α loss peak due to PI(BPDA/PDA), indicating that the degree of mixing in the blend became good compared with *Figure 6b*. Similar viscoelastic behaviour is observed for the PI(BPDA/ODA)/PI(PMDA/PDA) blend. We found that no α loss peak is observed for the blend despite the fact that homo-PI(BPDA/ODA) shows a clear α loss peak at 290°C[25]. Since PI(PMDA/PDA) does not show a clear T_g, if phase separation occurs, only the α loss peak due to PI(BPDA/ODA) should be observed. This is interpreted as a result that the blend is miscible so that segmental motions of PI(BPDA/ODA) were suppressed by rigid PI(PMDA/PDA). Accordingly we consider that in the PI(BPDA/PDA)/PI(PMDA/PDA) blend the disappearance of the α loss peak due to PI(BPDA/PDA) is attributed to the increase of the degree of mixing. The results show that the reduction of fluorescence intensity is strongly correlated to the changes of the viscoelastic data due to T_{cast}.

The changes of the density of the PI/PI blends due to T_{cast} are shown in *Figure 14*. Although the amount of change is small, the shapes of the curves are very similar to that in *Figure 12* except for the increase of the density at 120 or 130°C. The decrease of the density with increase of T_{cast} is interpreted as the decrease of intermolecular CT complex population, reflecting the molecular packing due to interpenetration between the distinct PIs[25]. Thus the intermolecular CT fluorescence is a sensitive indicator of the miscibility of PI/PI blends.

We now ask, why does the miscibility increase with increasing T_{cast}? We propose the following possibilities.

(1) The PAA/PAA blends possess a *UCST* (upper critical solution temperature) phase diagram.

(2) The homogeneous state in the solution is fixed due to rapid evaporation of solvent.

(3) The liquid-crystalline phase of PAA in solution melts at higher T_{cast} and becomes isotropic (PAA/PAA blends are easier to mix in the isotropic state than in the LC state).

It is known that the blends in which both component polymers have sufficiently large molecular weights do not generally show a *UCST* phase diagram because the entropy change of mixing is very low[13]. Since it is reasonable to suppose that the sudden changes at a certain temperature as shown in *Figures 11* and *13* are attributed to a transitional phenomenon, we consider now that the third factor contributes predominantly to the behaviour rather than the second. Recently Whang *et al.*[26] reported that an aromatic PAA in *N*-methylpyrrolidone (NMP) forms a lyotropic liquid crystal at room temperature, and becomes isotropic at more than 80°C. The results support our consideration about the effect of T_{cast}. However if melting of LC at higher temperature may bring about the increase of ΔS_{mix}, when cast at higher temperature, the possibility of case (1) remains.

Nature of intermolecular CT fluorescence

We have previously reported that various wholly aromatic PIs emit intermolecular CT fluorescence when excited at 350 nm and longer wavelength (450–550 nm)[22]. The existence of two excitation bands is consistent with the experimental results of Iida *et al.*[27], in which the photocurrent spectra of PI(PMDA/ODA) due to CT interactions possess two bands at approximately 350 and 460 nm.

Wachsman *et al.*[28] argued that for PI(PMDA/ODA) the increase of the CT fluorescence intensity with curing temperature could be due to two possible reasons. The first is an increase in the population of the coplanar state between pyromellitimide rings and diphenyl ether groups by conformational changes (intramolecular CT); and the second is the formation of the fluorescent sandwich structure (intermolecular CT). They opted for intramolecular CT. On the other hand, Erskine *et al.*[29] found that the long-wavelength absorption edge in the transmission spectra of Kapton film red-shifts with pressure (up to 120 kbar) and the observed changes are strictly reversible, and they concluded that the long-wavelength absorption band is attributed to the intermolecular CT complex between the pyromellitimide and diphenyl ether moieties. Their direct experimental results strongly support our opinion that the long-wavelength excitation band is due to intermolecular CT. From the results of our present study, it is obvious that the CT fluorescence emitted by a short-wavelength excitation (350 nm) is due to intermolecular CT. If the CT fluorescence occurs intramolecularly, the fluorescence of PI/PI blends ought to be independent of the blend morphologies. Accordingly we conclude from our present study and other spectroscopic data that both the short- and the long-wavelength excitation bands originate from the intermolecular CT interactions.

CONCLUSIONS

The fluorescence intensity as a function of blend ratio indicates that the miscibility of PI(BPDA/PDA)/

PI(PMDA/PDA) is better than that of PI(BPDA/PDA)/PI(PMDA/ODA) because the fluorescence intensity of the former is smaller at all blend ratios than that of the latter. This was supported by the results of dynamic mechanical analysis.

The domains in PI(BPDA/PDA)/PI(PMDA/PDA:ODA) reduced successively with increasing PDA content in the copolyimide, and the CT fluorescence intensity of the blends decreased successively.

It was clearly shown that, as T_{cast} increases, the miscibility of PI(BPDA/PDA)/PI(PMDA/ODA) and PI(BPDA/PDA)/PI(PMDA/PDA) increases, and the density and the fluorescence intensity drastically decreased. It was confirmed from dynamic mechanical analysis and optical microscopy and density measurements that the reduction of the intermolecular CT fluorescence intensity correlates strongly with the increase of the miscibility of the blends composed of fluorescent PI and non-fluorescent PI. This method is useful for PI/PI blends having very rigid polymer chains.

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REFERENCES

1 Kochi, M., Uruji, T., Iizuka, T., Mita, I. and Yokota, R. *J. Polym. Sci. (C)* 1987, **25**, 441

2 Yokota, R., Horiuchi, R., Kochi, M., Soma, H. and Mita, I. *J. Polym. Sci. (C)* 1988, **26**, 215

3 Takayanagi, M., Ogata, T., Morikawa, M. and Kai, T. *J. Macromol. Sci.-Phys. (B)* 1980, **17** (4), 591

4 Hwang, W. F., Wiff, D. R., Benner, C. L. and Helminiak, T. E. *J. Macromol. Sci.-Phys. (B)* 1983, **22** (2), 231

5 Numata, S., Kinjo, N. and Makino, D. *Polym. Eng. Sci.* 1988, **28**, 906

6 Stankovic, S., Guerra, G., Williams, D. J., Karasz, F. E. and MacKnight, W. J. *Polym. Commun.* 1988, **29**, 14; Guerra, G., Choe, S., Williams, D. J., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1988, **21**, 231; Guerra, G., Williams, D. J., Karasz, F. E. and MacKnight, W. J. *J. Polym. Sci. (B)* 1988, **26**, 301; Leung, L., Williams, D. J., Karasz, F. E. and MacKnight, W. J. *Polym. Bull.* 1986, **16**, 457

7 Bucknall, C. B. and Gilbert, A. H. *Polymer* 1989, **30**, 213

8 Harris, J. E. and Robson, L. M. *J. Appl. Polym. Sci.* 1988, **35**, 1877

9 Adduchi, J. M. 'Polyimides' (Ed. K. L. Mittal), Plenum Press, New York, 1984, Vol. 2, p. 1023

10 Tanunina, P. M., Gomoreva, Z. I., Lur'e, E. G., Vorob'ev, V. D., Dobrokhotova, M. L., Efimova, E. I. and Safronova, T. I. *Plast. Massy.* 1975, No. 9, 45

11 Smirnova, V. Ye., Bessonov, M. I., Zhukova, T. I., Koton, M. M., Kudryavtsev, V. V., Sklizkova, V. P. and Lebedev, G. A. *Polym. Sci. USSR* 1982, **24**, 1375

12 Yamamoto, Y., Kitahashi, M. and Etoh, S. *Polym. Prepr. Jpn.* 1988, **37**, 2396

13 Akiyama, S., Inoue, T. and Nishi, T. (Eds) 'Polymer Blends', CMC Press, Japan, 1981

14 Semerak, S. N. and Frank, C. W. *Macromolecules* 1981, **14**, 443; Thomas, J. W. and Frank, C. W. *Macromolecules* 1985, **18**, 1034

15 Amrani, F., Hung, J. M. and Morawetz, H. *Macromolecules* 1980, **13**, 649; Mikes, F., Morawetz, H. and Dennis, K. S. *Macromolecules* 1984, **17**, 60

16 Fredrickson, G. H. and Helfand, E. H. *Macromolecules* 1986, **19**, 2601

17 Halarly, J. L., Ubrich, J. M., Nunzi, J. M., Monnerie, L. and Stein, R. S. *Polymer* 1984, **25**, 956; Ubrich, J. M., Larbi, F. B. C., Halarly, J. L., Monnerie, L., Baner, B. J. and Han, C. C. *Macromolecules* 1986, **19**, 810

18 Holden, D. A. and Strauss, J. *Polym. Eng. Sci.* 1988, **28**, 1373

19 Albert, B., Jerome, R., Teyssie, P., Smyth, G., Boyle, N. G. and McBrierty, V. J. *Macromolecules* 1985, **18**, 388

20 Hasegawa, M., Kochi, M., Mita, I. and Yokota, R. *J. Polym. Sci. (C)* 1989, **27**, 263; Hasegawa, M., Kochi, M., Mita, I. and Yokota, R. *Eur. Polym. J.* 1989, **25**, 349

21 Kochi, M., Shimada, H. and Kambe, H. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 1979

22 Ree, M., Yoon, D. Y. and Volksen, W. (ACS Spring Conf.) *Polym. Mater. Sci. Eng.* 1989, **60**, 179

23 Bohn, L. 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut), 2nd Edn, Wiley, New York, 1975, p. 111-211

24 Bessonov, M. I., Koton, M. M., Kudryavtsev, V. V. and Lauis, L. A. (Eds) 'Polyimides', Plenum Press, New York, 1987, p. 194

25 Yokota, R., Doctoral Thesis, The University of Tokyo, 1990, p. 159

26 Whang, W. T. and Wu, S. C. *J. Polym. Sci. (A)* 1988, **26**, 2749

27 Iida, K., Waki, M., Nakamura, S., Ieda, M. and Sawa, G. *Jpn. J. Appl. Phys.* 1984, **23**, 1573

28 Wachsman, E. D. and Frank, C. W. *Polymer* 1988, **29**, 1191

29 Erskine, D., Yu, P. Y. and Freilich, S. C. *J. Polym. Sci. (C)* 1988, **26**, 465