Interdiffusion at polyimide interfaces

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Interdiffusion at interfaces between deuterated polyamic acid (d-PAA) and polyimide (PI) films was investigated with forward recoil spectrometry, an ion beam analysis technique. The PI films were prepared by spin coating a solution of PAA on a silicon substrate, followed by an anneal at a temperature T_i, which produced partial or complete conversion of the PAA to PI. An overlayer of d-PAA was added, in one set of samples by spin coating from solution, and in another set by transferring (in the absence of solvents) a dry d-PAA film onto the PI surface. The bilayer samples were then either annealed at a temperature T_d or allowed to stand at room temperature. No interdiffusion occurred in the solventless transfer samples for any combination of temperatures T_i or T_d from room temperature up to 400°C. Bilayers prepared by spin coating d-PAA from solution directly on partially cured PI films did, however, show significant interdiffusion distances w, which decreased with increasing values of T_i to immeasurable levels by $T_i = 200°C$. The decrease in w with increasing T_i is thought to be caused by a positive Flory parameter between PAA and PI which increases with the imide fraction in the PI film; the result is an increasing immiscibility between the swollen polymer layers. Subsequent annealing of these spin-coated bilayers at a temperature T_d up to 400°C was ineffective in producing any additional interdiffusion. The absence of any thermally activated interdiffusion (even for initially unimidized samples), with either the solventless-transfer or spin-coated preparation methods may be attributed to the rapid increase of the glass transition temperature of the polymer with imidization.

(Keywords: interdiffusion; adhesion; solvent; miscibility; polyimide)

INTRODUCTION

Polyimides are increasingly used in the electronics industry, especially as the dielectric material separating metal lines in integrated circuit interconnection and packaging technologies. However, such electronic systems of multiple conductor/polymer dielectric layers must have a reasonable level of adhesion between the polymer layers if failure (electrical or mechanical) is to be avoided. In a previous work[1] it was demonstrated that the adhesion between polyimide films correlates well with the amount of interdiffusion between such films. In this study we will explore two factors affecting polyimide interdiffusion: thermal conversion of polyamic acid (PAA) to the polyimide, and the presence of solvent molecules.

This study will show that interdiffusion between polyimide films is affected by two factors: the glass transition temperature T_g of the polymer, and the miscibility between the polymers in the two films. These factors have already been explored in other polymer systems[2]. Generally, the value of T_g determines the degree of mobility possible for the individual polymer molecules at a given temperature T; if T is not sufficiently higher than T_g, then the centre-of-mass motion of the molecules is 'frozen out', and interdiffusion is not possible. On the other hand, T_g can be lowered (and therefore the polymer mobility increased) by the addition of a solvent. The presence of the solvent will be seen to be crucial to interdiffusion in the polyimide system. The second factor, the miscibility of the polymers on either side of the interface, is also very important since a high enthalpy of interaction between unlike polymers (as measured by the Flory interaction parameter[3]) can reduce or prohibit interdiffusion of the two species, even when swollen by a solvent. While little is known about the thermodynamic interaction between PAA and the polyimide pyromellitic dianhydride oxydianiline (PMDA-ODA), our results indicate that the miscibility of PAA and polyimide is low.

EXPERIMENTAL

Materials

Our experiments measured the interdiffusion between a film (< 20 nm thick) of deuterated PAA (d-PAA) and an imidized or partially imidized PAA film of several micrometres thickness. This latter film was prepared from a solution of Du Pont 2545 Pyralin® PAA, which is based on PMDA-ODA, or poly[*N*,*N*′-bis(phenoxyphenyl) pyromellitamic acid]. *Figure 1* shows the cycloimidization reaction of PAA, which produces the polyimide poly[*N*,*N*′-bis(phenoxyphenyl)pyromellitimide] (which we shall call PI) plus two water molecules per monomer unit as a by-product. A solution of d-PAA in the solvent *N*-methyl-2-pyrrolidone (NMP) was contributed by IBM Almaden Research Center; the details of the

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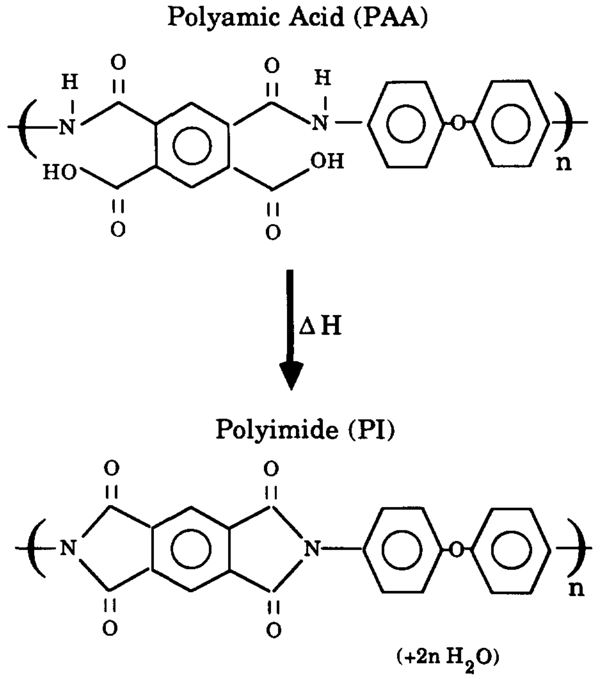

Figure 1 Conversion of PMDA-ODA-based polyamic acid (PAA) to polyimide (PI) by an imidization reaction

synthesis have been described in the literature[4]. The d-PAA was dissolved in either NMP or in dimethyl sulphoxide (DMSO).

Sample preparation

A PMDA-ODA substrate layer was created by spin coating a solution of Du Pont 2545 Pyralin® PAA on a silicon wafer at 600 rev min^{-1}, which resulted in a film about 7 μm thick. The coated wafer was spun for 6 min (to allow for some solvent evaporation) and then placed in a vacuum oven at 80°C for 1 h to remove more solvent. An anneal was performed for 1 h in vacuum or argon atmosphere at the imidization temperature T_i ($T_i = 150$, 165, 175, 185, 200, 300 or 400°C), allowing imidization (partial or complete, depending on T_i) of the PAA to the polyimide PMDA-ODA. For comparison, some samples were left uncured, which we designate with $T_i = 80$°C.

The d-PAA layer was applied over the PI substrate by one of two techniques:

1. *Spin-coating.* A solution of d-PAA in either NMP or DMSO was spun directly onto the PI layer.
2. *Solventless transfer.* Intermediate glass and water surfaces were used to transfer the d-PAA layer as a dry film to the PI surface. We shall see that these two methods of forming the bilayer d-PAA/PMDA-ODA samples can produce quite different interfacial diffusion properties. The samples were complete after annealing for 1 h at a temperature T_d of either room temperature (r.t.) or 400°C.

Experimental determination of concentration profiles

Forward recoil spectrometry[5] (FRES) was used to determine the concentration profile of the d-PAA as a function of depth into the PI substrate, and the data were analysed by comparison with the theoretical spectrum for an ideal sample. *Figures 2a* and *2b* show the FRES spectra for two bilayer d-PAA/PI samples for which $T_i = 150$°C and $T_d = 400$°C. For the sample whose spectrum is shown in *Figure 2a*, the d-PAA film was formed by spin coating a d-PAA/NMP solution onto the PI substrate, whereas for *Figure 2b* the solventless transfer method was used. An individual FRES spectrum represents the yield of hydrogen and deuterium nuclei recoiling from the sample, resulting from collisions with a 3 MeV $^4\mathrm{He}^{2+}$ ion beam. The highest energy nuclei, which form the 'edge' near channel 300, correspond to deuterium nuclei recoiling from the surface of the film. The edge near channel 200 marks the point where surface hydrogen nuclei (which have 1/2 the mass of deuterium nuclei, and therefore recoil with only about 7/10 the energy) enter the spectrum.

Depth information is present in the spectra, with lower channel numbers or nucleus energies corresponding to nuclei emerging from greater depths in the film sample. The depth–energy relationship is the result of energy losses (from inelastic collisions) suffered by the incident ion beam as it penetrates the film and similar losses by the recoiling hydrogen or deuterium nuclei as they pass through the film en route to the sample surface. The overlap of the hydrogen and the deuterium spectra begins

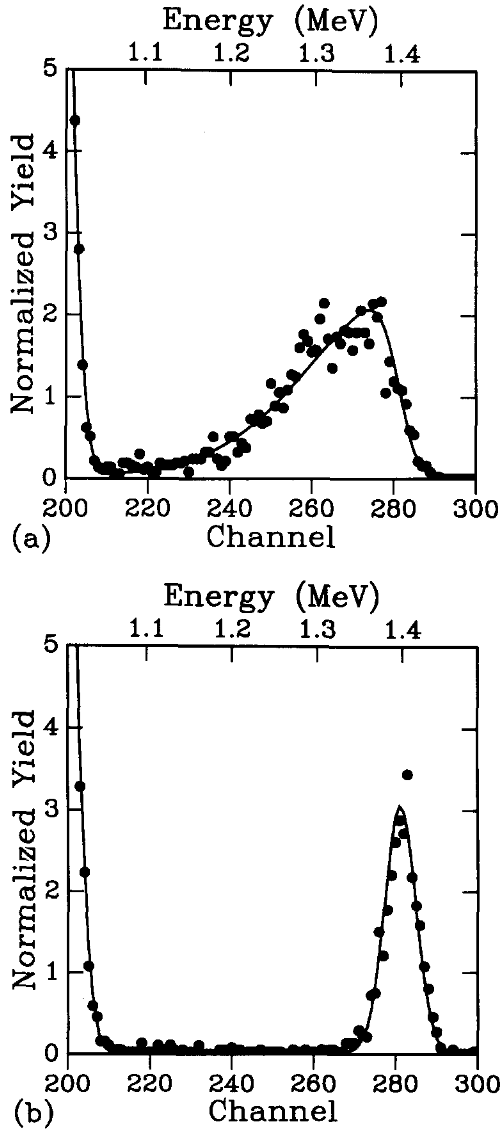

Figure 2 FRES spectra from bilayers of d-PAA/PI; $T_i = 150$°C, $T_d = 400$°C. Solid line represents equation (1), with interdiffusion distance w (equation (2)) adjusted for the best fit. (a) Bilayer formed by spin coating. Interdiffusion distance $w = 215$ nm. (b) Bilayer formed by solventless transfer. Interdiffusion distance $w = 19$ nm

with deuterium nuclei arriving from depths greater than 0.7 μm from the film surface, and therefore determines the depth window over which the d-PAA concentration (ϕ_{dpaa}) in the sample can be measured. The resolution of the technique is limited mainly by straggling of the nuclei as they pass through the stopper foil. Nuclei recoiling from a given depth x in the sample, previously mono-energetic, emerge from the stopper foil with an energy spread of about 45 keV about their mean energy. This full-width-at-half-maximum of the Gaussian instrumental resolution function corresponds to a depth resolution of about 80 nm.

The interdiffusion between the d-PAA film and the PI substrate was analysed by assuming that the d-PAA concentration profile is governed by Fick's laws, along with the boundary conditions corresponding to a thin film of thickness h diffusing into a semi-infinite matrix[6]:

$$\phi_{\mathrm{dpaa}} = \frac{1}{2}\left[\operatorname{erf}\left(\frac{h+x}{w}\right) + \operatorname{erf}\left(\frac{h-x}{w}\right)\right] \quad (1)$$

The interdiffusion distance w is expressed in terms of the time-averaged interdiffusion coefficient D and diffusion time t:

$$w = (4Dt)^{0.5} \quad (2)$$

A computer algorithm[7,8] simplifies comparison of the ϕ *versus* x simulation with the experimental data by converting the concentration and depth scales to the experimental variables, normalized yield and energy, respectively. The conversion of the volume fraction ϕ to normalized yield is made by using the fact that the number of nuclei recoiling from a given depth is proportional to the areal density of the corresponding atomic species at that depth. The depth scale is translated to an energy scale by employing a table of stopping powers[9]. Finally, a convolution is made with the Gaussian instrumental resolution function. The depth resolution of the method is determined by the standard deviation σ of the Gaussian function, about 50 nm. It has recently been shown[10] that time-of-flight spectrometry can be used to replace the stopper foil, resulting in an improvement in the resolution by at least a factor of two.

A least squares fit to the data, using equation (1), was made to determine w. The value of h was chosen to match the integrals of the simulation and experimental data. The ^{2}H portion of the spectrum was used as the error window in which the deviation of the simulation from the data was minimized. The ^{1}H portion of the spectrum provided the basis for normalizing the peak heights of the simulation and the data, allowing the correction of small variations in secondary ion and electron loss from the sample[11]. The best fit simulations of the two experimental spectra are shown as solid lines in *Figure 2*. The values for w in equation (1) were 215 nm for the spin-coated bilayer, and 19 nm for the solventless transfer bilayer. The latter interdiffusion distance is negligible compared to the standard deviation of the Gaussian instrumental resolution, and therefore represents a case in which there was no measurable interdiffusion. The theoretical spectrum becomes increasingly insensitive to the value of w for interdiffusion distances below 35 nm, which therefore defines w_{min}, the smallest measurable w value. The repeatability of w measurements greater than w_{min} was found to be about $\pm 25\%$.

RESULTS AND DISCUSSION

Figure 3 displays the interdiffusion distances w of d-PAA molecules in d-PAA/PI bilayer samples as a function of T_{i} of the PI substrate, for three different methods of sample preparation. The figure provides information about interdiffusion in three different regimes: (1) interdiffusion in the absence of solvent molecules – this diffusion should occur purely by thermal activation; (2) interdiffusion facilitated by the presence of a solvent; (3) interdiffusion resulting from post-annealing after the spin coating of the d-PAA layer. The interdiffusion distances measured in the solventless d-PAA/PI bilayers provide information regarding the first regime. One can see from *Figure 3* that no measurable interdiffusion occurred in the solventless transfer samples when annealed at $T_{\mathrm{d}} = 400$°C, for any value of T_{i} of the PI layer. The same result was found in these solventless transfer samples for all other choices of T_{d} in the range of r.t. to 400°C, and for annealing times at T_{d} between 5 min and 24 h. This evidence strongly suggests that thermally activated interdiffusion in the absence of solvents does not occur in the PI system.

Further evidence of the limited extent of thermally activated interdiffusion can be gathered from *Figure 3* by comparing the data from the spin-coated samples where T_{d} was either r.t. or 400°C. The spin-coated d-PAA/PI bilayers, prepared in the presence of the solvent NMP, do display interdiffusion for T_{i} values less than 200°C. We will discuss this dependence of the interdiffusion distance on T_{i} shortly. For the moment, however, we focus on the fact that samples in which T_{d} was 400°C do not show greater interdiffusion than the samples where $T_{\mathrm{d}} = $ r.t. The failure of the T_{d} anneal to produce additional measurable interdiffusion was noted in our previous studies[1,12], in which interdiffusion distances were found to be independent of T_{d} over the temperature range 150–400°C and independent of annealing time[13] at T_{d}. Since solvent is lost from the sample during the first few seconds of such an anneal, we expect that interdiffusion, were it to occur, would be driven by purely thermal activation. The null results for the effect of the T_{d} anneal are therefore likely to be another example of

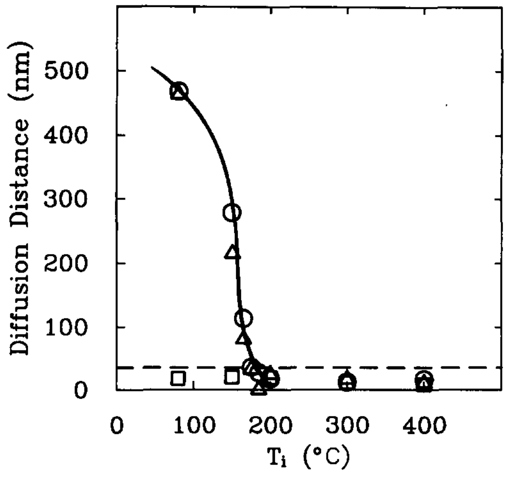

Figure 3 Interdiffusion distance w measured in bilayers of d-PAA/PI *versus* imidization temperature T_{i}. The solid line is a guide to the eye; diffusion distances below the dashed line (representing w_{min}) are not reliably measured. ○, Bilayer formed by spin coating, $T_{\mathrm{d}} = $ r.t.; △, bilayer formed by spin coating, $T_{\mathrm{d}} = 400$°C; □, bilayer formed by solventless transfer, $T_{\mathrm{d}} = 400$°C

the failure of thermally activated interdiffusion to occur in the absence of solvent molecules.

One factor likely to be responsible for the complete absence of thermally activated interdiffusion in our samples is the high value of T_g of polyimide, since one normally expects thermally activated interdiffusion to occur only at temperatures sufficiently above the T_g. The value (or even existence) of T_g for the polyimide PMDA-ODA is a topic of some disagreement, especially as changes in mechanical and thermal properties of PI, used by some[14–17] to place T_g near 400°C, may be linked to the process of segmental ordering which acts at such temperatures[18].

A further complication of the question of T_g is the fact that the imidization of PAA causes an increase in molecular rigidity, increasing the inherent glassiness of the polymer (raising T_g). Therefore, as one increases the temperature of the sample in an effort to exceed T_g, the subsequent increase in the imide fraction of the polymer would raise T_g, defeating the effort. It is this effect that explains the failure of thermally activated diffusion to appear even in bilayers of initially unimidized d-PAA and PAA annealed at 150°C. Because of the onset of the imidization reaction above 100°C, the T_g of such a bilayer would increase during the anneal, preventing interdiffusion. Presumably, if one were to anneal a PI bilayer at a temperature above the T_g of even fully imidized PI, one might be able to observe thermally activated interdiffusion. This hypothesis defies verification, since one would need to use temperatures above 400°C, the purported T_g of fully cured polyimide. Such temperatures would, however, also approach the decomposition temperature of the polymer, and therefore the results of the experiment would be ambiguous.

The factor limiting thermally activated interdiffusion – the necessity of heating the sample to temperatures sufficiently above T_g – can be overcome by introducing a solvent into the system. The significant values of w in *Figure 3* measured in spin-coated d-PAA/PI bilayers show that a solvent, acting as plasticizer, can lower the T_g of an unimidized or partially imidized PI film sufficiently to allow d-PAA/PI interdiffusion. The effect is also seen by comparing *Figures 4a–4c*, which are the FRES spectra obtained from bilayers of d-PAA and PI ($T_d = T_i = 150$°C) in which the d-PAA layer was applied by spin coating, solventless transfer, or solventless transfer followed by spin coating of pure NMP solvent, respectively. The values of w used in the fit were, respectively, 440 nm, 0 and 252 nm. It is clear from these values of w that adding solvent to the d-PAA/PI system can cause a significant amount of interdiffusion where none could otherwise take place (including annealing).

Figure 3 shows that the mere presence of solvent is not sufficient to cause d-PAA/PI interdiffusion, however. The value of w decreases with T_i of the PI film, dropping to a negligible value near 200°C. Given our previous argument that thermally activated interdiffusion in the PAA/PI system can be hampered by the increase of T_g with imide fraction in PI, one might suppose that the effect also plays a role in the T_i dependence of w. For instance, one could argue that the increase in T_g with T_i of the PI film would offset the plasticizing effect of the solvent, reducing the amount of interdiffusion possible. Indeed, PI films imidized above 200°C, and saturated with solvent, failed to show a T_g below the boiling point of the solvent[19], a result that would seem to preclude

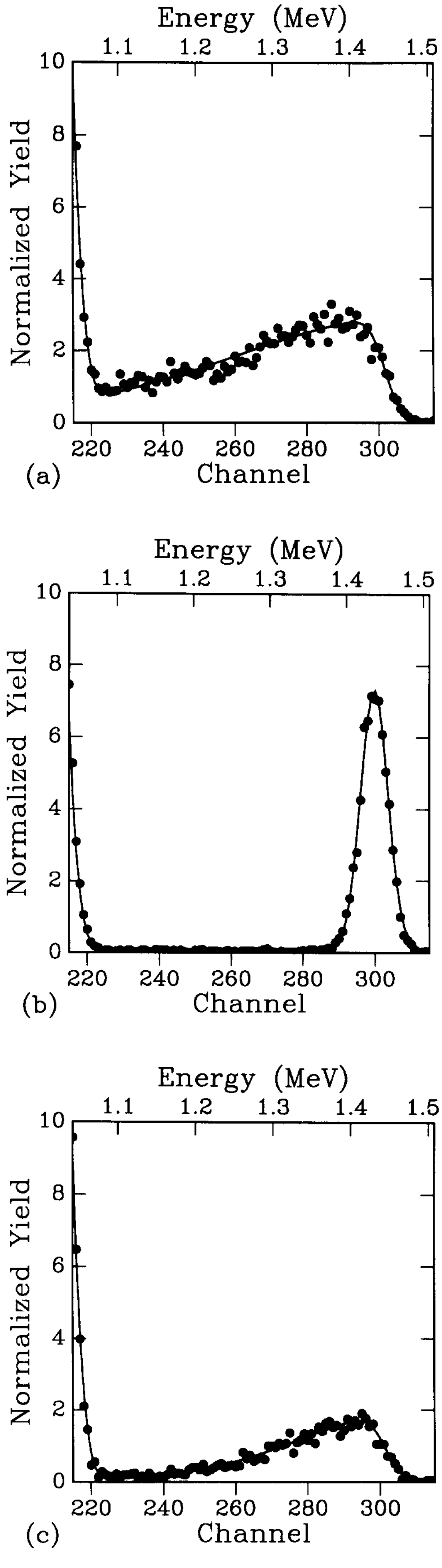

Figure 4 FRES spectra from bilayers of d-PAA/PI; $T_i = 150$°C, $T_d = 150$°C. Solid line represents equation (1), with interdiffusion distance w (equation (2)) adjusted for the best fit. (a) Bilayer formed by spin coating. Interdiffusion distance $w = 440$ nm. (b) Bilayer formed by solventless transfer. Interdiffusion distance $w = 0$ nm. (c) Bilayer formed by solventless transfer, followed by spin coating pure solvent. Interdiffusion distance $w = 252$ nm

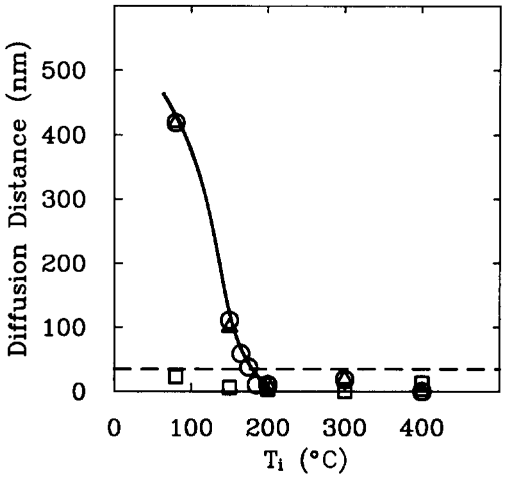

Figure 5 Interdiffusion distance w measured in bilayers of d-PAA/PI *versus* imidization temperature T_i. Solvent was DMSO. The solid line is a guide to the eye; diffusion distances below the dashed line (representing w_{min}) are not reliably measured. ○, Bilayer formed by spin coating, T_d = r.t.; △, bilayer formed by spin coating, T_d = 400°C; □, bilayer formed by solventless transfer, T_d = 400°C

interdiffusion at room temperature. As we shall see, however, this effect cannot be the sole factor governing interdiffusion in the PAA/PI system.

To explore further the role of the solvent in facilitating interdiffusion in the d-PAA/PI system, an experiment was conducted to discover if the choice of the solvent molecule had an effect on the amount of interdiffusion. Samples were prepared by spin coating or solventless transfer, but from DMSO-based rather than NMP-based solutions. The results for w as a function of T_i are displayed in *Figure 5*. Once again the samples prepared via solventless transfer showed no measurable diffusion, despite annealing at $T_d = 400$°C. Similarly, the T_d anneal did not appear to promote additional interdiffusion in the samples spin-coated from DMSO. In contrast to the NMP results, the DMSO solvent appeared to allow less d-PAA diffusion in those samples where interdiffusion was measurable.

It seemed possible that this minor difference between the DMSO and NMP results was due to the slightly higher vapour pressure of DMSO (66.7 Pa as opposed to 40.0 Pa for NMP[20]), reducing the time in which the solvent is present in concentrations sufficient to allow d-PAA diffusion. To check this idea, a modified method of sample preparation was used to ensure the maximum opportunity for the solvent to act. Rather than spin coating the d-PAA/solvent solution on a dry PI substrate, the PI layer was first soaked in the solvent (NMP or DMSO) for 90 min. The excess solvent was subsequently spun off, and immediately replaced with a solution of the d-PAA in solvent. This solution was allowed to stand on the PI for an additional 90 min before spinning, after which the samples were annealed in vacuum to remove the solvent. (The solvent exposure time was sufficient to allow the solvent to soak the sample completely, actually reaching the silicon substrate in some cases.)

Figure 6 displays the diffusion results from the solvent soaking experiment described above. First one notices that the d-PAA diffusion is not consistently affected by the choice of solvent, as it had been in the simple spin coating experiment. The w values of the d-PAA/DMSO samples, given the extra exposure time to the solvent, increased over those measured earlier, while the w values for the d-PAA/NMP samples remained close to those measured before. The similarity of the interdiffusion distances in the two sets of samples supports our hypothesis that evaporation can limit the effectiveness of the solvent in promoting interdiffusion during simple spin coating preparation.

The results from the soaking experiment can be seen to contradict the hypothesis that interdiffusion in polyimide films is governed entirely by T_g. Were T_g the primary factor, we would have expected the solvent exposure time to control w according to equation (2). The exposure time in the soaking experiment, nearly two orders of magnitude greater than the exposure time in the simple spin coating procedure, should therefore have resulted in an order of magnitude increase in w. As noted, the increased diffusion in the DMSO-treated samples was small, and w was nearly the same in the NMP-treated samples. Factors other than the increase of T_g with T_i must play a significant role in limiting interdiffusion in the PI system.

It would seem from the apparent time invariance of the interdiffusion distance that the d-PAA molecules must reach an equilibrium concentration profile at the solvent-swollen interface with the PI substrate. Were d-PAA molecules only partially miscible in the PI, one might expect such a concentration profile, corresponding to a diffuse interface separating the two phases[21–27] (see ref. 28 for more details). The diffuseness of the boundary layer, measured in our experiments as the interdiffusion distance, would be determined by the degree of miscibility. Therefore, as the imide fraction in the PI film increased with T_i, w would decrease.

One other effect which may hinder PAA/PI interdiffusion is the onset of order, either at the intermolecular or intramolecular levels[18,29–31], which occurs coincidentally with imidization in PAA films. One effect of this partial crystallinity (which increases with T_i) is a decreased solvent miscibility. This effect would serve to hinder the degree to which the T_g of the system could be lowered by the solvent. Another possible effect

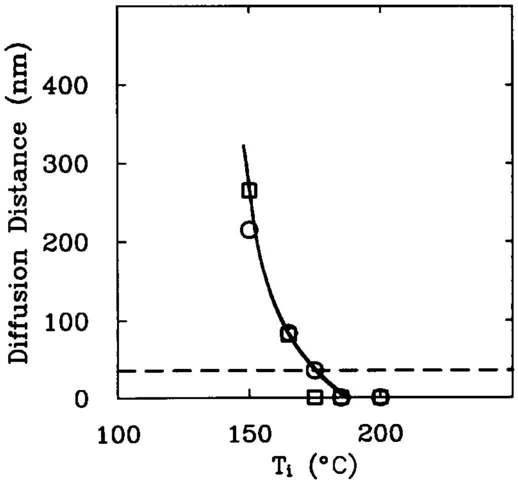

Figure 6 Interdiffusion distances w measured in bilayers of d-PAA/PI, formed by soaking the PI matrix with d-PAA/solvent solution, followed by spinning, *versus* imidization temperature T_i, T_d = 200°C. The solid line is a guide to the eye; diffusion distances below the dashed line (representing w_{min}) are not reliably measured. Solvent: ○, NMP; □, DMSO

of the crystallinity may be to slow the kinetics of PAA diffusion in PI. Unfortunately, little is known about interdiffusion in mixed amorphous/crystalline polymer systems such as this. One final consideration is the effect of the biaxial orientation exhibited by polyimide films imidized on a substrate. This orientation has been shown to affect the degree of crystallinity[32], and the amount and rate of solvent sorption in polyimide films[19], two factors just mentioned that may influence polymer interdiffusion in this system.

CONCLUSIONS

We have investigated the effect of thermal processing of PAA and the use of solvents on interdiffusion in the PAA/PI system. Measurable diffusion of d-PAA into a PI substrate imidized at a temperature T_i was found to take place only in the presence of solvent molecules. Thermally activated diffusion at a temperature T_d in the absence of solvents was not observed for any value of T_i between 80 and 400°C, or any value of T_d between room temperature and 400°C. The failure to find any thermally activated diffusion in our system was explicable in terms of the increase of T_g of PI with the degree of imidization.

Diffusion that was facilitated by the presence of solvents was seen to decrease with T_i to an unmeasurable level near 200°C. The concentration profile was also found to be stable with the time of exposure to the solvent. These results indicate that PAA and PI are immiscible, to a degree depending on the imide fraction in the PI film. Partial crystallinity of the PI film, known to increase with T_i, may also affect interdiffusion in this system.

As noted earlier, the pursuit of a better understanding of interdiffusion processes in polyimides may bring technological applications in the area of polyimide adhesion, perhaps promoting the optimization of electronic packaging applications that use polymer dielectrics. As an additional example of the apparent correlation between interdiffusion and adhesion, we note that the solventless transfer method of forming layered polyimide films, which in this study was shown to produce undiffused interfaces, was also seen to give samples with virtually no adhesion strength[33]. In future experiments, utilizing improvements in the FRES technique[10], we hope to expand our understanding of the interdiffusion of PAA and PI films in the regime of interdiffusion distances less than the 40 nm which currently limits us. It is clear from our study[1] of the correlation of interdiffusion and adhesion between polyimide films that the greatest changes in adhesion occur in this low interdiffusion distance regime. Such future studies may also resolve the matter of the effectiveness of the T_d anneal in increasing the adhesion of polymer films, while it fails to produce interdiffusion, at least at currently measurable levels.

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