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# Miscibility and phase properties of poly(aryl ether ketone)s with three high temperature all-aromatic thermoplastic polyimides

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Several semicrystalline poly(aryl ether ketone)s (PEK, PEEK and different isomers of PEKK) were melt-blended at $T > 400°C$ with three high temperature thermoplastic polyimides. The compatibility and crystallization properties of the blends were studied by differential scanning calorimetry (d.s.c.). Blends of a semicrystalline New-Thermoplastic PolyImide (N-TPI) showed some surprising differences in the fast-quenched amorphous samples. Its compatibility could be approximately ranked in the order PEKK > PEK ≫ PEEK, where PEEK was completely incompatible. For the case of PEK/N-TPI, extensive d.s.c. data on amorphous fast-quenched films blended at different temperatures between 400 and 455°C were used to construct a phase diagram showing an upper critical temperature of 440°C. Two other wholly aromatic non-crystalline polyimides, LARC-IA and LARC-ITPI, were also studied. These are difficult to process in their neat form due to high melt viscosity. In the case of LARC-IA, the addition of miscible or semi-miscible lower viscosity polymer such as PEKK lowers the melt viscosity dramatically. LARC-ITPI was completely incompatible in all cases. N-TPI and LARC-IA were also melt blended with different isomers of PEKK including PEKK(50T/50I), (60T/40I), (80T/20I) and (100T/0I), which have melting temperatures of 320, 310, 355 and 390°C, respectively, and equivalent glass transition temperatures of ~160°C; T/I refers to the ratio of 1,4 and 1,3 ketone linkages, respectively. Surprising differences were seen in the miscibility of the different PEKK isomers. PEKK(60T/40I) was the only PEKK miscible with N-TPI and LARC-IA at essentially all compositions. Tentative structure–property relationships for blend compatibility and the nature of the interactions leading to miscibility are discussed.

**(Keywords: polymer blends; poly(aryl ether ketone)s; polyimides)**

## INTRODUCTION

The issue of thermodynamic equilibrium in terms of the melt compatibility of semicrystalline polyimides with high glass transition temperature ($T_g$) is not well understood. This is due in part to difficulties in blending of high viscosity materials at high temperatures, and the possibility of chemical reactions at elevated temperatures[1]. Even though single-phase polyimide blends can be formed by solution casting, the blends are not in equilibrium nor are they miscible. The phase structure is frozen-in by the solvent casting process. In essentially all reported cases[2–7], phase separation occurred upon heating to $T > T_g$ unless the blends were completely immobilized by crystallinity or crosslinking. We have applied a technique of melt blending very small quantities of materials at very high temperatures, where one can be quite sure that equilibrium melt mixing has been reached[8]. Very short melt blending times are required, which is important since many of the materials of interest are generally processed close to or above their nominal degradation temperatures.

Previously[8], we studied melt-blended samples of a semicrystalline polyimide, New-Thermoplastic PolyImide [N-TPI; $T_g = 250°C$ and melting temperature ($T_m$) = 385°C], and found surprisingly large differences in the degree of miscibility with poly(aryl ether ketones) such as PEK, PEEK and PEKK(60T/40I), where T/I in the PEKK sample refers to the ratio of 1,4 to 1,3 ketone linkages, respectively (*Figure 1*). At blending temperatures of 410°C, PEKK(60T/40I) and N-TPI were essentially miscible at all concentrations, PEK was miscible with N-TPI only at high and low PEK concentrations and slightly compatible at intermediate concentrations, and PEEK and N-TPI were completely immiscible at all concentrations[8].

Ultem® 1000 ($T_g = 216°C$) is an amorphous poly(ether imide) which has been used in a variety of melt blending studies[9–11]. Ultem is miscible with other polymers only in rare instances, although compatible single-phase non-equilibrium blends can be made by casting from solution[2,3]. Examples of truly miscible pairs with Ultem include PEEK[9–11], PEKK(60T/40I)[11] and possibly other rigid polyimides[12]. Unfortunately, Ultem is difficult to process, is non-crystallizable with an intermediate $T_g$, has poor solvent resistance, and contains aliphatic (methyl) groups which lower its thermo-oxidative stability. Blends of N-TPI with liquid

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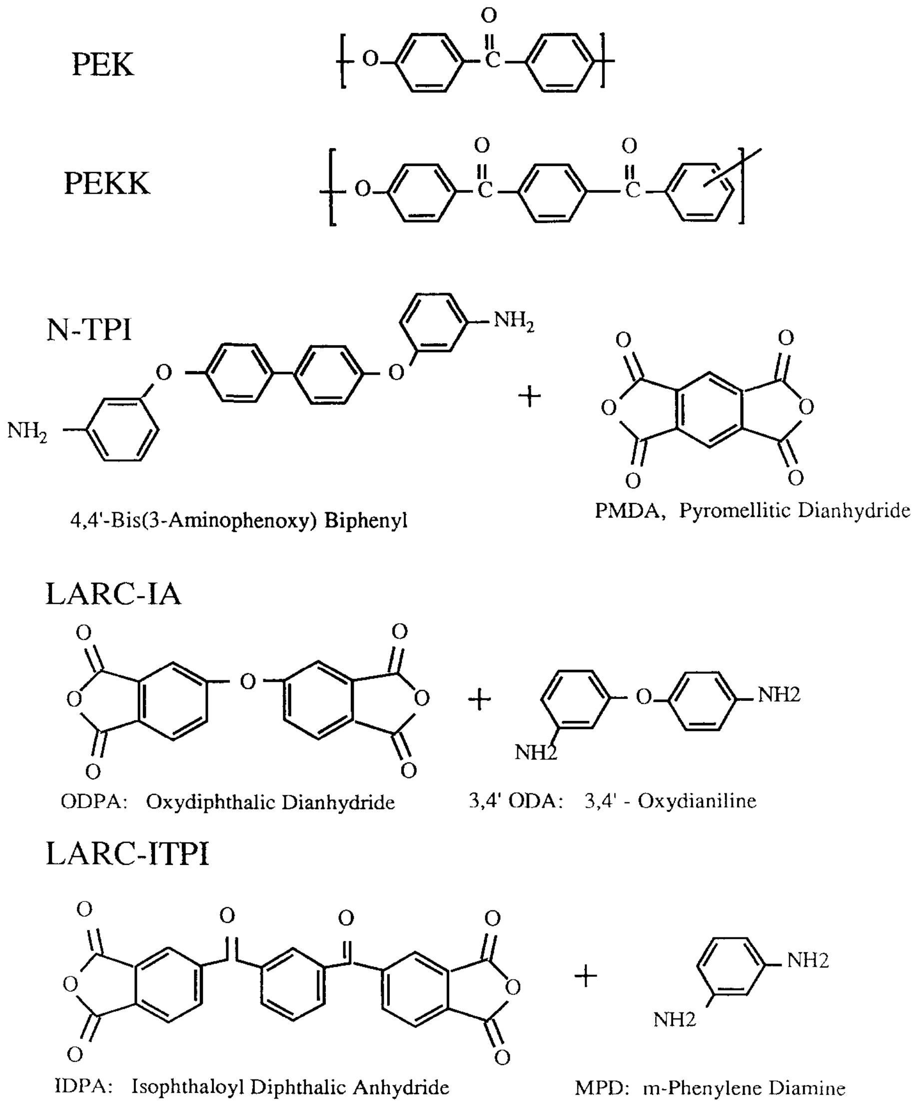

**Figure 1** Structure and composition of PEK, PEKK and the three polyimides. PEK contains all 1,4 ketone linkages, while the diagonal line for the last ketone bond in PEKK indicates that it consists of a mixture of 1,3 and 1,4 ketone linkages (see text for the four different PEKK isomers studied here)

crystalline polymers have been reported[13]. Other work on polyimide blends has been reviewed[1,5,14], including several examples where chemical interactions occur. Interesting examples include 'molecular composites' consisting of mixtures of rod-like and flexible polyimides[15].

In this study we have blended three all-aromatic polyimides with PEK and four different PEKKs: PEKK(50T/50I), (60T/40I), (80T/20I) and (100T/0I) with $T_m = 320$, 310, 355 and 390°C, respectively. PEK/N-TPI blends were studied previously[8], but here we emphasize the determination of the detailed phase diagram for this system at extremely high temperatures. The polyimides are Mitsui Toatsu's semicrystalline N-TPI, in addition to LARC-IA and LARC-ITPI (*Figure 1*) which are non-crystallizable polyimides with $T_g$s of 231 and 248°C, respectively. As was the case with poly(ether ether ketone) (PEEK)/N-TPI blends[8], no signs of any partial compatibility of LARC-ITPI were seen with any of the PEKKs or PEK, so no further results will be reported for this polyimide. Unlike N-TPI, LARC-IA is a mostly amorphous polyimide with borderline processability at 360–390°C. This temperature pushes the polymer stability limit so that the materials are very difficult to process without degrading them. The fact that it does not exhibit significant flow, even at ~330°C, indicates that there is some amorphous order in the form of a gel network or a low crystallinity state which cannot be easily detected.

If one considers PEKK or PEK as a viscosity modifier or a high-molecular-weight plasticizer, miscibility over the entire concentration range is of considerable technological importance in terms of improving the melt flow of polyimides such as Ultem[9], N-TPI and especially LARC-IA, which are difficult to process by themselves. If we can understand the phase properties of these, then design of compatible blends with good processability combined with retention of the high temperature properties of polyimide should be possible.

As was the case with PEK and PEEK[8], the chemical similarity of the PEKKs with the different T/I ratios leads one to expect some similarities in the blend properties. While there are some similarities, there are also many important differences in the degree of

**Table 1** Thermal properties obtained from d.s.c. first run data on originally amorphous blends of different PEKKs with N-TPI

| % PEKK | $T_{g,1}$ (°C) | $\Delta T_{g,1}$[a] (°C) | $T_{g,2}$ (°C) | $\Delta T_{g,2}$[a] (°C) | $T_{m,\text{N-TPI}}$ (°C) | $\Delta H_{\text{N-TPI}}$[b] ($J\,g^{-1}$) | $T_{m,\text{PEKK}}$ (°C) | $\Delta H_{\text{PEKK}}$[b] ($J\,g^{-1}$) | $W_{c,\text{N-TPI}}$[c] |
|---|---|---|---|---|---|---|---|---|---|
| *PEKK(50T/50I)* | | | | | | | | | |
| 100 | 156 | 6 | single $T_g$ | | [d] | [d] | 331 | 40 | 0 |
| 70 | 173 | 10 | single $T_g$ | | 380 | 12.9 | 330 | [e] | 0.37 |
| 30 | 185 | 14 | 223 | 13 | 383 | 26.5 | none | none | 0.33 |
| 0 | 246 | 10 | single $T_g$ | | 383 | 36 | [d] | [d] | 0.31 |
| *PEKK(60T/40I)* | | | | | | | | | |
| 100 | 156 | 8 | single $T_g$ | | [d] | [d] | 315 | 40 | 0 |
| 85 | 167 | 7 | single $T_g$ | | 375 | 5[e] | [e] | 5[e] | 0.29 |
| 75 | 170 | 14 | single $T_g$ | | 378 | 10.2 | none | none | 0.35 |
| 75 | 171 | 14 | single $T_g$ | | 379 | 11 | none | none | 0.38 |
| 65 | 179 | 25 | single $T_g$ | | 375 | 13 | none | none | 0.32 |
| 50 | 190 | 40 | single $T_g$[f] | | 375 | 21 | none | none | 0.36 |
| 30 | 215 | 28 | single $T_g$[f] | | 384 | 27 | none | none | 0.33 |
| 15 | 231 | 18 | single $T_g$ | | 384 | 29 | none | none | 0.29 |
| 0 | 246 | 10 | single $T_g$ | | 383 | 36 | [d] | [d] | 0.31 |
| *PEKK(80T/20I)* | | | | | | | | | |
| 100 | 159 | 6 | single $T_g$ | | [d] | [d] | 357 | 50 | 0 |
| 70 | 175 | 10 | single $T_g$ | | 383 | 4 | 355 | 27 | 0.11 |
| 30 | 183 | 16 | 234 | 14 | 384 | 18 | 355 | 10 | 0.22 |
| 30 | 184 | 16 | 235 | 16 | 384 | 17 | 354 | 8 | 0.21 |
| 15 | 183 | 12 | 233 | 16 | 384 | 30.5 | none | none | 0.38 |
| 0 | 246 | 10 | single $T_g$ | | 383 | 36 | [d] | [d] | 0.31 |
| *PEKK(100T/0I)* | | | | | | | | | |
| 100 | 159[g] | 8[g] | single $T_g$ | | [d] | [d] | 393 | 52 | 0 |
| 70 | 171 | 12 | single $T_g$ | | 385[h] | 7[h] | 385[h] | 30[h] | 0.20 |
| 30 | 177 | 12 | 241 | 11 | 384[h] | 22[h] | 390[h] | 12[h] | 0.27 |
| 0 | 246 | 10 | single $T_g$ | | 383 | 36 | [d] | [d] | 0.31 |

[a] Determined from departure point from d.s.c. baseline
[b] Values of the enthalpy of fusion were calculated from melting endotherms during first d.s.c. runs on originally amorphous blends
[c] The values of the N-TPI fraction crystallinity ($W_{c,\text{N-TPI}}$) were normalized to the volume fraction of N-TPI present in the blends using $W_{c,\text{N-TPI}} = \Delta H_{\text{N-TPI}}/(116 \times \text{wt fraction N-TPI})$, where $116\,J\,g^{-1}$ is the heat fusion[25] for 100% crystalline N-TPI
[d] Not applicable for pure component
[e] These are qualitative estimates because crystallization and melting of PEKK overlaps with N-TPI crystallization
[f] Broad glass transitions were shown to be two glass transitions (see text)
[g] Data from amorphous PEKK(100T/0I) had to be estimated because of difficulties in quenching a purely amorphous sample
[h] Because PEKK(100T/0I) and N-TPI have about the same melting point, $\Delta H$ is estimated from the exotherms because these peaks are well separated

compatibility of the different PEKK isomers with N-TPI and LARC-IA. We have concentrated on amorphous blend properties so the crystallization rate differences between the PEKKs and PEK do not influence our conclusions on melt miscibility. The effect of crystallization was also systematically studied here, because of its importance in the resulting blend morphologies and material properties.

## EXPERIMENTAL

### *Materials*

The composition of the three polyimides, PEK and PEKK are shown in *Figure 1*. N-TPI is from Mitsui Toatsu—it is composed of 4,4′-bis(3-aminophenoxy)-biphenyl and pyromellitic dianhydride (PMDA), and has a weight-average molecular weight ($M_w$) of ~20 000 g mol$^{-1}$. LARC-IA is a non-crystalline polyimide made with oxydiphthalic dianhydride (ODPA) and 3,4′-oxydianiline (ODA), and has a $T_g$ of 231°C. LARC-ITPI is a non-crystalline polymer with a $T_g$ of 248°C and the structure given in *Figure 1*. It is immiscible at all concentrations with the PEKKs, so it will not be discussed further. Glass transitions, melting points and heats of fusion are given in *Tables 1* and *2* for the pure materials except LARC-ITPI.

PEK (Victrex® 220P) is from ICI. The PEKK series was made at Du Pont and consists of polymers with different terephthalic/isophthalic (T/I) ratios (*Figure 1*) including PEKK(50T/50I), (60T/40I), (80T/20I) and (100T/0I). All have glass transitions of ~160°C with $T_m$ = 320, 310, 355 and 390°C, respectively[16]. Both PEKK(60T/40I) and PEKK(80T/20I) are believed to be random copolymers in terms of the placement of 1,3 *versus* 1,4 ketone linkages[16]. PEKK(50T/50I) is an alternating copolymer and PEKK(100T/0I) is a homopolymer which contains all *para* (e.g. 1,4) ketone linkages. The $M_w$s are ~30 000 g mol$^{-1}$ for the PEKKs. The PEKKs have widely varying crystallization rates which increase substantially with the increase in melting temperatures[16]. The maximum bulk crystallization rates vary in the order PEKK(100T/0I) > PEK

**Table 2** Thermal properties obtained by d.s.c. for originally amorphous blends of different PEKKs with non-crystallizable LARC-IA

| %PEKK | $T_{g,1}$ (°C) | $\Delta T_{g,1}$ (°C) | $T_{g,2}$ (°C) | $\Delta T_{g,2}$ (°C) | $T_{m,PEKK}$ (°C) | $\Delta H_{PEKK}$[a b] (J $g^{-1}$) |
|---|---|---|---|---|---|---|
| *PEKK(60T/40I)* | | | | | | |
| 100 | 156 | 8 | | | 315 | 40 |
| 85 | 163 | 8 | single $T_g$ | | 313 | 2.1 |
| 70 | 174 | 12 | single $T_g$ | | none | none |
| 30 | 203 | 12 | single $T_g$ | | none | none |
| 15 | 220 | 9 | single $T_g$ | | none | none |
| 0 | 231 | 5 | | | | |
| *PEKK(80T/20I)* | | | | | | |
| 100 | 159 | 6 | | | 357 | 50 |
| 70 | 170 | 6 | 215 | 12 | 350 | 30 |
| 30 | 177 | 6 | 219 | 8 | 351 | 14 |
| 0 | 231 | 5 | | | | |
| *PEKK(100T/0I)* | | | | | | |
| 100 | 159 | 8 | | | 393 | 52 |
| 70 | 170 | 8 | 212 | 8 | 393 | 30 |
| 30 | 177 | 6 | 222 | 6 | 387 | 15 |
| 0 | 231 | 5 | | | | |

[a] First d.s.c. runs on originally amorphous films

[b] Values of the enthalpy of fusion ($\Delta H$) were calculated from melting endotherms

> PEKK(80T/20I) ≫ N-TPI > PEKK(50T/50I) > PEKK(60T/40I). It is interesting to note that PEKK(100T/0I) is somewhat faster than PEK, and that PEK, PEKK(100T/0I) and PEKK(80T/20I) are all orders of magnitude faster than N-TPI or PEKK(60T/40I).

### *Methods*

The blending procedure has been described previously[8]. Only small amounts of materials can be easily blended in this way, which is an advantage in cases of limited material availability. The blending method consists of pressing and shearing molten polymer films (~0.05 g total) on a hot plate between sheets of Kapton® and then quenching. The sample is then removed from the Kapton, folded, and the process repeated five to 10 times. The total exposure to the high temperatures in the melt for five blending cycles is typically only tens of seconds, which allows degradation to be minimized. Due to the small film areas ($A \approx 200\,\mathrm{mm}^2$), relatively high shear and elongational forces can be applied by hand. Equilibration of the blend phase morphology can be tested by obtaining a differential scanning calorimetry (d.s.c.) trace on a blend, and then reblending the same sample several more times before performing d.s.c. a final time. In this way one can check for further changes in $T_g$ (i.e. changes in phase compositions) as well as thermal degradation.

The blend films were quenched from $T > 390°C$ to ~20°C at about 300°C $s^{-1}$ by pressing against a cold brass block, in order to obtain completely amorphous films with a phase structure frozen-in and representative of that in the melt. The phase-separated films are clear, both in the phase contrast microscope and by the naked eye. This is presumably because the refractive indices are quite similar. Crystallization is very fast for 100% PEKK(100T/0I) so a purely amorphous film could not be obtained. The crystallization rate in the semi-compatible blends was decreased enough that it was possible to prepare essentially amorphous samples of these materials in most cases.

We use blending temperatures between 400 and 455°C for determination of the phase diagram of PEK and N-TPI in amorphous fast-quenched blends. The blending temperatures were 410 ± 5°C for N-TPI and the other PEKKs. For LARC-IA/PEKK and LARC-ITPI/PEKK mixtures we generally used 395–410°C. All polymers were dried at about $T_g$ under vacuum for 24 h before melt blending.

Colour change was minimal in all blends used in this study. Samples exhibiting a slight colour change generally showed identical thermal behaviour to those that retained their original transparent orangish colour from the polyimide. More useful than colour observations, was the monitoring of N-TPI's ability to recrystallize. Either in the blend or in the pure state, slight degradation of N-TPI causes a very dramatic decrease in its ability to recrystallize. This was checked routinely, especially for our samples blended at the highest temperatures of ~460°C. One can also check for chemical interaction between blend components which could be detected in terms of a suppression of N-TPI crystallization. We never saw any evidence of this.

A Du Pont 9900 thermal analysis station was used with a heating rate of 20°C $\mathrm{min}^{-1}$ unless otherwise indicated.

## RESULTS

### *Phase diagram for PEK/N-TPI*

In the previous work[8], we had the good fortune to discover a system where the components at ~400°C were clearly miscible at concentrations rich in either component, yet they are clearly incompatible at concentrations between ~20 to 60% N-TPI in PEK. Because of N-TPI crystallinity, phase diagrams cannot be easily explored below its melting temperature of ~385°C. Because both PEK and N-TPI have nominal degradation temperatures at around 410°C, it was believed that it would be difficult to study the system at the higher temperatures required to obtain at least a qualitative phase diagram. Fortunately, upon perfecting our skills in melt blending of the polymers, we found that we could actually attain blending temperatures of >460°C without significant degradation.

After fast quenching, miscibility was determined by observing whether the d.s.c. $T_g$ of the amorphous blend follows the Gordon–Taylor equation. $T_g$ is defined as the centre point or approximate inflection point of the heat capacity change, and the breadth of the glass transition ($\Delta T_g$) is determined in terms of the points of departure from the d.s.c. baseline[17].

$$T_g = (T_{g,1} + rT_{g,2}W_2/W_1)/(1 + rW_2/W_1) \qquad (1)$$

In equation (1), $T_g$ is in Kelvin, $r = \rho_1 \Delta\alpha_2/\rho_2\Delta\alpha_1$, $\rho$ is the density, $\Delta\alpha$ is the change in thermal expansion coefficient from the solid to liquid state, and $W$ is the weight fraction. It is generally necessary to use $r$ as an adjustable parameter[18]. We have used $r = 0.55$ for the solid curve in *Figure 2*. If the glass transition of the blend is narrow and close to the Gordon–Taylor curve, then the blend is miscible. $\Delta T_g$ in *Figure 2* is indicated by the vertical bars. If the glass transition as measured

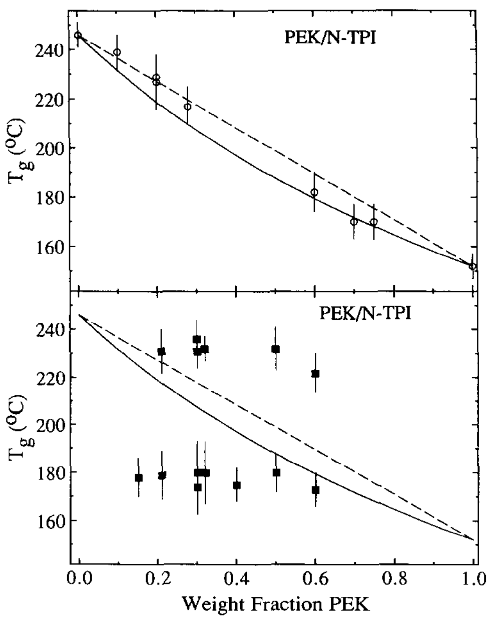

**Figure 2** Representative $T_g$ data *versus* PEK weight fraction for PEK/N-TPI blends. Miscible blends are indicated in the top and phase-separated blends are indicated in the bottom. The blending temperatures used for the miscible blends (top) were high enough to drive the system to single-phase behaviour, while the blending temperatures for the bottom of the figure were low enough that the system was in the two-phase region. This phase behaviour is more clearly indicated in *Figure 3*, which also shows the range of temperatures that was used (400 to 455°C). The vertical bars represent the breadth of the glass transitions as determined from the departure points from the d.s.c. baseline. The solid curves were calculated using the Gordon–Taylor equation and the linear average (dashed line) is shown for comparison

by d.s.c. is broad, this indicates some phase separation, whether or not the centre of the glass transition is close to the Gordon–Taylor curve. Broad glass transitions will be discussed further below in terms of d.s.c. enthalpy relaxation experiments[19]. Two separate glass transitions are also seen in many cases (bottom, *Figure 2*). Indirect evidence of the degree of compatibility is also routinely obtained from the crystallization kinetics measured by d.s.c. If the kinetics are changed, as is determined by the peak temperature of cold crystallization, then this is another signature of partial compatibility, but not necessarily complete miscibility. No discrepancies between the different methods were ever seen in blends deemed compatible by the glass transition studies.

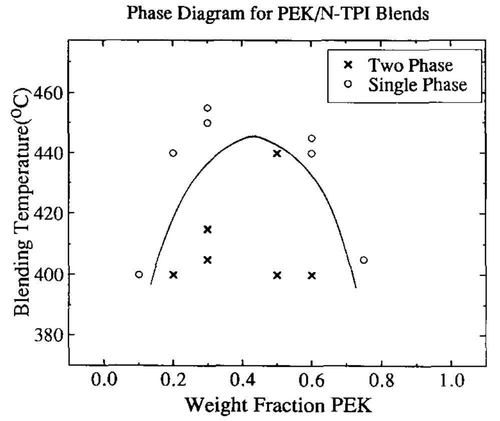

**Figure 3** Phase diagram determined for PEK/N-TPI blends by d.s.c. glass transition studies of fast-quenched amorphous blends. The upper critical temperature is ~440°C

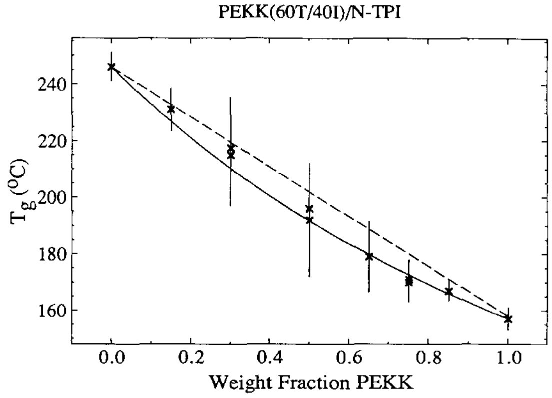

**Figure 4** D.s.c. glass transitions measured at 20°C min$^{-1}$ *versus* blend composition for PEKK(60T/40I)/N-TPI amorphous films blended at 405°C. The vertical bars represent the breadth of the glass transition as determined from the departure points from the d.s.c. baseline. The solid curves were calculated using the Gordon–Taylor equation and the linear average (dashed line) is shown for comparison

Representative $T_g$ data *versus* PEK weight fraction indicate both miscible and phase-separated blends at the same composition (*Figure 2*). The reason for this is that the data in *Figure 2* were obtained at different temperatures between 400 and 455°C, and temperature affects the degree of compatibility. The d.s.c. determined phase diagram is shown in *Figure 3*, where the $y$-axis is the actual blending temperature. It is seen that the phase diagram is slightly asymmetric, showing that the PEK-rich blends are slightly more 'miscible' than the N-TPI-rich blends. Although detailed phase diagrams were not obtained, this trend of the asymmetric phase properties has been seen indirectly once before[8], and is also seen or the rest of the blends studied here which are borderline compatible. The approximate critical point for this very high upper critical temperature is 440°C and occurs at a PEK fraction of about 0.4 (*Figure 3*).

### *Amorphous PEKK/N-TPI blends*

First d.s.c. runs of the rapidly quenched samples from the equilibrium melt were used to examine the phase morphology in the melt, i.e. single phase or biphasic. In the biphasic cases, the $T_g$s are used to estimate the phase compositions, as was discussed above. The glass transitions *versus* composition for PEKK(60T/40I)/N-TPI are shown in *Figure 4*[8]. The data in *Figure 4* and *Table 1* indicate that there is a single $T_g$ that approximately follows the Gordon–Taylor equation with $r = 0.65$. The glass transitions are sharp for $W_{\text{N-TPI}} \leq 35\%$ and relatively sharp for $W_{\text{N-TPI}} = 85\%$. At $W_{\text{N-TPI}} = 50$ and 70%, the glass transitions are broad indicating partial phase separation into N-TPI-rich and poor phases. To prove that these are not single broad $T_g$s but are actually two overlapping but separate $T_g$s, the method of inducing an enthalpy relaxation by selective annealing (physical ageing) below the lower glass transition for extended times was used[19,20]. A d.s.c. heating run on an amorphous 50/50 blend, cooled slowly to room temperature from 230°C, gives a smooth but

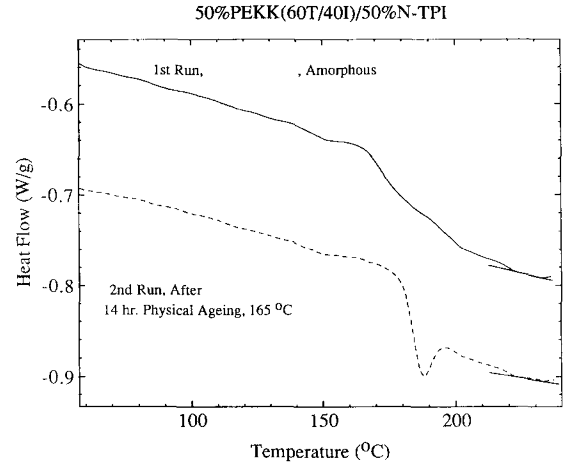

**Figure 5** D.s.c. heating scans taken at 20°C min$^{-1}$ for an amorphous 50% N-TPI/50% PEKK(60T/40I) film blended at 405°C. The first run corresponds to data taken after slow cooling (0.5°C min$^{-1}$) from 230 to 20°C. The second run corresponds to the run after 14 h of annealing at 165°C (see text). In both cases, there is evidence of two individual but overlapping glass transitions

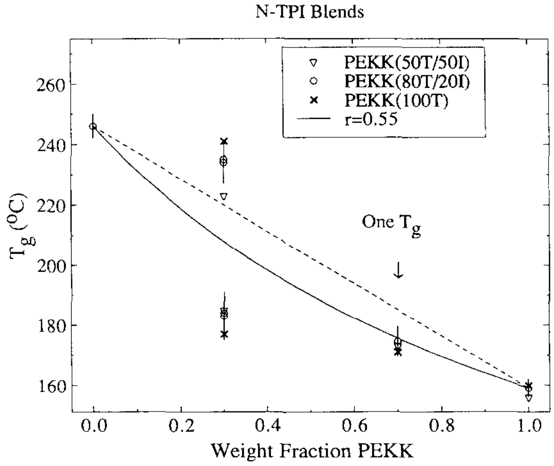

**Figure 6** Glass transitions from first d.s.c. run *versus* composition of originally amorphous films blended at 410°C. The different PEKKs blended with N-TPI are listed in the inset and $r$ is the Gordon–Taylor fitting parameter for the solid curve. The vertical bars are the values of $\Delta T_g$ for the PEKK(80T/20I) blends. See *Figure 2* caption for explanations

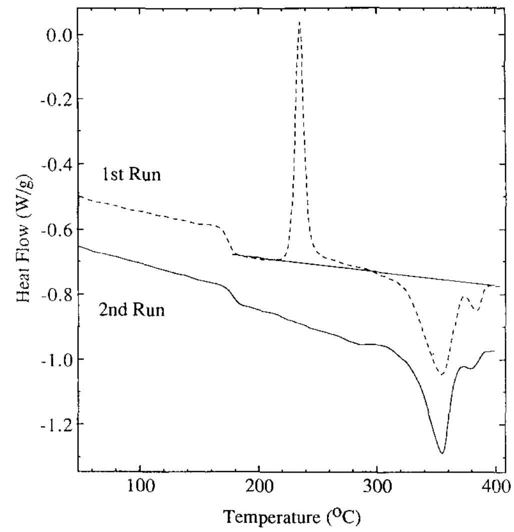

**Figure 7** First and second d.s.c. runs for the miscible 70% PEKK(80T/20I)/30% N-TPI films blended at 410°C. The first run d.s.c. data show a $T_g$ at 174°C, a $T_c = 235$°C for the PEKK crystallization, $T_{m,PEKK} = 354$°C and $T_{m,N\text{-}TPI} = 383$°C. The second run for the crystallized blend also shows a clear single $T_g$ and two melting endotherms

fairly broad glass transition (*Figure* 5)[8]. The result of physically ageing the 50/50 blend by annealing at 165°C for 14 h ($T_g = \sim 190$°C) gives rise to strong enthalpy relaxation seen as a sharp local minimum near the middle of the original broad glass transition. This proves that there are actually two overlapping transitions due to a two-phase morphology, and is also the case for some of the broad glass transitions seen in amorphous blends of PEK/N-TPI[8]. One phase is slightly rich in N-TPI and one is rich in PEKK(60T/40I). Similar d.s.c. results subsequent to physical ageing have been seen previously for a blend that was also shown independently by neutron scattering to be partially phase-separated[20]. Based on the data in *Figure 4*, where the glass transitions are broad but never separate into two clear $T_g$s, we expect that PEKK(60T/40I) is more 'compatible' with N-TPI than PEK. Also, we expect that the critical temperature would be slightly lower in the PEKK(60T/40I) blends because of this. This has not been fully investigated.

The data for the amorphous N-TPI blends with the other PEKKs are given in *Figure 6* and *Table 1*. For all three PEKKs, single narrow glass transitions are seen at 70% PEKK, indicating single-phase behaviour at this composition. The single $T_g$s at 70% PEKK agree with the Gordon–Taylor equation with $r = 0.55$ (solid curve, *Figure 6*). Although the two separate $T_g$s seen at 70% N-TPI are quite sharp, they are significantly different from the pure phase $T_g$s, indicating partial compatibility for all three PEKKs at this blend composition (*Figure 6* and *Table 1*). The reproducibility is good as is indicated by the results for two independently mixed blends at 30% PEKK(80T/20I), and the double glass transitions indicate strong phase separation. The bars in *Figure 6* represent the breadth of the glass transitions as they are determined from the departure from the d.s.c. baseline[17] for the PEKK(80T/20I) blends.

An example of the raw data is shown in *Figure 7*, where the first and second d.s.c. runs are given for the miscible 70% PEKK(80T/20I)/30% N-TPI blend. The first run d.s.c. data show a $T_g$ at 174°C, a crystallization temperature ($T_c$) = 235°C for the PEKK crystallization, $T_{m,PEKK} = 354$°C and $T_{m,N\text{-}TPI} = 383$°C. The crystallization temperature for the N-TPI cannot be clearly seen because of the high dilution, but presumably occurs in the region around 260°C where a slight exothermic departure from baseline can be seen in the first d.s.c. run (*Figure 7*). No exotherms are seen in the second d.s.c. run, as would be expected for a pre-crystallized blend.

D.s.c. data for a typical amorphous phase-separated blend, along with data for the pure polymers, are shown in *Figure 8* for 30% PEKK(80T/20I)/70% N-TPI. This detection of two clear $T_g$s, two exotherms and two endotherms is typical of this class of blends with the more rapidly crystallizing PEKKs or PEK. N-TPI/PEK has been shown to exhibit similar features[8]. Interesting

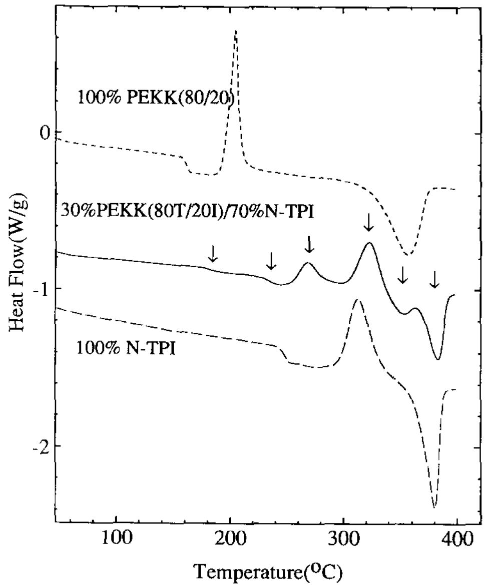

**Figure 8** D.s.c. data for the two pure polymers and for a typical amorphous phase-separated blend [30% PEKK(80T/20I)/70% N-TPI] made at 410°C. The arrows from left to right indicate, respectively, the $T_g$ of the PEKK-rich phase, the N-TPI phase $T_g$, the PEKK crystallization exotherm, the N-TPI exotherm, the PEKK endotherm and the N-TPI endotherm (see text)

semicrystalline morphological features can be obtained when one component clearly crystallizes before the other.

The compositions of each phase can be estimated from the degree of variation of $T_g$ from the pure phase values. The most phase mixing for the 70% N-TPI blends in *Figure 6* was seen for PEKK(50T/50I), as indicated by the depression of the $T_g$ of the N-TPI phase from 246 to 223°C. PEKK(60T/40I) (*Figure 4*) was even slightly more compatible than PEKK(50T/50I), but this may be in part related to the fact that PEKK(50T/50I) is essentially a homopolymer while PEKK(60T/40I) is a random copolymer. The $T_g$ of the PEKK(50T/50I) phase is also increased by ~28°C for this 70% N-TPI blend, showing substantial dilution of this phase by N-TPI, as would be expected based on the phase diagram for a related system, PEK/N-TPI (*Figure 3*).

*Amorphous blends of PEKKs and PEK with LARC-IA*

Pure LARC-IA is essentially non-crystalline and shows no sign of a crystallization endotherm or exotherm by d.s.c. It has a sharp glass transition at 231°C but does not exhibit significant flow until about 330°C. The samples were melt blended at ~395–410°C. The same PEKKs and PEK were studied as with N-TPI, except that PEKK(50T/50I) was not included because of its similarity to PEKK(60T/40I). There is a remarkable but ill-understood difference where it is observed that PEKK(60T/40I) is miscible (single $T_g$) over the entire composition range, while the other two PEKK isomers are phase-separated with two $T_g$s over the entire range (*Figure 9*, *Table 2*). This latter feature can be contrasted with the case of N-TPI with the different PEKKs, where there was complete miscibility for the 70% PEKK blends for all the PEKKs (*Figure 6*). There is slight phase mixing at all compositions for PEKK(80T/20I) and PEKK(100T/0I) as indicated by the shift in the two $T_g$s from their pure component values in *Figure 9* and *Table 2*. The same is true for the PEK blends with LARC-IA as is shown in *Figure 10*. In fact, PEK, PEKK(80T/20I) and PEKK(100T/0I) show very similar behaviour in their blends with both N-TPI and LARC-IA. This should be contrasted with PEEK/N-TPI blends which are completely immiscible and no shift in $T_g$ is seen[8]. The vertical bars on the PEKK(80T/20I) data points in *Figure 9* indicate that the glass transitions are sharp at all compositions studied.

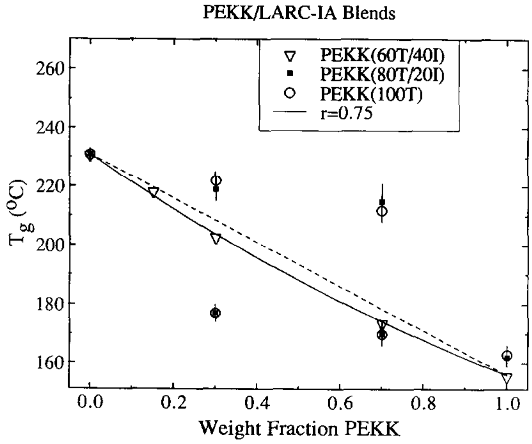

**Figure 9** Glass transitions from amorphous films blended at 400°C *versus* composition. The different PEKKs blended with LARC-IA are listed in the inset. The vertical bars are the values of $\Delta T_g$ for the PEKK(80T/20I) blends. See *Figure 2* caption for explanations

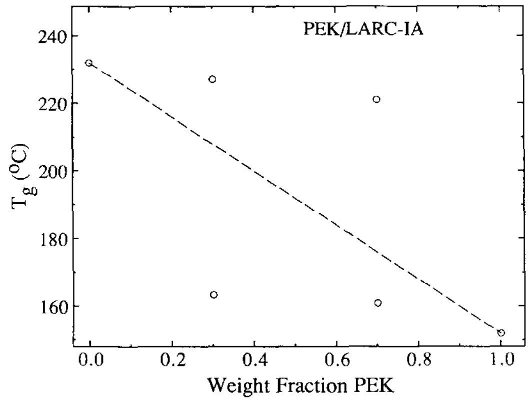

**Figure 10** Glass transitions of amorphous films of PEK/LARC-IA *versus* PEK weight fraction. The samples were blended at 400°C. The double glass transitions indicate that they are phase-separated at the weight fractions indicated. All glass transitions were narrow. See *Figure 2* caption for explanations

*Semicrystalline PEKK/N-TPI blends*

As was discussed earlier[8], in originally amorphous miscible blends with only 25% N-TPI, the slow crystallizing PEKK(60T/40I) exhibits little crystallization during cooling at $3°C\,min^{-1}$ from 400°C, as determined by a second d.s.c. heating. This is mainly because the increase in $T_g$ of the amorphous phase dilutes and, more importantly, restricts mobility of the PEKK. The same trend occurs with the slow crystallizing PEKK(50T/50I) (data not shown), where a small amount of N-TPI severely prohibits PEKK crystallization. On the other hand, PEKK(80T/20I) and PEKK(100T/0I) are fast crystallizing materials compared with PEKK(60T/40I)

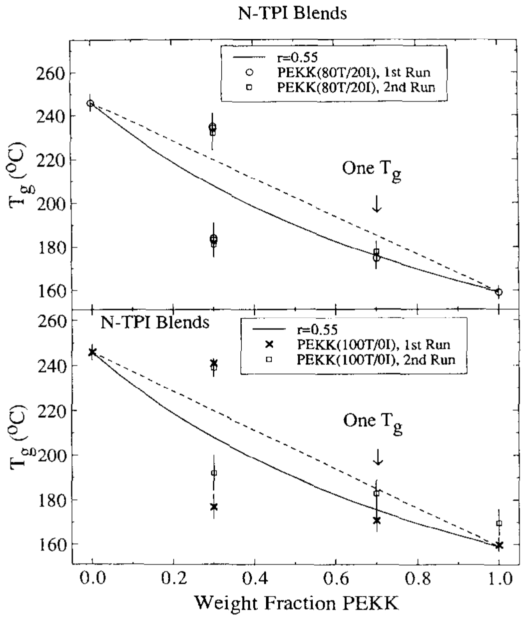

**Figure 11** Glass transitions for amorphous (first run) and semicrystalline (second run) N-TPI/PEKK blends. Data are shown for blends of PEKK(80T/20I) (top) and PEKK(100T/0I) (bottom) blended at 410°C. See *Figure 2* caption for explanations

or N-TPI. The high melting points of 355 and 390°C for PEKK(80T/20I) and PEKK(100T/0I), respectively, could also be of some use in extending the high temperature properties of the blends. The data are summarized in *Table 1*, showing significant crystallization of the various PEKKs in most cases. In addition, in most cases except at very low N-TPI concentrations, the N-TPI crystallinity fraction ($W_{c,\text{N-TPI}}$) normalized by the weight fraction of N-TPI in the blend remains at high levels about the same as the N-TPI homopolymer (i.e. $W_{c,\text{N-TPI}} = 0.31$) (*Table 1*).

*Figure 11* shows that there are small increases of ~4°C in $T_g$ for the d.s.c. second runs, which were performed on blends crystallized during slow cooling at ~3°C min$^{-1}$ from 410°C. The data corresponding to first d.s.c. runs in *Figure 11* were taken on amorphous blends. The N-TPI phases are already quite pure from the 30% PEKK blends, so no significant change in $T_g$ is seen due to depletion of PEKK from that amorphous phase. This is the opposite of the case of completely miscible PEEK/Ultem blends, where PEEK is strongly depleted from the amorphous phase as it crystallizes, leading to broadening and substantial increases in $T_g$ (ref. 11). For the PEKK(100T/0I) blends in *Figure 11* (bottom), crystallization leads to an increase in the PEKK phase $T_g$ in both blends and pure PEKK(100T/0I). The glass transitions also broaden slightly. Both the increase in $T_g$ and the broadening are due to the constraining effect of crystallites on the amorphous motions, similar to the case of pure semicrystalline materials[17]. The depletion of PEKK(100T/0I) from the amorphous phase also contributes to a slight elevation and broadening of the glass transition due to an increase in the concentration of the high $T_g$ polyimide in the amorphous polyimide-rich phase.

One other indication that there is partial compatibility is the slowing down of the PEKK crystallization. In some cases separate exotherms for PEKK-rich phases and N-TPI-rich phases can be easily resolved in the first d.s.c. run (e.g. *Figure 8*), and slowing down or acceleration (i.e. N-TPI crystallization is sometimes accelerated due to plasticization by PEKK) of crystallization can be estimated by examining the cold crystallization peak position.

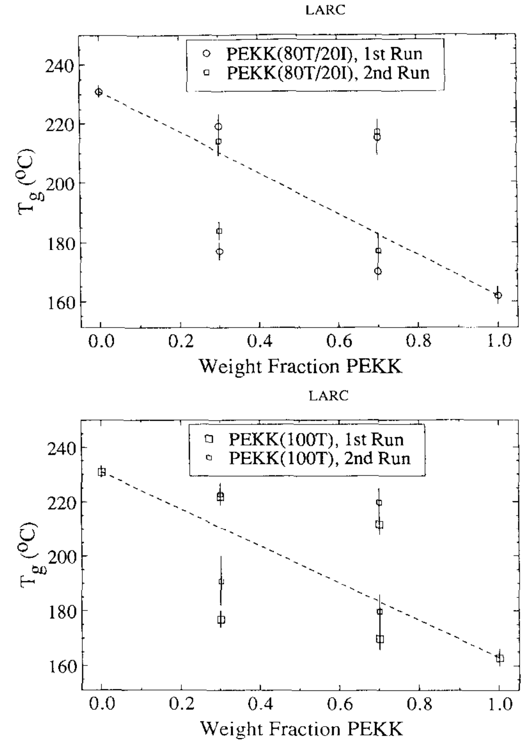

**Figure 12** D.s.c. glass transitions *versus* composition for amorphous (first run) and semicrystalline (second run) LARC-IA/PEKK blends. (Top) LARC-IA blends with PEKK(80T/20I) and (bottom) PEKK(100T/0I) blended at ~400°C. See *Figure 2* caption for explanations

### *Semi-crystalline PEKK/LARC-IA blends*

The major difference between N-TPI and LARC-IA is that LARC-IA is non-crystallizable (in the unoriented state). No crystallization is observed in PEKK(60T/40I) blends at concentrations ≤70% PEKK(60T/40I) (*Table 2*). The integrated melting peaks ($\Delta H$) are given in *Table 2*. For PEKK(80T/20I) and PEKK(100T/0I), the crystallization kinetics are slowed down consistent with the determination of partial phase mixing in the blends as was determined by the glass transition studies above. The extent of PEKK crystallization is still high as can be seen from the relatively high values of $\Delta H_{\text{PEKK}}$ at all blend compositions for PEKK(80T/20I) and PEKK(100T/0I) in *Table 2*.

The glass transitions for the lower $T_g$ PEKK-rich phases increase with crystallinity and in some cases broaden slightly, as can be seen in the second d.s.c. runs on crystallized blends (*Figure 12*). This is due to the same reasons discussed above for N-TPI blends, i.e. the amorphous phase is depleted of the low $T_g$ component as it crystallizes. The upper $T_g$ for the 70% PEKK(100T/0I)/30% LARC-IA 70/30 blend (*Figure 12*, bottom) also increases slightly due to crystallization of the PEKK, i.e. the PEKK(100T/0I) can crystallize out of both the PEKK-rich and PEKK-poor phases!

## DISCUSSION

Specific interactions such as hydrogen bonding, charge transfer, acid–base interactions and ion–dipole interactions are possible enthalpic driving forces for miscibility[21]. Preliminary ultraviolet–visible (u.v.–vis.) spectra taken on the blends showed no evidence of charge transfer complexation in miscible N-TPI/PEKK blends although this is known to occur in other polyimide systems[22,23]. Hydrogen-bond interactions have been detected between polybenzimidazole (PBI) imidazol amine units and the polyimide (Ultem) phthalimide carbonyl units in solidified solvent-cast blends[2,24]. No such interaction exists between PEKK and the polyimides studied here. Also, we are interested in interactions in the melt at the extremely high temperatures used for our blending, where these specific interactions would presumably become significantly weaker. Normally a lower critical temperature is seen for polymers which hydrogen bond, but our system(s) exhibit an upper critical temperature (*Figure 3*) which is typical for many polymer/polymer pairs that lack strong specific interactions like hydrogen bonding[21]. Dispersion forces are non-specific enthalpic interactions present in all materials. Hydrogen bonding and other dipole–dipole interactions will depend on chain structure, and spacing and orientation of the interacting dipoles. There are some similarities between the chain structures of the polyimides and PEKKs, and since the molecular weights are not high, it is possible that dipole–dipole or related interactions are enough to promote miscibility. We now turn to the discussion of the effect of subtle structural changes of PEK, PEEK and the PEKKs on miscibility within the polyimides.

The previous study[8] showed the surprising result that the higher ether content polymer, poly(ether ether ketone) (PEEK), was completely incompatible with N-TPI while PEK and PEKK(60T/40I) were completely miscible at some concentrations and partially compatible at others. Examining the structures of the polyimides, it is possible that the higher content of the more 'flexible' ether linkages in PEEK, and/or the ~120° ether bond angles, change its ability to interact with the very rigid polyimides. The degree of 'compatibility' can be ranked roughly as PEKK $>$ PEK $\gg$ PEEK, i.e. the highest ketone-containing polymers seem to be the most compatible. Among the different PEKK isomers, PEKK(60T/40I) is the most 'compatible'. This is especially clear from the data in *Figure 9*, where PEKK(60T/40I) is completely miscible with LARC-IA over the entire concentration range while PEKK(80T/20I) and PEKK(100T/0I) show substantial phase separation at both compositions tested. PEKK(60T/40I) is also the most 'compatible' with N-TPI, although the difference is not as dramatic as in the blends with LARC-IA. It is possible that the higher fraction of 1,3 ketone linkages in PEKK(60T/40I), compared with PEKK(80T/20I) and PEKK(100T/0I), could contribute to a more disordered chain structure allowing interactions with the rigid but 'disordered' polyimides which also contain a substantial fraction of 1,3 linkages (*Figure 1*). The difference between PEKK(60T/40I) and PEKK(50T/50I) may be due to the latter being a homopolymer, i.e. one with a more regular structure (see Experimental and ref. 16).

In the ~5–20% PEKK range, PEKK acts as a high-molecular-weight 'plasticizer' for the very viscous polyimides, and one can obtain at least an order of magnitude decrease in the melt viscosity of the pure polyimide. We have shown that complete or at least substantial compatibility exists in this concentration regime at ~410°C, and improved processability should be achieved.

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