Hydrogen bonding in polybenzimidazole/polyimide systems: a Fourier-transform infra-red investigation using low-molecular-weight monofunctional probes

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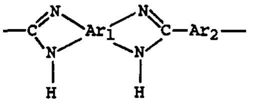
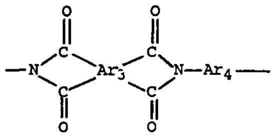
To elucidate the nature of the specific interactions occurring in polybenzimidazole/polyimide (PBI/PI) miscible blends, a Fourier-transform infra-red investigation on these polymers in the presence of low-molecular-weight monofunctional compounds was undertaken. In the case of PBI the probe compounds were proton-accepting molecules (aliphatic ketones) able to form hydrogen-bonding interactions with the polymeric substrate. In the case of the two investigated polyimides, poly([2,2'-bis(3,4-dicarboxyphenoxy)phenylpropane]-2-phenylenebisimide) (Ultem 1000) and the condensation product of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 5(6)-amino-1-(4'-aminophenyl)-1,3,3'-trimethylindane (XU 218), the carbonyl functional group in the probes was replaced by a hydroxyl group. This approach allowed us to conclude that in PBI/PI blend systems a hydrogen-bonding interaction occurs between the polymeric components.

(Keywords: hydrogen bonding; polybenzimidazole/polyimide blends; Fourier transform infra-red)

INTRODUCTION

Recently a novel class of miscible polymer blends based on aromatic polybenzimidazoles (PBI) and aromatic polyimides (PI) has been discovered[1]. The generic structures of the two components can be represented as:

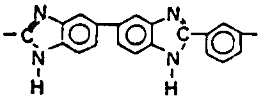

Aromatic Polybenzimidazole


Aromatic Polyimide

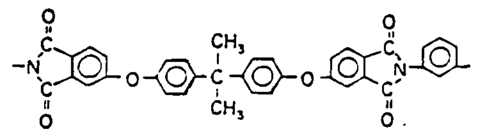
where Ar$_i$ represents any one of a number of aromatic moieties. In particular, blends of the materials listed in *Table 1* (PBI/Ultem 1000 and PBI/XU 218) have been extensively investigated[1,2] (see *Table 1* for full names of chemicals). Both PBI/Ultem 1000 and PBI/XU 218 blends were found to be miscible over the entire composition range. Miscibility was evidenced by the presence of single T_g values and well defined single tan δ relaxations intermediate between those of the components, and by the formation of clear films[1]. In a wide variety of blend systems the occurrence of specific interactions between the components is considered the major driving force towards miscibility. To detect the existence of such interactions, an initial investigation on the PBI/XU 218 and on the PBI/Ultem 1000 blends was undertaken using Fourier-transform infra-red spectroscopy (*FT*i.r.). This technique has met with considerable success in characterizing miscible polymer systems. Composition-dependent frequency shifts as well as band-shape variations have been observed and interpreted on the basis of specific intermolecular interactions occurring between the components[3–7]. In the case of the PBI/PI

Table 1 Chemical structures and codes for compounds used

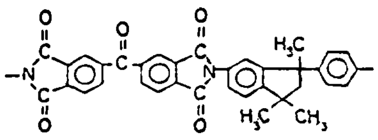
Poly(2,2'(*m*-phenylene)-5,5'-bibenzimidazole)
(PBI; Celanese Corporation; $T_g = 420°C$)



Poly([2,2'-bis(3,4-dicarboxyphenoxy)phenylpropane]-2-phenylenebisimide)
(Ultem 1000; General Electric Company; $T_g = 220°C$)



Condensation product of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 5(6)-amino-1-(4'-aminophenyl)-1,3,3'-trimethylindane
(XU 218; Ciba-Geigy Corporation; $T_g = 320°C$)



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systems a frequency shift of up to 55 cm^{-1} in the N–H stretching region in PBI and up to 6 cm^{-1} in the carbonyl stretching absorptions in the PIs were observed; these shifts were eliminated by thermally induced phase separation. The experimental results indeed suggested that miscibility in these blends derives from specific intermolecular interactions, but the nature of these interactions was not definitively identified. Three possibilities were mentioned:

(a) hydrogen-bonding interaction between the >N–H groups of PBI and the carbonyl groups of PI;

(b) π-orbital interactions between the imide and imidazole rings; and

(c) a charge-transfer interaction between the phthalimide and the benzimidazole fused-ring systems.

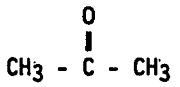
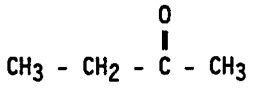
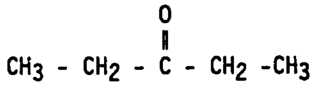
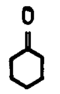
The aim of the present investigation is thus to establish the nature of the interaction in the PBI/PI system. The previous study showed that the shifts in the blend spectra occurred in the stretching regions of two functional groups, >N–H and C=O, which could act as proton donor and proton acceptor, respectively[8,9]. Therefore the presence of hydrogen-bonding interactions was investigated first. A method was needed to evaluate the proton-donating capability of PBI as well as the ability of the PIs to act as proton acceptors. The use of low-molecular-weight monofunctional molecules as probes to measure the hydrogen-bonding potential of compounds is well documented in the literature: it was first used by Gordy[10] and later re-examined by Crowley *et al.*[11] and by Nelson *et al.*[12]. More recently Cangelosi and Shaw[13] have studied the interaction of hydrogen-bonding probes in a wide variety of 'acid' and 'base' polymer matrices and have ranked the various polymers according to their hydrogen-bonding ability. This approach seems promising for the systems under investigation and so an *FT*i.r. study of PBI and PIs in the presence of a series of probe compounds was undertaken. The purpose of the study is twofold:

(i) to test if PBI and the PIs are actually able to form hydrogen bonds and to derive a comparative measure of their hydrogen-bonding potential; and

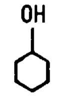
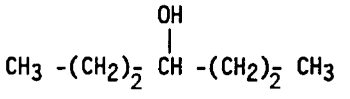
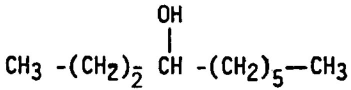
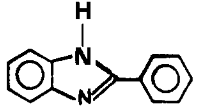
(ii) to study the spectral features associated with hydrogen-bond formation and eventually comparing these features with those observed in the spectra of the PBI/PI blends.

Table 2 Probes used with PBI and PI

(a) With PBI

Formula	Name	B.p. (°C)
 $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$	Acetone	56
 $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$	Methyl ethyl ketone	80
 $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$	Diethyl ketone	102
	Cyclohexanone	155

(b) With PIs

Formula	Name	B.p. (°C)
	Cyclohexanol	160
 $CH_3-(CH_2)_2\overset{OH}{\overset{\|}{CH}}-(CH_2)_2CH_3$	4-Heptanol	158
 $CH_3-(CH_2)_2\overset{OH}{\overset{\|}{CH}}-(CH_2)_5-CH_3$	4-Decanol	210
	2-Phenylbenzimidazole	–

EXPERIMENTAL

Materials

The PBI was kindly supplied by Celanese Corp. in the form of a finely ground powder. The Ultem 1000 (General Electric Co.) had reported molecular weights of $\bar{M}_w = 30\,000 \pm 10\,000$ and $\bar{M}_n = 12\,000 \pm 4000$. The XU 218 (Ciba-Geigy Corp.) had an inherent viscosity of 0.65 dl g^{-1} (0.5% solution in *N*-methylpyrrolidone at 25°C). All the polymers were used as received. The 'base' (electron-donating) and the 'acid' (electron-accepting) probes used in the present study are listed in *Table 2*. All the compounds used except 4-heptanol (Lancaster Synthesis Ltd) were Aldrich 'Spectranalized' grade and were purified and dried as required before use.

Sample preparation

The procedure for incorporating the probes into the polymer matrices was selected in accord with the affinity of the probes for the different polymers. For example, PBI was found to be readily swollen by acetone and methyl ethyl ketone at room temperature, so that a thin PBI film, prepared and dried according to the method described in a previous paper[2], was immersed in the respective liquids and removed periodically for *FT*i.r. spectra. In the case of diethyl ketone and cyclohexanone, because of the extremely low absorption rate at room temperature, the swelling was carried out at 90 and 140°C, respectively.

This procedure was not suitable for incorporating the probe compounds into either of the polyimides. In fact, even after very long periods (168 h) no trace of the absorbed 'acid' probes was detected by *FT*i.r. in the polymer matrices. An alternative method was therefore used in which the polymer and the probe were first dissolved in methylene chloride. Thin films (2–5 μm) were then cast onto glass plates and carefully removed after most of the solvent had evaporated. To remove the last traces of methylene chloride, the films were dried at 100°C for 12 h. Thermogravimetric (t.g.a.) measurements were performed to check the absence of residual CH_2Cl_2 and to determine the amount of probe incorporated into the polymer films.

Techniques

I.r. spectra were obtained at 2 cm^{-1} resolution with a Brüker–IBM IR 30 *FT*i.r. spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector. The scanned wavenumber range was 4800–400 cm^{-1} and 4593 data points were collected for each spectrum. The frequency scale was internally calibrated with a reference helium–neon laser to an accuracy of 0.2 cm^{-1}. Typically 200 spectra were signal-averaged in the conventional manner to reduce spectral noise. All the films used in this study were sufficiently thin to be within an absorbance range where the Beer–Lambert law is obeyed. All the spectra were taken in absorbance.

The t.g.a. measurements were performed on a Perkin–Elmer TGS2 thermobalance under nitrogen using a heating rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

PBI behaviour

Few details have been reported to date regarding the vibrational spectroscopy of PBI[14,15]; to interpret the results in the following section, a preliminary examination of the PBI infra-red spectrum was undertaken.

PBI (see *Table 1*) is completely amorphous, with a reported T_g of 420°C. The i.r. spectrum of PBI in the region 4800–400 cm^{-1} is shown in *Figure 1*. Below 2000 cm^{-1} the spectrum is characterized by relatively narrow peaks attributed to localized normal vibrations of the phenyl groups. A broader band attributed to highly coupled conformationally sensitive modes is detected at 1336 cm^{-1} (ref. 14). For the present investigation the occurrence of a 'window' in the 2000–1700 cm^{-1} region is of particular interest; this allowed the detection and analysis of the carbonyl stretching band of a probe compound without interference. The most relevant region for the present study is above 2000 cm^{-1}. The PBI spectrum recorded at room temperature shows in this region a relatively sharp peak at 3415 cm^{-1} superimposed on a very broad absorption approximately centred at 3145 cm^{-1}; a third, low-intensity, peak is detected at 3063 cm^{-1}.

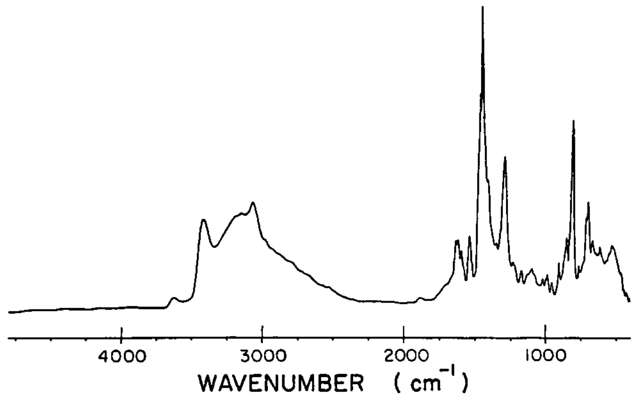


Figure 1 *FT*i.r. spectrum of PBI

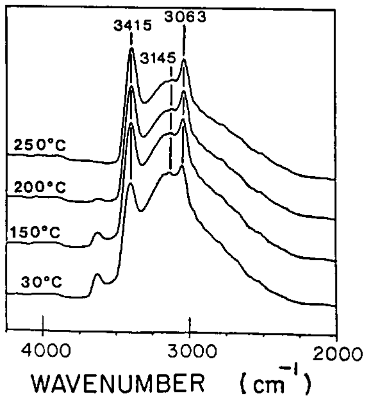
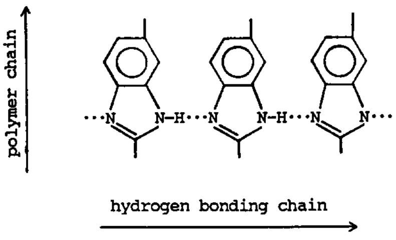


Figure 2 *FT*i.r. spectra of PBI from 4000 to 2100 cm^{-1} recorded at 30, 150, 200 and 250°C

In this spectral region the N–H stretching absorptions are expected to occur and it is reasonable to assume that the complex shape of this band changes as a function of temperature. In *Figure 2* the PBI spectra in the 4000–2100 cm^{-1} region recorded at different temperatures are shown. It is observed that, as the temperature increases, the sharp absorbance at 3415 cm^{-1} increases in intensity at the expense of the broad absorption at 3145 cm^{-1}. The band system shows an isosbestic point at approximately 3350 cm^{-1}. This behaviour is reversible; in fact, when the film is cooled to room temperature, the absorption band gradually recovers its original shape. Typically, after 168 h at 25°C in an inert atmosphere, a spectrum coincident with the initial one is obtained. These spectral features are indicative of the occurrence of an equilibrium between free and self-associated N–H groups. The peak at 3415 cm^{-1} can be attributed to the free N–H groups while the characteristically broad band at 3145 cm^{-1} is attributed to the self-associated ones. Upon heating the sample, a significant number of intermolecular hydrogen bonds are broken, causing an increase in the intensity of the unassociated N–H stretching band at the expense of the absorption due to the self-associated species.

The intermolecular hydrogen-bonding interaction occurring in PBI can be schematically depicted as follows:



It is likely that both the completely unassociated N–H groups and the terminal groups of the hydrogen-bonded chains contribute to the absorption at 3415 cm^{-1}. The breadth of the band due to self-associated groups is related, among other effects, to the presence of hydrogen-bonded chains of different lengths, each one absorbing at a slightly different frequency[8].

The peak at 3063 cm^{-1} seems to be only marginally affected by temperature and can be reasonably attributed to the aromatic C–H stretching modes.

The above interpretation of the PBI spectral features is consistent with the fact that both imidazole and benzimidazole (low-molecular-weight analogues of PBI) are known to form strong intermolecular interactions through hydrogen bonding[16–18]. In particular, the imidazole vibrational behaviour in CCl_4 solution has been widely investigated: spectral features similar to those previously discussed have been observed in the N–

H stretching region, and have been interpreted in the same way.

To determine the hydrogen-bonding potential of PBI, low-molecular-weight probes carrying a single proton-acceptor group were selected; a carbonyl functionality was preferred because the latter gives rise to a sharp, well defined peak in a spectral region where PBI does not absorb. The probe compounds were chosen with the simplest possible molecular structures to minimize the possibility of other interactions and to simplify the spectral interpretation. On this basis it follows that the best-suited compounds for the present purposes are the linear and cyclic aliphatic ketones. Thus in *Figure 3* the spectra of PBI films containing acetone recorded at various swelling times are shown: the absorption centred at 1704 cm^{-1} (acetone $\nu_{C=O}$) is observed to increase gradually with time. The other two main bands of the probe compound, centred at 1332 and 1228 cm^{-1} respectively, also increase in the same fashion. The normalized absorbance of the 1704 cm^{-1} peak allows the quantitative determination of the absorbed acetone: the results of such measurements are reported in *Figure 4*. The kinetic curve presents an initial linear trend followed by a plateau; the acetone absorption can be considered complete after 70 h and the maximum amount of probe absorbed in these experimental conditions was found to be 15.2 wt%.

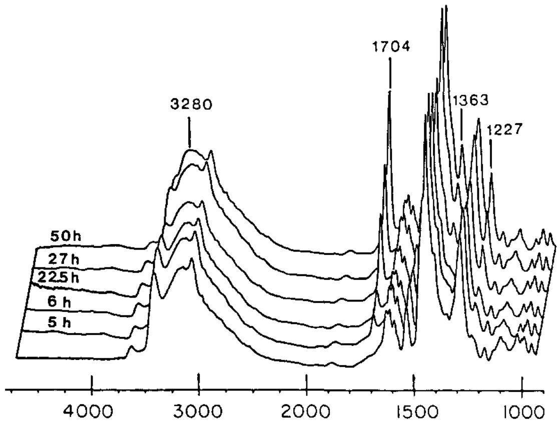


Figure 3 Spectra of PBI swollen in liquid acetone at room temperature for various swelling times

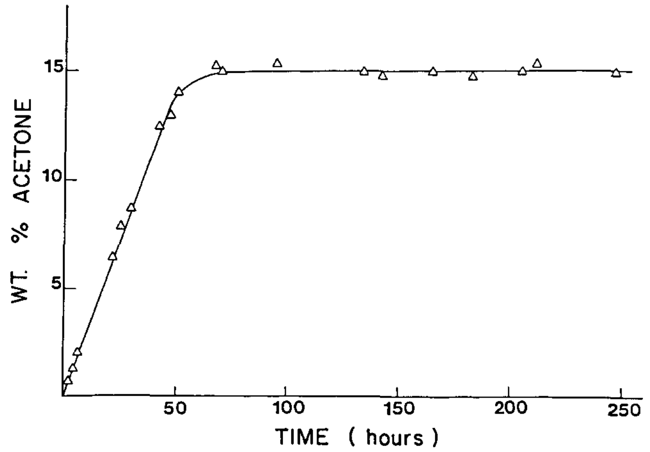


Figure 4 Weight per cent of acetone absorbed in PBI at room temperature as a function of the swelling time

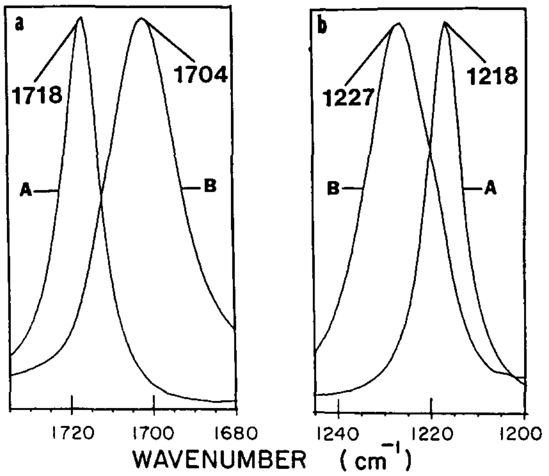


Figure 5 *FT*i.r. spectra of acetone in PBI (traces B) and of a 0.05 M solution of acetone in CCl_4 (traces A) in two different absorption regions

From *Figure 3* it is apparent that a substantial modification of the complex N–H absorption lying in the 3500–2200 cm^{-1} region is brought about by the incorporation of acetone into the PBI matrix. In this case also the observed modification is gradual, following the kinetics of the swelling process. We first discuss below the spectral details associated with the probe compound and then focus on the N–H stretching band system.

It is well established that the formation of hydrogen bonds has a marked effect on the frequency as well as on the band shape of the absorption of the proton acceptor. In particular, in the case of a carbonyl acceptor, hydrogen bonding reduces the force constant of the C=O bond, thereby producing a decrease in the stretching frequency. This interaction also causes the C=O band to broaden considerably, though no major intensity effects are observed. On the other hand, hydrogen bonds act as constraints to both in-plane and out-of-plane deformation vibrations, thus producing a frequency shift to higher wavenumbers for these modes[8,19].

In *Figure 5a* the $\nu_{C=O}$ stretching absorption of acetone in PBI (trace B) and the same band recorded in a 0.05 M solution of acetone in CCl_4 (trace A) are compared. Because of the non-polar nature of CCl_4 the acetone carbonyl can be considered unperturbed in the latter environment and the absorption recorded can be taken as a reference state[13,19]. It is observed that the band in PBI shifts towards lower wavenumbers by 14 cm^{-1} with respect to the reference state; the band shape still remains highly symmetrical but a considerable broadening occurs (the width at half-height increases from 11 cm^{-1} to 20 cm^{-1}). The 1218 cm^{-1} absorption region of acetone in CCl_4 and the same peak recorded in PBI are shown in *Figure 5b*. In this case a spectral subtraction was performed to remove the contribution of CCl_4 and PBI respectively; in both the cases a 'clean' result was obtained in the region of interest. It is observed that the peak recorded in PBI shifts towards higher wavenumbers by 9 cm^{-1} and that a considerable band broadening occurs. The acetone peak at 1218 cm^{-1} has been attributed to a mixed mode to which both a C–C asymmetric stretching vibration and a C=O in-plane deformation contribute. The strong contribution of this latter mode was confirmed by the observation that this band shifts and broadens on the high-frequency side by addition of small amounts of methanol to acetone CCl_4 solutions[20].

Essentially the same effect is observed in the present case. Both the above effects clearly indicate the formation of a hydrogen-bonding interaction between the acetone carbonyls and a proton-donor group in the PBI matrix. In particular, the symmetrical $\nu_{C=O}$ band shape and the fact that the band position does not change on increasing the probe concentration seem to indicate that most of the acetone molecules interact with the PBI proton-donor groups, possibly through the formation of a 1:1 adduct[21–23]. The proton-donating groups of PBI can be readily identified as the N–H groups of the benzimidazole ring. This accounts for the strong perturbation observed in the 3500–2200 cm^{-1} spectral region. The effects of hydrogen bonding on the fundamental stretching vibrations of the donor groups have been thoroughly investigated; the weakening of the force constant of the donor–H group causes the related stretching frequencies to shift to lower wavenumbers. Since donor–H is a single bond, the effect is much more pronounced than that observed for an acceptor group such as C=O. The shifted absorptions are much broader than the corresponding ones of the unassociated groups; an increase in the integrated intensities of these bands is also generally observed[19]. In the present system it is observed that, by increasing the amount of absorbed acetone, the free N–H stretching peak at 3415 cm^{-1} decreases in intensity. Concurrently a broadening and a shift towards higher wavenumbers of the complex absorption at 3144 cm^{-1} (self-associated N–H groups) occurs. For the highest values of absorbed acetone, the band system is no longer resolved into two different contributions but exhibits a broad spectral shape with a maximum approximately centred at 3280 cm^{-1} and a shoulder at 3415 cm^{-1}. These features are due to the increase in strength of a new band at ~3280 cm^{-1} associated with the stretching modes of the N–H groups hydrogen-bonded to the acetone carbonyls. The complex overall shape of the absorption at high acetone contents is related to a simultaneous equilibrium involving free and self-associated N–H groups as well as N–H groups hydrogen-bonded to carbonyls. It is worth noting at this point that the [N–H]/[C=O] ratio reaches a maximum value in our experimental conditions of 2/1. It is clearly difficult to derive further quantitative information about the relative concentration of the above-mentioned species. Qualitatively, however, it seems that the new contribution at 3280 cm^{-1} appears mainly at the expense of the free N–H peak at 3415 cm^{-1}, thus suggesting that the unassociated N–H groups are more available to form hydrogen-bonding interactions with the carbonyls than are the self-associated ones. It is noted that the difference between the stretching frequency of free and associated species is proportional to the strength of the hydrogen bond[3,4,19]. Thus, on average, the strength of the interaction between N–H and C=O groups ($\nu_s \simeq 3280\ cm^{-1}$) is less than that of the self-associated N–H groups ($\nu_s \simeq 3144\ cm^{-1}$).

The interactions of PBI with methyl ethyl ketone (MEK), diethyl ketone (DIK) and cyclohexanone (CYK) have been investigated and compared to consolidate the results obtained with acetone. It was found that substantial quantities of MEK can also be incorporated into the PBI matrix by swelling a thin PBI film at room temperature immersed in the solvent. The swelling process is, however, much slower in this case. For DIK and CYK, swelling had to be carried out at higher temperatures (90 and 140°C respectively) to allow sufficient quantities of the probes to diffuse into the polymer matrix. This probably reflects an unfavourable interaction of the hydrocarbon moiety in the probe as well as a size effect. However, in all cases (see *Figure 6*) the overall spectral features closely resemble those noted in *Figure 3* for acetone. The results obtained for all the probe compounds are summarized in *Table 3*. We note, first, that the maximum position in the N–H stretching region is practically coincident in all cases. This is partially due to the intrinsic broadness and complexity of the absorption in this region, which prevents the detection of subtle differences among the various spectra. On the other hand, the carbonyl shifts observed for MEK, DIK and CYK are very close to each other, while acetone gives rise to a significantly lower shift. This indicates that all the ketones studied, except acetone, form hydrogen bonds with PBI of very similar strengths. The observation that CYK interacts more strongly than acetone with an electron-accepting polymer is not without precedence; Cangelosi and Shaw have reported similar behaviour in a wide variety of 'acid' polymers[13]. They argued that, since no large electronic differences are expected in the functional groups of the two molecules, the increased interaction strength in cyclohexanone should be attributed largely to steric factors, namely to the restricted motion of the side-chains in cyclohexanone, rendering the carbonyl group more accessible. In our

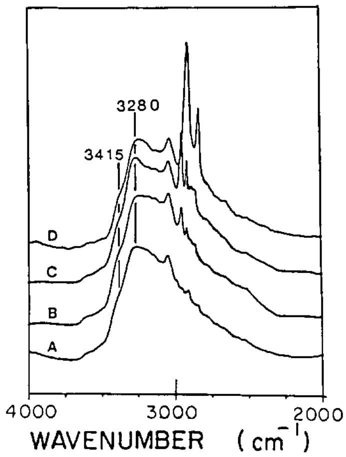


Figure 6 The 4000–2100 cm^{-1} region of the PBI spectrum in the presence of the various investigated probes: (A) PBI+acetone; (B) PBI+MEK; (C) PBI+DIK; (D) PBI+CYK

Table 3 Carbonyl absorption shifts observed in *FT*i.r. spectra of PBI/probe mixtures

Probe	Carbonyl location in CCl_4 (cm^{-1})	Carbonyl location in PBI (cm^{-1})	Carbonyl shift (cm^{-1})	Maximum position in the 3500–2200 cm^{-1} region[a]
Acetone	1718	1704	14	3280±5
Methyl ethyl ketone	1721	1702	19	–
Diethyl ketone	1719	1701	18	3285±5
Cyclohexanone	1717	1698	19	3280±5

[a] Averages of five measurements

system this explanation is contradicted by the fact that the other two linear ketones investigated, MEK and DIK, show practically the same carbonyl shift as CYK. The reason for the anomalous weakness of the interaction involving acetone is not entirely clear. It has been suggested that the weaker basicity of this molecule with respect to other aliphatic ketones could be attributed to a decreased stability of the resonance structure representative of its basic form[13]. As already mentioned, in ref. 13, using acetone and CYK as basic probes, the hydrogen-bonding ability of various proton-donating polymers was ranked by comparing the carbonyl shifts observed in the different polymer/probe mixtures. In *Tables 4* and *5* the results obtained with PBI are compared to those of ref. 13. Such a comparison, both in the case of acetone (*Table 4*) and in the case of CYK (*Table 5*), points to a strong hydrogen-bonding potential of PBI. In fact, with both the probe compounds, none of the polymers investigated in ref. 13 was found to produce a higher shift in the carbonyl location than PBI. We note that other effects including changes in the dielectric constant of the medium can play a role in determining the overall shift of the probe carbonyl absorption. It is, however, generally accepted that, when relatively strong interaction occurs, it largely determines the C=O band location, the other effects being comparatively smaller[19]. On this basis it seems reasonable to compare, at least qualitatively, the C=O shifts of the same probe molecule in different polymer matrices.

Thus the results obtained in this section can be summarized as follows:

(i) At room temperature, PBI is strongly self-associated through intermolecular hydrogen bonding.

(ii) This polymer is able to form hydrogen-bonding interactions with carbonyl compounds.

(iii) The strength of these interactions is higher than that observed for other proton-donating polymers.

The latter result leads to the conclusion that the hydrogen-bonding potential in PBI could be exploited in the form of new miscible polymer blends with proton-accepting components.

Table 4 Interaction of polymer matrices with acetone

Polymer	Carbonyl location (cm^{-1})	Carbonyl shift (cm^{-1})
Polybenzimidazole	1704	14
Phenoxy[a]	1709.0	8.8
Poly(vinyl chloride)[a]	1711.3	6.5
Polystyrene[a]	1716.2	1.6

[a] Data from ref. 13

Table 5 Interaction of polymer matrices with cyclohexanone

Polymer	Carbonyl location (cm^{-1})	Carbonyl shift (cm^{-1})
Polybenzimidazole	1698	19
Nitrocellulose[a]	1701.7	15.9
Phenoxy[a]	1704.5	13.1
Poly(vinylidene fluoride)[a]	1707.3	10.3
Poly(vinyl chloride)[a]	1707.5	10.1
Cellulose acetate butyrate[a]	1710.5	7.1
Polystyrene[a]	1713.8	3.8

[a] Data from ref. 13

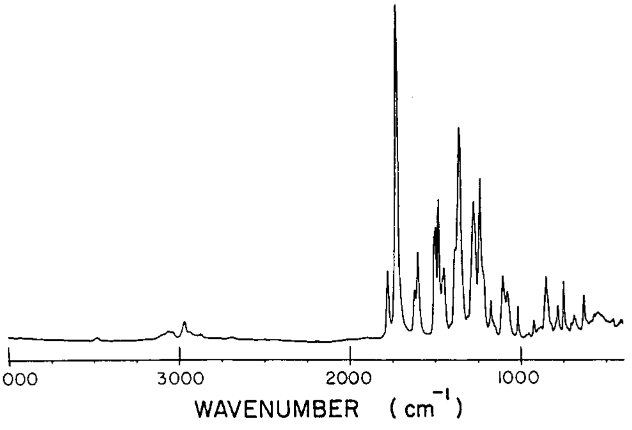


Figure 7 *FT*i.r. spectrum of Ultem 1000

Ultem 1000

To test the ability of Ultem 1000 to act as proton acceptor and to analyse the spectral features associated with hydrogen-bond formation, the spectrum of this polyimide in the presence of a series of proton-donating compounds was also investigated.

First, the main characteristics of the Ultem 1000 i.r. spectrum (*Figure 7*) are briefly discussed. The complex molecular structure of this polymer renders the definitive assignments of its vibrational modes difficult, but on the basis of previous investigations[24,25] some tentative assignments can be made. In the 1800–1700 cm^{-1} region the characteristic doublet due to the symmetric and asymmetric stretching of the imide carbonyls (1779 and 1727 cm^{-1} respectively) is observed. At lower wavenumbers the spectrum shows relatively sharp peaks attributed to the aromatic substituents (1619 cm^{-1}; 1601 cm^{-1}; the complex system centred at 1479 cm^{-1}); broader, conformationally sensitive bands appear at 1385 cm^{-1} and at 1276 and 1238 cm^{-1}. In the high-frequency region, the $-CH_3$ asymmetric and symmetric stretching vibrations occur at 2969 and 2873 cm^{-1} respectively, while the aromatic ν_{CH} modes give rise to an ill-defined triplet centred at 3068 cm^{-1}. A sharp, low-intensity absorption probably due to the $\nu_{C=O}$ overtone is detected at 3485 cm^{-1}. In the analysis below we focus on the 1800–1700 cm^{-1} carbonyl region and on the O–H, N–H stretching region (3600–3400), where the probe compounds are expected to absorb.

The various probes used are listed in *Table 2*. Their chemical structures resemble those of the proton-accepting compounds used with PBI, with a hydroxyl group replacing the carbonyl functionality. As mentioned, it was found that the simple swelling technique previously used is not successful with the polyimides. None of the tested aliphatic alcohols is absorbed by Ultem 1000 to any significant extent at either ambient or at higher temperatures. For this reason probe incorporation was achieved by the alternative method discussed above. The residual solvent and the probe content in the polymer films were evaluated by means of thermogravimetry (see *Figures 8* and *9*). For the pure polyimides it was found that, after 24 h at ambient temperature, 3–4 wt% of residual methylene chloride was still present in the films (*Figure 8*, trace A). This residual was completely removed by drying the films at 100°C for 12 h (*Figure 8*, trace B). To avoid the concurrent evaporation of the probes during the final drying

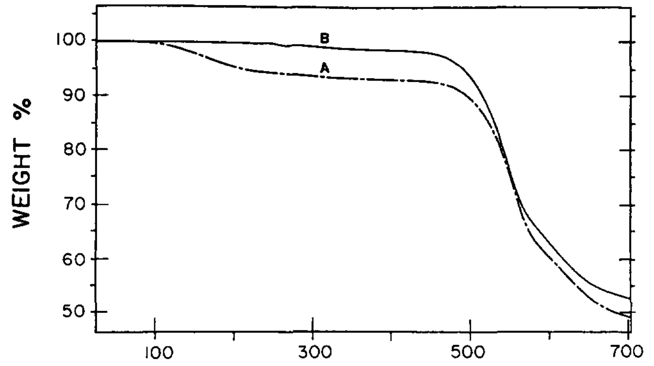


Figure 8 Thermogravimetric measurements on pure Ultem 1000: (A) sample after the casting procedure; (B) sample after the drying procedure

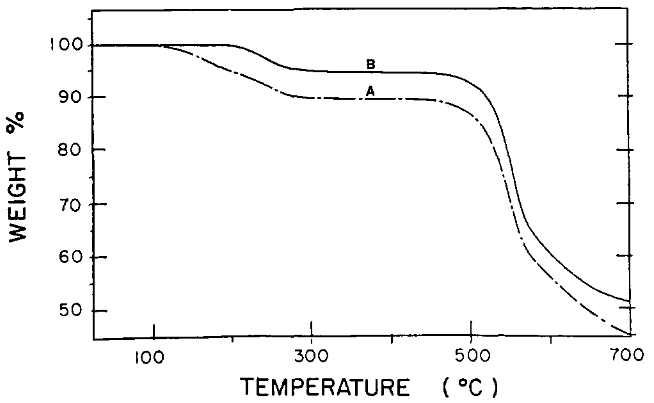


Figure 9 Thermogravimetric measurements on the Ultem 1000/cyclohexanol mixture: (A) sample after the casting procedure; (B) sample after the drying procedure

procedure, non-volatile long-chain aliphatic alcohols were selected. From the t.g.a. measurements performed on the polymer/probe mixtures (*Figure 9*) it is clearly seen that the drying process selectively removes the residual CH_2Cl_2 while leaving the probe essentially trapped in the polymer film. The t.g.a. results are summarized in *Table 6*; in all cases the probe content as obtained by t.g.a. is very close to the expected value, thus confirming the reliability of the method.

The 4000–2500 cm^{-1} region of the Ultem 1000 spectrum in the presence of the various proton-donating compounds is reported in *Figure 10*. In spectrum B (Ultem 1000/cyclohexanol mixture) a symmetrical, rather broad, peak is observed in the O–H stretching region at 3558 cm^{-1}.

Again we may compare the hydroxyl band location in the polymer substrate with its location in a diluted CCl_4 solution, where the O–H groups can be considered to be in an unperturbed state. The spectrum of a diluted (0.5 M) solution of cyclohexanol in CCl_4 displays a sharp, intense band at 3622 cm^{-1} due to the stretching vibrations of the free O–H groups, together with a very broad, asymmetric absorption centred at 3343 cm^{-1}, attributed to the self-associated hydroxyls; in the present case the reference band is the one at 3622 cm^{-1}. The shift towards lower wavenumbers and the broadening of the O–H band shape found in the polymer/probe mixture strongly suggest the formation of a hydrogen-bonding interaction between the probe and the polymer matrix. The magnitude of the shift (64 cm^{-1}) can be regarded as a relative indication of the hydrogen-bonding strength. It is noted that no bands due to probe self-association are evident in the spectra of the mixtures. This indicates that by using a low probe content it is possible to maximize the polymer–probe interaction and to avoid self-association phenomena. However, at higher probe contents a poorly resolved absorption in the 3520–3120 cm^{-1} region appears (self-associated O–H groups); at the same time after the casting process the polymer films appear hazy. Evidently when an excess of the second component is trapped in the matrix, a phase separation occurs and the resulting peaks are detected. This effect indicates the necessity of using small amounts of a second component to simplify the spectral interpretation.

The presence of the donor group is expected to produce a spectroscopically detectable perturbation in the environment of the interacting proton-acceptor group, which, in this case, is likely to be the imide carbonyl. In *Figure 11* the spectra of Ultem 1000 (trace A) and of the Ultem 1000/cyclohexanol mixture (trace B) in the 1850–1650 cm^{-1} region are shown. A subtle shift (2 cm^{-1}) of the 1727 cm^{-1} band towards lower wavenumbers is observed in the spectrum of the mixture; an even smaller shift is detected in the 1780 cm^{-1} absorption. The effect is only slightly above the experimental uncertainty but it was found to be reproducible in several mixtures of analogous composition as well as in mixtures containing the other investigated probes. The very small effect detected in the carbonyl region is reasonable because of

Table 6 Thermogravimetric analysis of Ultem 1000/probe mixtures

	Amount of second component (wt %)	
Mixture	Nominal	T.g.a.
Ultem 1000/cyclohexanol	6.0	6.2
Ultem 1000/4-heptanol	5.2	5.0
Ultem 1000/4-decanol	5.8	5.5
Ultem 1000/PhBim (A)	4.9	5.0
Ultem 1000/PhBim (B)	9.2	8.3

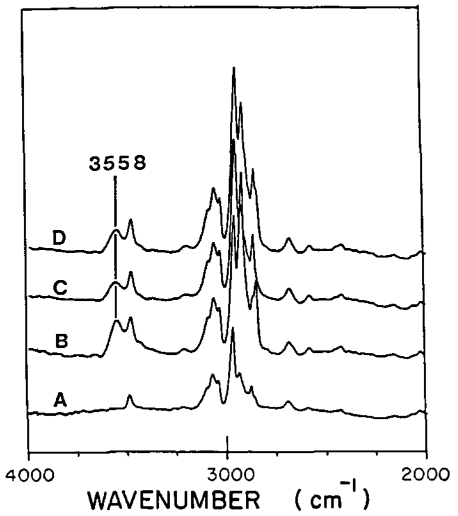


Figure 10 The 4000–2500 cm^{-1} region of the Ultem 1000 spectrum in the presence of the various investigated probes: (A) pure Ultem 1000; (B) Ultem 1000/cyclohexanol; (C) Ultem 1000/4-heptanol; (D) Ultem 1000/4-decanol

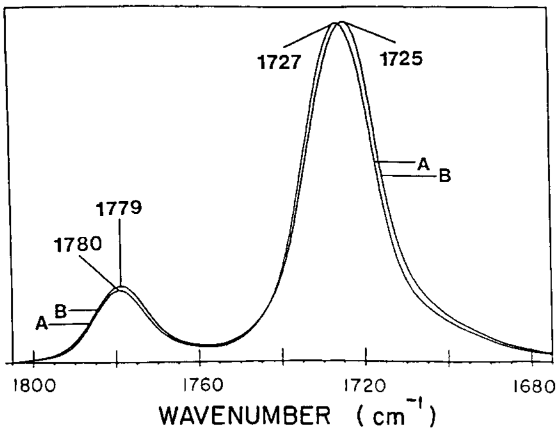


Figure 11 The 1850–1650 cm^{-1} region of the spectrum of: (A) Ultem 1000; (B) Ultem 1000/cyclohexanol mixture

Table 7 Interactions of polymer matrices with cyclohexanol

Polymer	O–H location (cm^{-1})	O–H shift (cm^{-1})
Polyimide, XU 218	3564	58
Poly(pivalolactone)[a]	3566	59
Polyimide Ultem 1000	3558	64
Poly(butanediol 1,4-terephthalate)[a]	3556	69
Polyacetal[a]	3550	74
Poly(ε-caprolactone)[a]	3538	97
Poly(vinyl methyl ether)[a]	3486	136

[a] Data from ref. 13

the small amount of probe compound that can be incorporated into the polymer substrate.

The results obtained with cyclohexanol were confirmed with the other probes. In particular, it was found that, within the error limits of the *FT*i.r. technique, the hydroxyl groups associated with all the probes behave identically both in CCl_4 solution and in the polymer mixtures (see *Figure 11*). This indicates that the strength of the probe–polymer interaction does not depend on the geometry and size of the probe molecule, in contrast to the previous findings involving the proton-accepting compounds acetone and cyclohexanone. As already mentioned, the shift of the O–H peak relative to its position in CCl_4 is an indication of the hydrogen-bonding strength in a polymer/probe mixture. It is possible to compare the shift observed in the Ultem 1000/cyclohexanol mixture with those found for a number of different proton-accepting polymers[13] (see *Table 7*). It can be seen that Ultem 1000 produces one of the smallest shifts and thus can be considered a comparatively poor proton-accepting polymer.

The solution method used to prepare the Ultem 1000/probe mixture is somewhat more versatile than the swelling process. Taking advantage of this fact a model compound whose chemical structure more closely resembles that of PBI was incorporated into Ultem 1000 to reproduce the spectral features observed in the PBI/Ultem 1000 blends. The compound selected for this purpose was 2-phenylbenzimidazole (PhBim), whose chemical structure is shown in *Table 2*. It was possible to prepare polymer/probe mixtures of different composition (5.0 and 8.3 wt% of PhBim respectively). The films of both mixtures appeared clear after the solution casting process and no absorptions due to probe–probe self-association were detected in the i.r. spectra (see *Figure 12*). A rather broad absorption is observed in the N–H stretching region, at 3370 cm^{-1}; its intensity increases with increasing PhBim content in the polymer substrate. In a dilute CCl_4 solution (1×10^{-3} M) the free N–H stretching vibration of the model compound gives rise to a sharp peak at 3475 cm^{-1}. The shift towards lower wavenumbers (105 cm^{-1}) and the substantial band broadening observed in the polymer/probe mixtures are again indicative of hydrogen-bonded N–H groups. In *Figure 13* the same spectra shown in *Figure 12* but in the 1800–1680 cm^{-1} region are reported, together with the Ultem 1000 spectrum for comparison. A shift towards lower wavenumbers which increases with increasing PhBim content in the mixture is observed in the 1727 cm^{-1} imide band; the peak develops an asymmetry on the low-frequency side. A small, barely detectable, shift (1 cm^{-1}) is found also in the 1780 cm^{-1} band. These effects, in agreement with the previous findings, indicate that the N–H groups of the model compound interact preferentially with the imide carbonyls of the polymer substrate.

As a final test the spectrum of a 10/90 wt% PBI/Ultem 1000 blend was itself analysed (*Figures 12* (C) and *13* (D)). It can be seen that, both in the 4000–2500 cm^{-1} and in the carbonyl region, the features observed in the blend

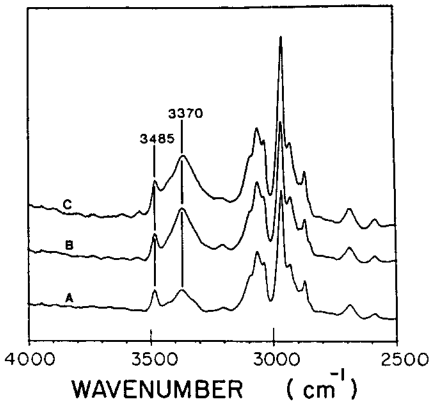


Figure 12 *FT*i.r. spectra in the 4000–2500 cm^{-1} region of: (A) Ultem 1000/PhBim 5.2%; (B) Ultem 1000/PhBim 8.3%; (C) 10/90 wt% PBI/Ultem 1000 blend

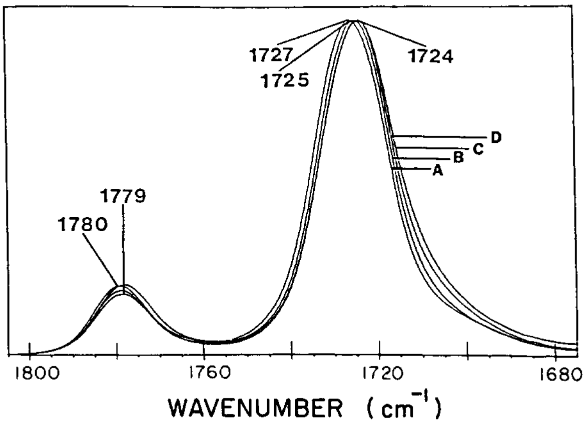


Figure 13 *FT*i.r. spectra in the 1850–1650 cm^{-1} region of: (A) Ultem 1000; (B) Ultem 1000/PhBim 5.2%; (C) Ultem 1000/PhBim 8.3%; (D) 10/90 wt% PBI/Ultem blend

spectrum are the same as those found in the Ultem 1000/PhBim mixtures. The same conclusions can, therefore, be drawn: a hydrogen-bonding interaction between the N–H groups of PBI and the imide carbonyls of Ultem 1000 occurs upon blending the two polymeric components. The interaction causes the appearance of a rather broad absorption at 3370 cm^{-1} attributed to the N–H groups interacting with the carbonyls and a shift of the 1727 cm^{-1} $\nu_{a,C=O}$ towards lower wavenumbers. A more complete analysis of the vibrational behaviour of the PBI/Ultem 1000 blend system over the whole composition range will be discussed in a subsequent paper.

XU 218

Some results concerning the behaviour of XU 218 polyimide as a proton-accepting polymer have been obtained. The spectrum of this polymer in the 4000–400 cm^{-1} region is shown in *Figure 14*. In the carbonyl region three well defined absorptions at 1780, 1726 and 1676 cm^{-1} are detected: they are due, respectively, to the already discussed symmetric and asymmetric stretching vibrations of the imide carbonyls and to the stretching mode of the benzophenone carbonyl. The low frequency at which this group absorbs is due to its extensive conjugation with the two adjacent phenyl rings.

A series of polymer/probe mixtures was prepared using the same low-molecular-weight compounds and the same technique used with Ultem 1000. The probe content was evaluated as before using t.g.a.: the results of such measurements are summarized in *Table 8*. In *Figure 15* the 3800–2500 cm^{-1} spectral region of the pure polyimide (trace A) and of two representative polymer/probe mixtures (traces B and C) are shown. The peak observed at 3564 cm^{-1} in spectrum B (XU 218/cyclohexanol mixture) and that at 3373 cm^{-1} in spectrum C (XU 218/PhBim mixture) closely resemble the absorbances observed in analogous mixtures with Ultem 1000 with respect to band shape and position. This indicates that the XU 218 is also able to form hydrogen bonds with proton-donating compounds. The relative strength of such interactions, as evaluated from the O–H shift in the XU 218/cyclohexanol mixture (see *Table 7*), is found to be of the same order of magnitude as the interactions formed by Ultem 1000; however, with respect to other proton-accepting polymers, XU 218 is found to be one of the least able.

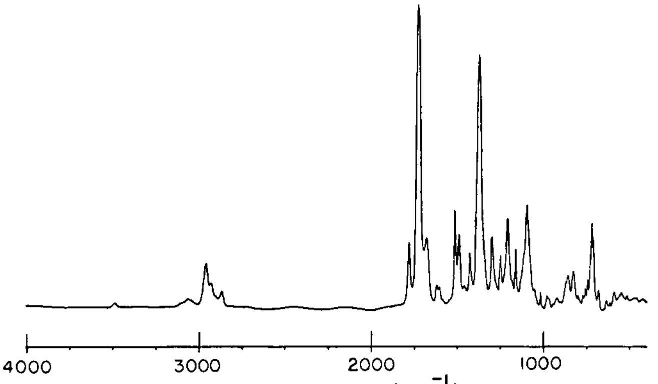


Figure 14 *FT*i.r. spectrum of XU 218

Table 8 Thermogravimetric analysis of XU 218/probe mixtures

Mixture	Amount of second component (wt %)	
	Nominal	T.g.a.
XU 218/cyclohexanol	5.3	5.3
XU 218/4-heptanol	5.2	5.0
XU 218/4-decanol	5.2	5.1
XU 218/PhBim (A)	5.1	4.8
XU 218/PhBim (B)	9.2	9.3

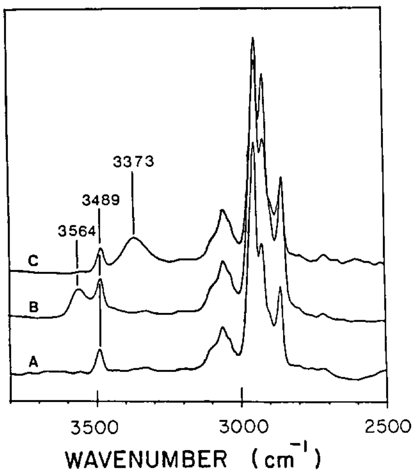


Figure 15 *FT*i.r. spectra in the 4000–2500 cm^{-1} region of: (A) XU 218; (B) XU 218/cyclohexanol; (C) XU 218/PhBim 9.2%

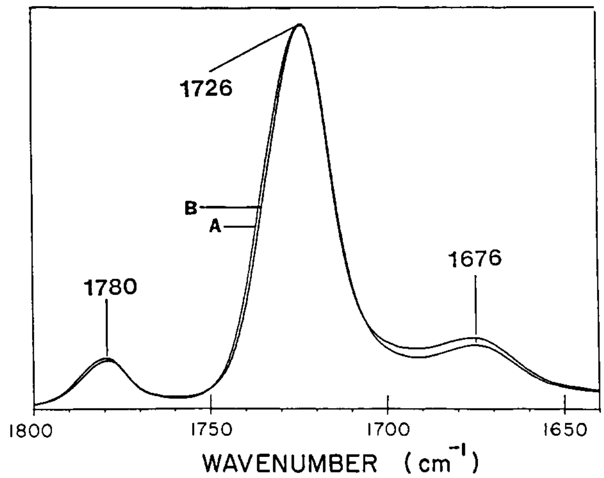


Figure 16 *FT*i.r. spectra in the 1850–1650 cm^{-1} region of: (A) XU 218; (B) XU/PhBim 9.2%

Surprisingly, in contrast with the previous results obtained with Ultem 1000, no detectable shifts were observed in the carbonyl region for all the investigated mixtures of XU 218 (see *Figure 16*). This effect could be tentatively explained by assuming that both the imide and the benzophenone carbonyls interact with the probe compounds. In this instance the number of carbonyls of the same type actually interacting decreases, making the already subtle shift undetectable. An investigation possibly involving other spectroscopic techniques is required to clarify this point.

CONCLUSIONS

The use of low-molecular-weight monofunctional compounds was found to be helpful in assessing the hydrogen-bonding potential of PBI and of two commercial polyimides, Ultem 1000 and XU 218. Using this approach it was possible to establish that PBI can act as a strong proton donor through the N–H groups of the benzimidazole ring. On the other hand, it was found that the two polyimides are able to act as proton acceptors, though their hydrogen-bonding potential is weak compared to that in other proton-accepting polymers. By using a model compound whose chemical structure closely resembles that of PBI, it was possible to conclude definitively that in PBI/Ultem 1000 blends hydrogen-bonding interactions take place between the components.

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