Miscibility and complexation behaviour of poly(styrene-*co*-allyl alcohol)/poly(*N,N*-dimethylacrylamide) and poly(styrene-*co*-allyl alcohol)/poly(2-ethyl-2-oxazoline) systems

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The miscibility and complexation behaviour of two isomeric tertiary amide polymers, poly(*N*,*N*-dimethylacrylamide) (PDMA) and poly(2-ethyl-2-oxazoline) (PEOx), with poly(styrene-*co*-allyl alcohol) (SAA) containing 4.5 and 6.5 wt% of hydroxyl groups has been studied. PDMA and SAA form complexes from methyl ethyl ketone (MEK) solutions when the PDMA contents in the feed are not more than 50 and 75 wt% for SAA(4.5)/PDMA and SAA(6.5)/PDMA, respectively. However, they do not form complexes from tetrahydrofuran (THF) or *N*,*N*-dimethylformamide (DMF) solutions. On the other hand, PEOx does not form complexes with SAA from any of the three solvents used. We have previously reported that another isomeric tertiary amide polymer, poly(*N*-methyl-*N*-vinylacetamide) (PMVAc), can form interpolymer complexes with SAA from MEK solutions over the entire feed composition range and from THF solutions when the feed is rich in SAA. These observations show that the abilities of the three isomeric tertiary amide polymers to form complexes with SAA are in the order of PMVAc > PDMA > PEOx. *FT*i.r. spectroscopy studies demonstrate that intermolecular hydrogen bonding interactions contribute to the miscibility and complex formation in these blends.

(Keywords: interpolymer complexes; polymer miscibility; hydrogen bonding)

INTRODUCTION

In a recent paper[1], we reported the interpolymer complexation between poly(styrene-*co*-allyl alcohol) (SAA) and poly(*N*-methyl-*N*-vinylacetamide) (PMVAc). Mutual precipitation occurs from methyl ethyl ketone (MEK) solutions for all feed compositions and from tetrahydrofuran (THF) solutions when the feed is rich in SAA. However, interpolymer complexes do not form from *N*,*N*-dimethylformamide (DMF) solutions. Thus, the nature of the solvent, as well as the feed composition, has profound effects on interpolymer complexation. This is because in a polymer/polymer/solvent system, if the affinity between the two unlike polymers is stronger than those of the two polymer/solvent pairs, interpolymer complexation may occur, and in contrast, a stronger favourable interaction of the polymer/solvent pair prevents the formation of interpolymer complexes. Fourier-transform infra-red (*FT*i.r.) spectroscopy results show that the driving force for forming interpolymer complexes in the SAA/PMVAc system is hydrogen bonding between the aliphatic hydroxyl groups in SAA and the tertiary-amide-type carbonyl groups in PMVAc.

The majority of the previously reported hydrogen-bond-type polymer complex systems involve one component polymer containing pendent carboxyl or phenolic hydroxyl groups as proton donors, such as poly(acrylic acid) (PAA)/poly(*N*-vinylpyrrolidone) (PVP)[2], poly(methacrylic acid)/PVP[2,3], PAA/poly(vinyl methyl ether) (PVME)[4], PAA/poly(2-ethyl-2-oxazoline) (PEOx)[5,6], poly(*p*-vinylphenol) (PVPh)/poly(*N*,*N*-dimethylacrylamide) (PDMA)[7], PVPh/PEOx[7], and phenol-formaldehyde resin/PDMA[8]. As PDMA and PEOx are isomeric with PMVAc and can form complexes with carboxyl and phenolic hydroxyl containing polymers, it is of interest to investigate whether they can also form interpolymer complexes with SAA.

In this work, the miscibility and complexation behaviour of SAA/PDMA and SAA/PEOx systems was studied by differential scanning calorimetry (d.s.c.) and *FT*i.r. The differences between the two polymeric tertiary amides in their complexation behaviour with SAA are discussed, and are also compared to the behaviour of PMVAc.

EXPERIMENTAL

Materials

The two samples of poly(styrene-*co*-allyl alcohol) used in this study, which contained 4.5 and 6.5 wt% of hydroxyl groups, were provided by Scientific Polymer

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Products and were dried *in vacuo* at 90°C for at least 2 days before use. These two copolymers were denoted as SAA(4.5) and SAA(6.5), respectively. Based on gel permeation chromatography (g.p.c.) measurements, the number- and weight-average molecular weights of SAA(4.5) and of SAA(6.5) were found to be 2140 and 4040, and 1750 and 3260 g mol^{-1}, respectively. The glass transition temperature (T_g) of SAA(4.5) is 55°C, while that of SAA(6.5) is 48°C.

Poly(*N*,*N*-dimethylacrylamide) (PDMA), with a T_g value of 118°C, was obtained by solution polymerization in 1,4-dioxane at 80°C for 4 h using 2,2′-azobisisobutyronitrile (AIBN) as the initiator. The number- and weight-average molecular weights of the PDMA were found to be 12000 and 19600 g mol^{-1}, respectively. Poly(2-ethyl-2-oxazoline) (PEOx) was provided by the Dow Chemical Company, and had number- and weight-average molecular weights of 38500 and 61500 g mol^{-1}, respectively. The T_g of this PEOx is 56°C.

Preparation of polymer complexes and blends

Polymer complexes between SAA and PDMA, or PEOx, were obtained by the mixing of solutions which each contained 0.1 g of polymer per 10 ml of solvent. White precipitates, which were formed immediately upon mixing, were separated from the solution by centrifugation and washed with solvent. The supernatant liquids were allowed to evaporate to obtain residual blends. For systems which did not form interpolymer complexes, the clear solutions were allowed to evaporate slowly to obtain blends. All the complexes and blends were then dried *in vacuo* at 90°C for at least 7 days; they were then stored in a desiccator to prevent absorption of moisture. The nitrogen contents of the polymer complexes and also their residual blends were determined by elemental analysis.

Glass transition temperature (T_g) *measurements*

The glass transition temperatures (T_gs) of all of the samples were measured with a Perkin–Elmer DSC-4 differential scanning calorimeter. As PDMA and PEOx are highly hygroscopic, all the samples were preheated to 150°C and held at that temperature for 15 min to ensure complete removal of any moisture or residual solvent. A scanning rate of 20°C min^{-1} was used, and the T_g was taken as the initial onset of the change of slope in the d.s.c. curve. All of the reported T_g values are taken as averages obtained from several runs.

Fourier transform infra-red (FT*i.r.*) *characterization*

Infra-red spectra were recorded on a Perkin–Elmer 1725X *FT*i.r. spectrophotometer. Sixty-four scans were signal-averaged at a resolution of 2 cm^{-1}. The spectra which were recorded at elevated temperatures were obtained by using a SPECAC high-temperature cell, equipped with an automatic temperature controller, which was mounted in the spectrophotometer. The sample chamber was purged with N_2. Samples for *FT*i.r. analyses were prepared by casting THF solutions onto KBr discs and then drying the products *in vacuo* at 90°C for at least 2 days.

RESULTS AND DISCUSSION

Complexation behaviour of SAA with PDMA and PEOx

Both SAA(4.5) and SAA(6.5) can form complexes with PDMA from methyl ethyl ketone (MEK) solutions depending on the feed composition. Data on the yields and compositions of the polymer complexes and the corresponding residual blends, together with their T_g values are compiled in *Tables 1* and *2*.

Table 1 Experimental data obtained for the SAA(4.5)/PDMA system

Feed composition PDMA content		Polymer complexes				Residual blends		
(wt%)	(mol%)	Yield (wt%)	PDMA content (mol%)	T_g (°C)	Product[a]	Yield (wt%)	PDMA content (mol%)	T_g (°C)
10	9.4	13.2	64.1	110	C	86.8	1.1	62
25	23.8	24.8	68.8	113	C	75.2	7.0	63
50	48.4	33.7	76.4	116	C	66.3	34.4	68
75	73.9	–	–	–	M	–	–	107
90	89.5	–	–	–	M	–	–	112

[a] C = complex formation, M = miscible blend

Table 2 Experimental data obtained for the SAA(6.5)/PDMA system

Feed composition PDMA content		Polymer complexes				Residual blends		
(wt%)	(mol%)	Yield (wt%)	PDMA content (mol%)	T_g (°C)	Product[a]	Yield (wt%)	PDMA content (mol%)	T_g (°C)
10	9.0	18.4	49.2	105	C	81.6	≈0.0	56
25	23.0	33.4	53.9	110	C	66.6	6.6	58
50	47.2	47.9	56.3	110	C	52.1	38.4	71
75	72.8	67.1	76.5	113	C	32.9	65.1	92
90	89.0	–	–	–	M	–	–	113

[a] C = complex formation, M = miscible blend

For the SAA(4.5)/PDMA system, mutual precipitation occurred when the feed was relatively rich in SAA(4.5). The yields of the complexes increased with increasing PDMA contents in the feed, and ranged from 13.2 to 33.7 wt%. The compositions of the complexes, ranging from 64.1 to 76.4 mol% of PDMA, depended on the feed compositions. The corresponding *N,N*-dimethylacrylamide/allyl alcohol (DMA/AA) molar ratios in the complexes are in the range of 7.4–13.3. These large ratios indicate that there are a large number of DMA segments which are not in close contact with the hydroxyl groups as the AA segments are sparsely distributed along the copolymer chains. The glass transition temperatures of these complexes are in the range of 110–116°C and are higher than those of corresponding miscible blends with similar compositions, indicating a strong association between unlike polymer chains. For feed compositions of 10–25 wt% of PDMA, practically all of the PDMA has been complexed with SAA(4.5), leaving just a small amount of PDMA in the residual blend. The low PDMA contents in the residual blends are also reflected by their low T_g values, which are close to that of SAA(4.5).

SAA(6.5), with a higher allyl alcohol content, formed complexes with PDMA at SAA contents as low as 25 wt% in the feed. The yields of the complexes increased with increasing PDMA contents in the feed and had values which were higher than those of the corresponding SAA(4.5)/PDMA complexes. These results demonstrate that a higher allyl alcohol content in SAA promotes its complexation with PDMA. The compositions of the complexes, ranging from 49.2 to 76.5 mol% of PDMA, depended on the feed compositions. The corresponding DMA/AA molar ratios in these complexes are in the range of 2.9–9.7, which are considerably smaller than those of the SAA(4.5) system. A larger number of AA segments in SAA(6.5) allow more DMA segments to be in close contact with the hydroxyl groups, thus giving rise to smaller DMA/AA ratios in the complexes. For feed compositions of 10–25 wt% PDMA, the residual blends are practically devoid of PDMA, hence giving rise to low T_g values.

Complexation between SAA and PDMA did not occur in *N,N*-dimethylformamide (DMF) solutions and only miscible polymer blends were obtained. This is because DMF itself is also a tertiary amide and can therefore effectively compete with PDMA in forming hydrogen bonds with the allyl alcohol segments in SAA. As illustrated in *Figures 1* and *2*, the T_g *versus* composition curves of both the SAA(4.5)/PDMA and SAA(6.5)/PDMA systems cast from DMF are 'S-shape' in form, which are commonly observed for blends involving hydrogen bonding interactions[9,10], and which can be simulated by the Kwei equation[9]:

$$T_g(\text{blend})=(w_1T_{g1}+kw_2T_{g2})/(w_1+kw_2)+qw_1w_2$$

where k and q are fitting constants, and have values of 5 and 110, and 4 and 85 for the SAA(4.5)/PDMA and SAA(6.5)/PDMA systems, respectively.

Unlike the SAA/PMVAc system, complexation between SAA and PDMA did not occur upon mixing their THF solutions. This observation suggests that the interpolymer interaction between SAA and PDMA is weaker than that between the SAA/PMVAc pair. It is worthwhile to note here that the T_g *versus* composition curve for SAA(4.5)/PDMA cast from THF solutions is quite close to the composition 'average line', while the curve for SAA(6.5)/PDMA cast from THF solutions is S-shaped, with k and q values of 3 and 50, respectively. This suggests that a higher allyl alcohol content in SAA results in a greater extent of intermolecular hydrogen bonding between SAA and PDMA.

In contrast, PEOx did not form complexes with either SAA(4.5) or SAA(6.5) from MEK, THF or DMF solutions. As the T_g values of SAA(4.5), SAA(6.5) and PEOx are close to each other, a single T_g observed for these blends may not be regarded as an indication of miscibility. However, all of the SAA/PEOx blends cast from MEK, THF and DMF solutions were transparent and remained so up to 300°C. This transparency is not a result of matching the refractive indices of the polymers,

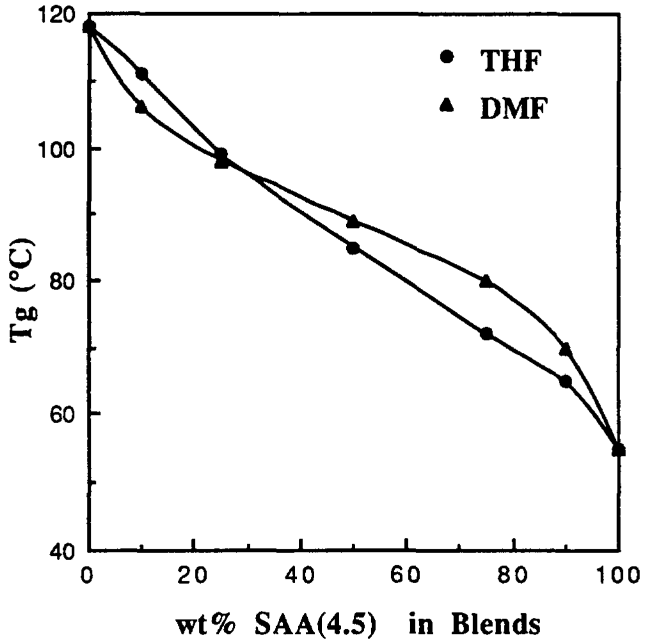

Figure 1 T_g *versus* composition curves of SAA(4.5)/PDMA miscible blends cast from DMF (▲) and THF (●) solutions

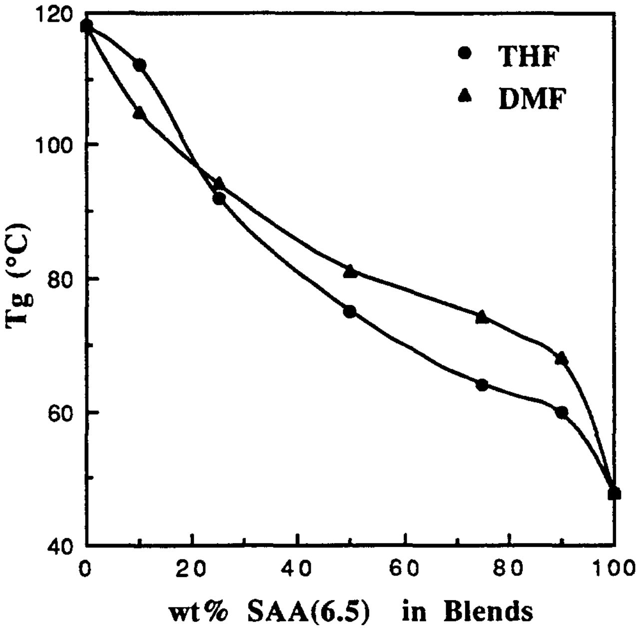

Figure 2 T_g *versus* composition curves of SAA(6.5)/PDMA miscible blends cast from DMF (▲) and THF (●) solutions

as the values are 1.57, 1.56 and 1.51 for SAA(4.5), SAA(6.5) and PEOx, respectively (estimated by the Vogel method[11]). Therefore, the optical clarity of the blends can be an indication of miscibility. The miscibility of PEOx with SAA is further confirmed by the *FT*i.r. studies, as will be discussed in the following section.

FT*i.r. characterization*

Infra-red spectroscopy can be used to detect the existence of hydrogen bonding interactions in polymer blends. Coleman and his co-workers[12–14] have successfully employed this technique to investigate the miscibility behaviour of hydrogen-bonding-type polymer blends. Here, we present our *FT*i.r. studies of the blends of SAA/PDMA and SAA/PEOx.

Carbonyl region of SAA/PDMA blends

Figure 3 shows the infra-red spectra of the carbonyl stretching region between 1550 and 1750 cm^{-1} of SAA(6.5), PDMA, and a SAA(6.5)/PDMA blend containing 10 wt% PDMA, and, in addition, the spectrum of the blend after subtracting the SAA(6.5) absorption. All of the samples were cast from THF solutions and their spectra were recorded at 90°C to eliminate the interference of moisture. PDMA (curve A) has a strong absorption centred at 1643 cm^{-1} for the free carbonyl band, while SAA(6.5) (curve B) has a band at 1600 cm^{-1} due to the vibration of the aromatic rings in its polymer chain. A new band at 1626 cm^{-1} appears in the spectra of the SAA(6.5)/PDMA blend (curves C and D) which can be attributed to carbonyl groups in PDMA hydrogen bonded with hydroxyl groups in SAA(6.5). As shown in *Figure 4*, an increase in SAA(6.5) content in the blends leads to an increase in the relative intensity of the hydrogen bonded carbonyl band at 1626 cm^{-1}, when compared with the free carbonyl band at 1643 cm^{-1}, indicating that more of the carbonyl groups are involved in hydrogen bonding with the hydroxyl groups when the SAA content in the blends is increased.

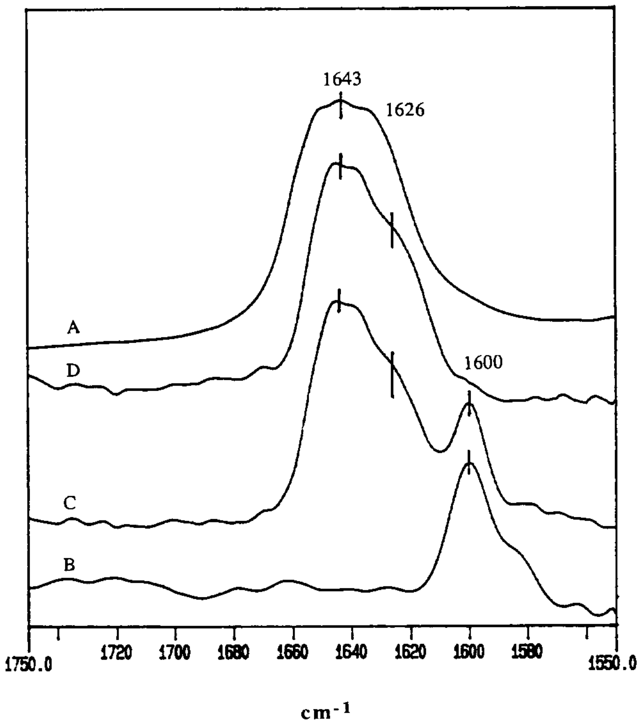

Figure 3 *FT*i.r. spectra of the carbonyl region, recorded at 90°C, of samples cast from THF solutions: (A) PDMA; (B) SAA(6.5); (C) SAA(6.5)/PDMA containing 10 wt% PDMA; (D) the spectrum obtained by subtracting the absorption of SAA(6.5) in this region from spectrum C

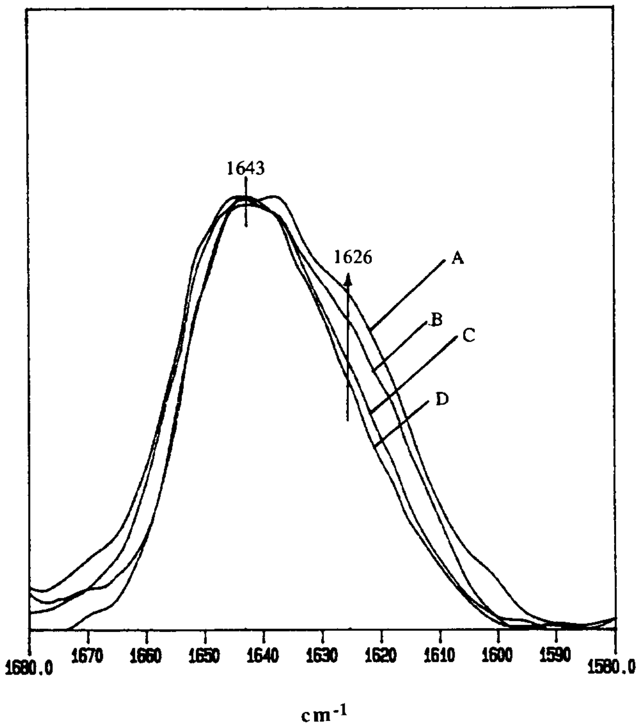

Figure 4 *FT*i.r. spectra of the carbonyl region, recorded at 90°C (after subtracting the SAA absorption), of samples of SAA(6.5)/PDMA miscible blends, cast from THF solutions, containing: (A) 10; (B) 25; (C) 50; (D) 100 wt% of PDMA

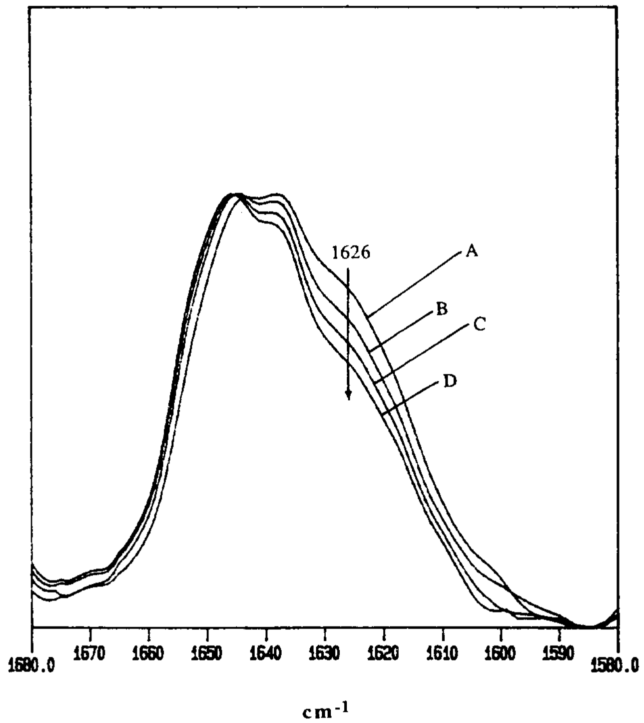

Figure 5 *FT*i.r. spectra of the carbonyl region (after subtracting the SAA absorption) of samples of SAA(6.5)/PDMA miscible blends containing 10 wt% PDMA, cast from THF solutions, recorded at: (A) 90; (B) 120; (C) 150; (D) 180°C

Figure 5 shows the *FT*i.r. spectra of the carbonyl region of the SAA(6.5)/PDMA blend containing 10 wt%

of PDMA (after subtracting the SAA absorption) as a function of temperature. The intensity of the peak at 1626 cm^{-1} for the hydrogen bonded carbonyls decreases as the temperature is raised from 90 to 180°C. This observation illustrates a general trend that an increase in temperature accelerates the dissociation of intermolecular hydrogen bonding in the polymer blends.

Hydroxyl region of SAA/PDMA blends

The spectra of the corresponding hydroxyl stretching band can also provide information on the intermolecular hydrogen bonding between the component polymers. *Figure 6* shows the hydroxyl region of SAA(6.5)/PDMA blends cast from THF solutions and recorded at 90°C. The spectrum of SAA(6.5) (curve A) has a band at 3578 cm^{-1} attributed to free hydroxyl groups, and a broad band centred at 3422 cm^{-1} which represents a broad distribution of hydrogen bonded or self-associated hydroxyl groups. As the PDMA content in the blend increases, the intensity of the free hydroxyl band at 3578 cm^{-1} decreases, indicating that more free hydroxyl groups are involved in intermolecular association with the carbonyl groups. This peak almost disappears when the PDMA content reaches 75 wt% in the blend (see curve E). In addition, the centre of the broad hydrogen bonded hydroxyl band shifts from 3422 cm^{-1} for SAA(6.5) to 3467 cm^{-1} for the blend containing 75 wt% of PDMA. The frequency shift of the hydroxyl groups in SAA(6.5) which are hydrogen bonded with the carbonyl groups in PDMA, with respect to the free hydroxyl groups ($\Delta\nu = 111$ cm^{-1}), which can be used as a measure of the average strength of the intermolecular interactions, is smaller than that of the self-associated hydroxyls ($\Delta\nu = 156$ cm^{-1}). In contrast, the frequency shift of the hydroxyl groups in SAA which are hydrogen bonded with the carbonyl groups in PMVAc is larger than that of the self-associated hydroxyls[1]. These results suggest that intermolecular interaction between SAA and PMVAc is stronger than that between SAA and PDMA, and is in agreement with the experimental observation that PMVAc has a stronger ability to form complexes with SAA, when compared with PDMA.

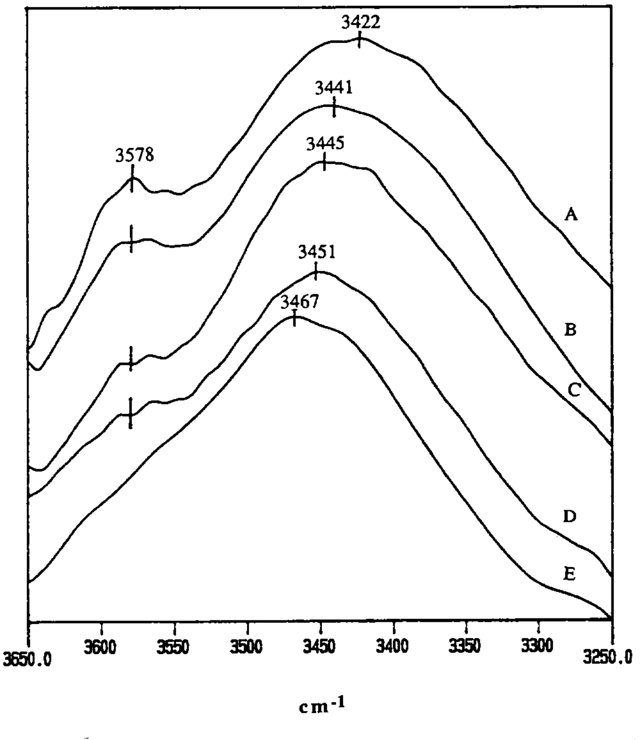

Figure 6 *FT*i.r. spectra of the hydroxyl region, recorded at 90°C, of samples of SAA(6.5)/PDMA miscible blends, cast from THF solutions containing: (A) 0; (B) 10; (C) 25; (D) 50; (E) 75 wt% PDMA

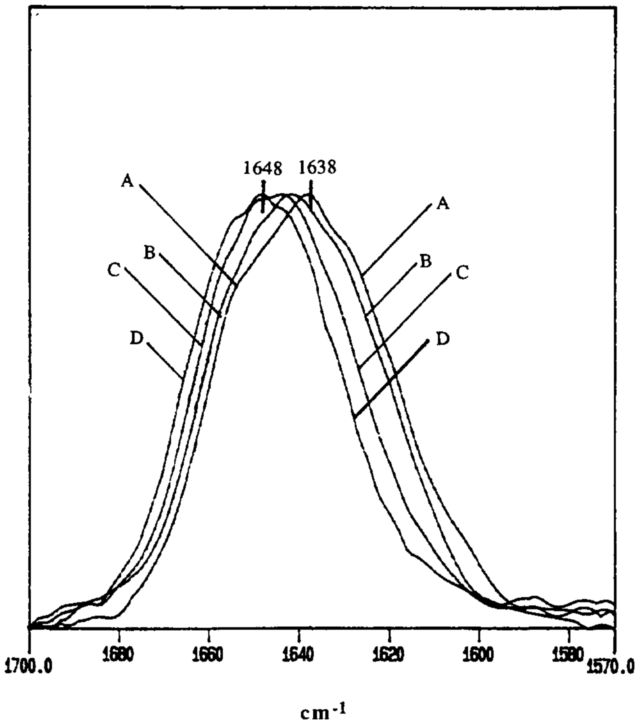

Figure 7 *FT*i.r. spectra of the carbonyl region, recorded at 90°C (after subtracting the SAA absorption) of samples of SAA(6.5)/PEOx miscible blends, cast from THF solutions, containing: (A) 10; (B) 25; (C) 50; (D) 100 wt% of PEOx

Carbonyl region of SAA/PEOx blends

Figure 7 shows the carbonyl stretching region for blends of SAA(6.5)/PEOx (after subtracting the SAA absorption) cast from THF solutions and recorded at 90°C. PEOx (curve D) has a band centred at 1648 cm^{-1}. As the content of SAA(6.5) is increased in the blend, the centre of the carbonyl band gradually shifts to lower frequencies, which can be considered as evidence for intermolecular association. When compared with the SAA/PDMA blend, which has an obvious shoulder at 1626 cm^{-1}, representing the contribution of the hydrogen bonded carbonyl groups, the carbonyl region of the SAA/PEOx blend does not show a clear shoulder, indicating that the difference in frequency between the free carbonyl band and the hydrogen bonded carbonyl band of SAA/PEOx is smaller than that of the SAA/PDMA system. This observation indicates a weaker intermolecular hydrogen bonding interaction between SAA and PEOx, when compared with SAA/PDMA. The existence of interpolymer hydrogen bonding in SAA/PEOx is also confirmed by the temperature dependence of the carbonyl region for the blends containing 25 wt% PEOx. As shown in *Figure 8*, an increase in temperature causes the intensity at 1631 cm^{-1} to decrease, and the intensity at 1648 cm^{-1} to increase.

Hydroxyl region of SAA/PEOx blends

Figure 9 shows the hydroxyl stretching region of SAA(6.5)/PEOx blends, with different compositions, cast

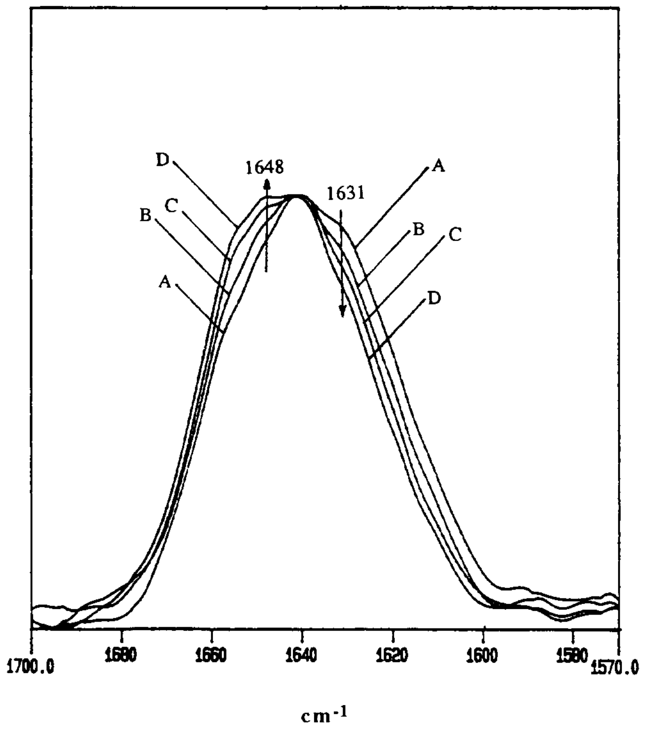

Figure 8 *FT*i.r. spectra of the carbonyl region (after subtracting the SAA absorption) of samples of SAA(6.5)/PEOx miscible blends containing 25 wt% PEOx, cast from THF solutions recorded at: (A) 60; (B) 90; (C) 120; (D) 150°C

from THF solutions and recorded at 90°C. With an increasing concentration of PEOx, the band shifts from 3422 cm^{-1}, for the pure self-associated hydroxyl groups, to higher frequencies, and is accompanied by a decrease in the intensity of the band at 3578 cm^{-1}, which is assigned to the free hydroxyl band. This phenomenon is similar to that observed in the SAA(6.5)/PDMA system.

CONCLUSIONS

PDMA forms interpolymer complexes with SAA from MEK solutions at feed compositions of not more than 50 and 75 wt% of PDMA, for SAA(4.5)/PDMA and SAA(6.5)/PDMA, respectively, but does not form complexes from THF and DMF solutions. Interpolymer complexation does not occur between SAA and PEOx from MEK, THF or DMF solutions.

The abilities of the three isomeric polymers to form intermolecular complexes with SAA are in the order PMVAc > PDMA > PEOx. *FT*i.r. spectroscopic studies show that the hydrogen bonding between the hydroxyl groups in SAA and the carbonyl groups in polymeric tertiary amides initiates the intermolecular complexation, and that the relative strengths of their hydrogen bonding interactions is in agreement with their abilities to form interpolymer complexes.

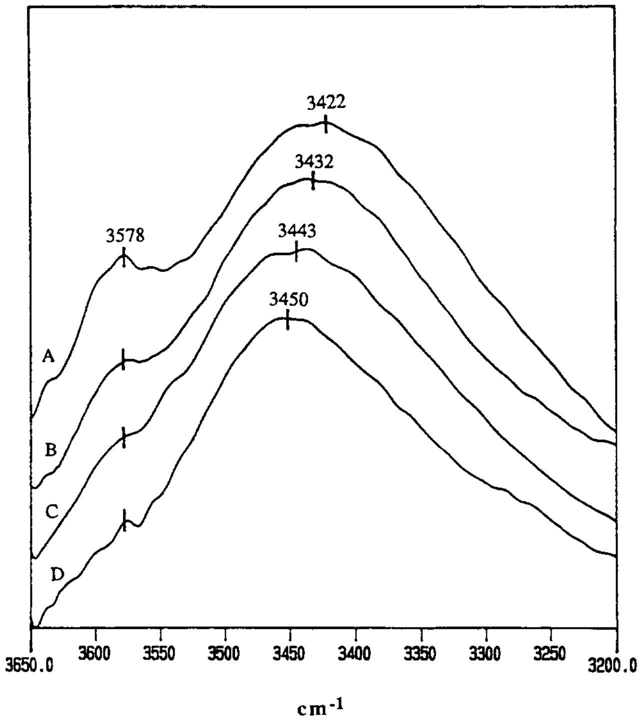

Figure 9 *FT*i.r. spectra of the hydroxyl region, recorded at 90°C, of samples of SAA(6.5)/PEOx miscible blends, cast from THF solutions, containing: (A) 0; (B) 10; (C) 25; (D) 50 wt% PEOx

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