Interpolymer complexes in the poly(styrene-*co*-allyl alcohol)/poly(*N*-methyl-*N*-vinylacetamide) system

Jie Dai, S. H. Goh*, S. Y. Lee and K. S. Siow
Department of Chemistry, National University of Singapore, Singapore 0511, Republic of Singapore
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Poly(styrene-*co*-allyl alcohol) (SAA) with hydroxyl contents of 4.5 and 6.5 wt% can form intermolecular complexes with poly(*N*-methyl-*N*-vinylacetamide) (PMVAc) depending on the nature of the solvent(s) and the feed compositions that are used. When methyl ethyl ketone was used as the solvent, complexation between SAA and PMVAc occurred at all feed compositions, but when tetrahydrofuran was used as the solvent, complexation occurred only when the feed was rich in SAA. However, only miscible blends were formed from *N,N*-dimethylformamide, a strong hydrogen bond breaking solvent. The compositions of the complexes are in the range of 50–70 mol% and 55–74 mol% of PMVAc for the SAA(4.5)/PMVAc and SAA(6.5)/PMVAc systems, respectively. Fourier transform infra-red spectroscopic studies showed the existence of hydrogen bonding interactions in the blends.

(Keywords: interpolymer complexes; poly(styrene-*co*-allyl alcohol); poly(*N*-methyl-*N*-vinylacetamide))

INTRODUCTION

Since the combined entropy contributions to the free energy involved in mixing two polymers is negligibly small, specific intermolecular interactions are generally required for the miscibility of polymer blends. If such interactions are strong enough to allow adequate long continuous intermolecular association along the different polymer chains, they can form interpolymer complexes. In their review of interpolymer complexes, Bekturow and Bimendina[1] classified interpolymer complexes into several types, which were based on the nature of the dominating interactions, such as stereocomplexes between stereoisomers caused by van der Waals interactions, polyelectrolytes or polyionic complexes stabilized mainly by ionic bonds, and complexes formed through hydrogen bonding.

Among the previously reported hydrogen bonding type of complexes, the majority of them are complexes between polyacids (proton donors) and water-soluble nonionic polymers (proton acceptors), such as poly(acrylic acid) (PAA)/poly(*N*-vinylpyrrolidone) (PVP)[2], poly(methacrylic acid) (PMAA)/PVP[2,3], PAA/poly(ethylene glycol) (PEG)[2], PAA/poly(vinyl methyl ether) (PVME)[4] and PAA/poly(ethyl oxazoline) (PEOx)[5]. Recently, Kwei and co-workers[6–8] reported the complex formation between phenol–formaldehyde resins or poly(vinylphenol) (PVPh), and tertiary amide polymers such as poly(*N,N*-dimethylacrylamide) (PDMA) and PEOx in several solvents. Their results indicated that although the phenolic hydroxyl group was a weaker proton donor than the carboxylic acid group in polyacids, polymers containing the former group can also form complexes with tertiary amide polymers. These results prompted us to further investigate whether polymers containing aliphatic hydroxyl groups, which are even weaker proton donors when compared to the phenolic species, can also form complexes with polymers containing substituted amide groups.

In our study, we chose poly(styrene-*co*-allyl alcohol) (SAA) as the proton donor and poly(*N*-methyl-*N*-vinylacetamide) (PMVAc) as the proton acceptor. It will be shown that SAA and PMVAc can form polymer complexes or miscible blends, depending on the nature of the solvent(s) and the feed compositions that are used.

EXPERIMENTAL

Materials

Two samples of poly(styrene-*co*-allyl alcohol) with reported hydroxyl group contents of 5.4–6.0 and 7.3–8.0 wt% were provided by Scientific Polymer Products and were dried *in vacuo* at 90°C for at least 2 days before use. Based on the relative difference in intensity between the phenyl protons at 6.3–7.4 ppm (5H) in the styrene repeat units and the protons of the hydroxymethyl groups at 2.8–3.95 ppm (3H) in the allyl alcohol repeat units in the n.m.r. spectra, the actual hydroxyl contents of the two SAA copolymers were found to be 4.5 and 6.5 wt%, respectively. The two copolymers are identified as SAA(4.5) and SAA(6.5) in this paper. The molecular weights of the polymers were determined with a Waters 410 gel permeation chromatograph, using polystyrene as a standard. The number- and weight-average molecular weights of SAA(4.5) were found to be

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* To whom correspondence should be addressed

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2140 and 4040, respectively, while those of SAA(6.5) were found to be 1750 and 3260, respectively.

N-methyl-*N*-vinylacetamide was purchased from Fluka and distilled at 5°C/12 mmHg before use. The distilled monomer was then polymerized 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 PMVAc were found to be 9550 and 15 000, respectively.

Preparation of polymer complexes and blends

Polymer complexes of SAA/PMVAc were obtained by mixing solutions containing 0.1 g of polymer per 10 ml of solvent. White precipitates formed immediately upon mixing; these were separated from the solution by centrifugation, washed with solvent and then dried *in vacuo* at 90°C for 1 week. For systems which did not form interpolymer complexes, the solutions were allowed to evaporate slowly, before the drying process, for at least 2 days. All of the complexes and the blends were stored in a desiccator to prevent absorption of moisture, and the nitrogen contents of the polymer complexes were determined by elemental analysis.

Glass transition temperature (T_g) *measurements*

A Perkin-Elmer DSC-4 differential scanning calorimeter was used to determine the glass transition temperatures (T_gs) of both the polymer complexes and the miscible blends. As PMVAc is highly hygroscopic, all the samples were preheated to 150°C and held at this temperature for 15 min to ensure the complete removal of any moisture and residual solvent. The scanning rate was 20°C min^{-1} and the T_g was taken as the initial onset of the change of slope in the differential scanning calorimetry (d.s.c.) curve. All of the reported T_g values are taken as the average 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}. Spectra 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. A N_2 purge was used to remove moisture in the sample chamber. Samples for *FT*i.r. analyses were prepared by solution casting onto KBr discs and then drying *in vacuo* at 90°C for at least 2 days.

Table 1 Experimental data of the SAA(4.5)/PMVAc system

Solvent	Feed composition PMVAc content (wt%)	(mol%)	Product[a]	Polymer complex Yield (wt%)	PMVAc content (mol%)	T_g (°C)
MEK	10	9.4	C	6.1	55.5	110
MEK	25	23.8	C	21.6	66.0	113
MEK	50	48.4	C	39.2	69.7	111
MEK	75	73.9	C	55.4	70.6	114
MEK	90	89.5	C	64.9	74.1	113
THF	10	9.4	C	4.3	60.2	114
THF	25	23.8	C	7.7	62.9	118
THF	50	48.4	C	9.4	69.1	119
THF	75	73.9	M	–	–	125[b]
THF	90	89.5	M	–	–	129[b]

[a] C, complex formation; M, miscible blend
[b] Represents the T_g of a miscible blend

Table 2 Experimental data of the SAA(6.5)/PMVAc system

Solvent	Feed composition PMVAc content (wt%)	(mol%)	Product[a]	Polymer complex Yield (wt%)	PMVAc content (mol%)	T_g (°C)
MEK	10	9.0	C	12.7	40.0	112
MEK	25	23.0	C	32.2	49.7	111
MEK	50	47.2	C	44.5	59.0	111
MEK	75	72.8	C	58.1	65.4	117
MEK	90	89.0	C	26.2	70.1	128
THF	10	9.0	C	6.9	59.8	114
THF	25	23.0	C	16.3	59.6	115
THF	50	47.2	C	21.7	63.5	118
THF	75	72.8	C	14.9	68.0	118
THF	90	89.0	M	–	–	128[b]

[a] C, complex formation; M, miscible blend
[b] Represents the T_g of a miscible blend

RESULTS AND DISCUSSION

Complex formation

Both SAA(4.5) and SAA(6.5) formed complexes with PMVAc in methyl ethyl ketone (MEK) solutions. The yields, as well as the compositions of the complexes, are shown in *Tables 1* and *2*.

For the SAA(4.5)/PMVAc system, the yields of complexes increased with an increasing PMVAc content of the feed. The compositions of the complexes, ranging from 55.5 to 74.1 mol% of PMVAc, depended on the feed composition. A similar dependence on feed composition has been observed for other systems, such as PVPh/PDMA[8], PVPh/PEOx[8] and PAA/ PEOx[5]. The T_gs of these complexes are in the range 110–114°C.

For the SAA(6.5)/PMVAc system, the yields of complexes also increased with the increasing PMVAc content of the feed, except for the case when the feed contained 90 wt% PMVAc. The compositions of the complexes, ranging from 40.0 to 70.1 mol% of PMVAc, also depended on the feed composition.

In contrast, when tetrahydrofuran (THF) was used as the solvent, SAA(4.5) formed complexes with PMVAc only when the feed contained 10–50 wt% PMVAc, and the yields of the complexes were much smaller than those obtained from the corresponding MEK solutions. For feed compositions of 75 and 90 wt% PMVAc, complexation did not occur. However, the blends that are obtained are miscible, as shown by their optical clarity and the existence of a single T_g in each blend.

SAA(6.5), with a higher allyl alcohol content, formed complexes with PMVAc for feed compositions of 10–75 wt% PMVAc, with the yields of these complexes being higher than those of the corresponding SAA(4.5)/ PMVAc complexes. The results show that a higher allyl alcohol content promotes complexation with PMVAc.

Complexation between SAA and PMVAc did not occur in *N*,*N*-dimethylformamide (DMF) and only miscible polymer blends were formed. *Figures 1* and *2* show, respectively, the T_g *versus* composition curves for DMF-cast SAA(4.5)/PMVAc and SAA(6.5)/PMVAc

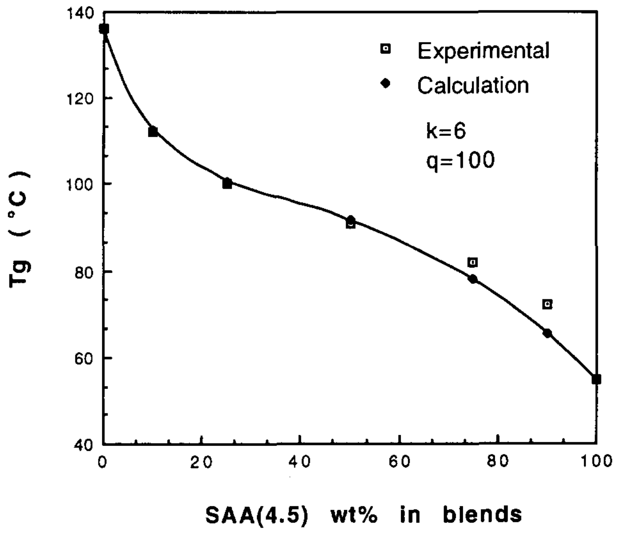

Figure 1 T_g *versus* composition curve of miscible blends of SAA(4.5)/PMVAc cast from DMF solutions

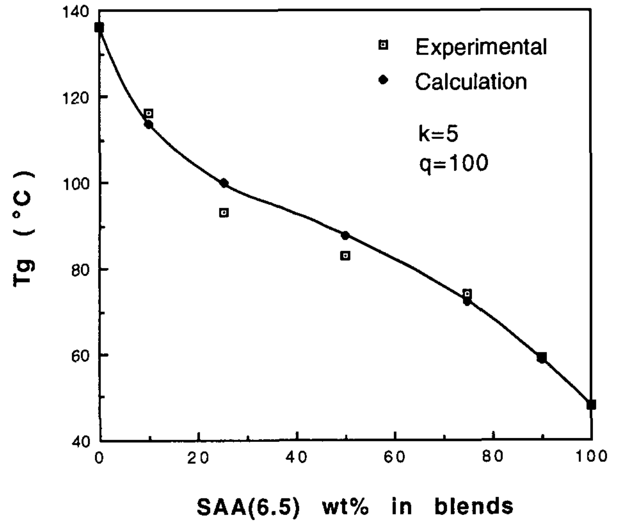

Figure 2 T_g *versus* composition curve of miscible blends of SAA(6.5)/PMVAc cast from DMF solutions

blends. Both of these curves are 'S-shape' in form, which can be satisfactorily fitted by the Kwei equation[10]:

$$T_g(\text{blend}) = (w_1 T_{g_1} + k w_2 T_{g_2})/(w_1 + k w_2) + q w_1 w_2$$

where k and q are fitting constants, and have values of 6 and 100, and 5 and 100 for the SAA(4.5)/PMVAc and SAA(6.5)/PMVAc systems, respectively. These 'S-shaped' T_g–composition curves are commonly observed for blends involving hydrogen bond interactions[9,10].

It has been previously established that since solvent can participate in hydrogen bond interactions, the nature of the solvent used has a profound effect on the formation of interpolymer complexes[1–3]. Complexation does not occur in a solvent which can effectively compete against this interpolymer association. Drago and co-workers[11] determined the enthalpies of adduct formation between t-butyl alcohol and various bases and found that there was a linear relationship between the enthalpy values and the frequency shift of the hydroxyl band. The latter are in the order, DMF > THF ≫ acetone, indicating a strong affinity between the hydroxyl moiety and DMF. Therefore, it is reasonable to conclude tht DMF competes effectively with PMVAc for the hydroxyl group of SAA, thus preventing the formation of interpolymer complexes. Wang and co-workers[7] have reported that PVPh forms complexes with PDMA in acetone and dioxane, but not in DMF.

FT *i.r. characterization*

Infra-red spectra can provide valuable information about intermolecular interactions in polymer blends. Coleman and his co-workers[12–14] have performed extensive work in this area. Their results show that the hydroxyl stretching vibration band at 3700–3100 cm^{-1} and the carbonyl stretching vibration band at 1800–1600 cm^{-1} are sensitive to hydrogen bonding from both the self-association of hydroxyl groups between like polymer chains, and also the intermolecular interactions between the hydroxyl groups in one chain and the carbonyl groups in another polymer chain. The frequency shifts of the above bands, caused by the crosslinking effect of hydrogen bonding along the polymer chains, and the relative intensity differences between the free and hydrogen bonded carbonyls can be employed to qualitatively (or even quantitatively) determine the extent of intermolecular hydrogen bonding which occurs between the different components in polymer blends. As SAA contains hydroxyl groups and PMVAc contains tertiary-amide type carbonyl groups in their polymer chains, blends of SAA/PMVAc are ideal systems for *FT*i.r. characterization. Hence, we have used this technique to show the existence of hydrogen bonding between the hydroxyl groups in SAA and the carbonyl groups in PMVAc.

Figure 3 shows the carbonyl stretching region, recorded at 140°C, of pure PMVAc and its miscible blends with SAA(4.5), for samples cast from DMF solutions. This temperature was chosen because it was higher than the

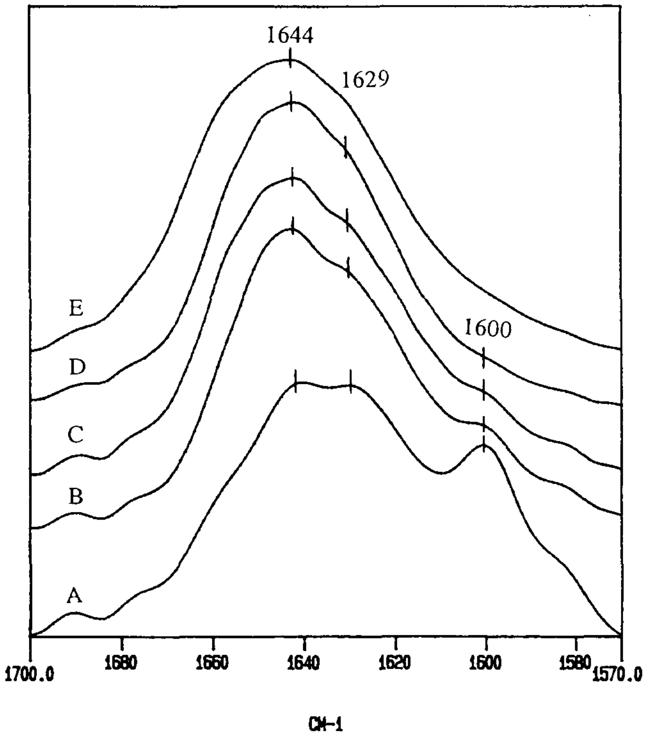

Figure 3 *FT*i.r. spectra, recorded at 140°C, of the carbonyl stretching region of pure PMVAc and its miscible blends with SAA(4.5) cast from DMF solutions: (A) 10; (B) 25; (C) 50; (D) 75 and; (E) 100 wt% PMVAc

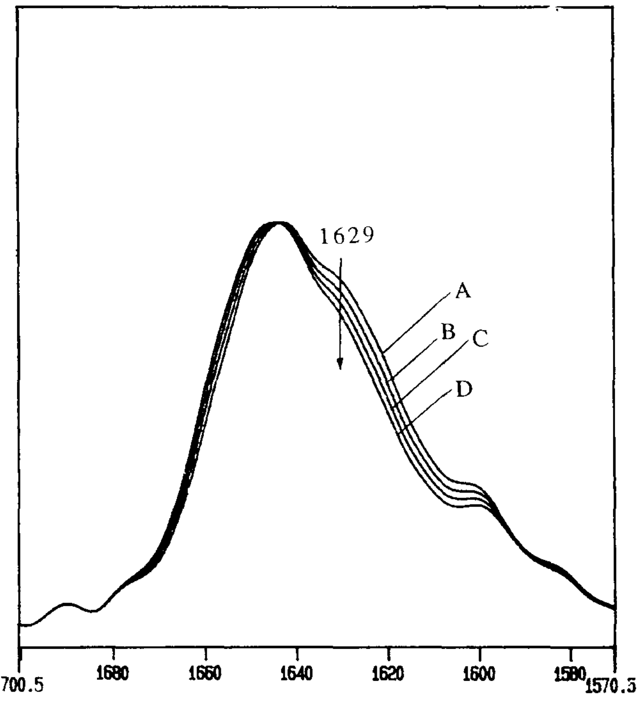

Figure 4 *FT*i.r. spectra of the carbonyl stretching region of the SAA(4.5)/PMVAc miscible blend containing 25 wt% PMVAc, cast from DMF solutions, recorded at: (A) 140°C; (B) 160°C; (C) 180°C and; (D) 200°C

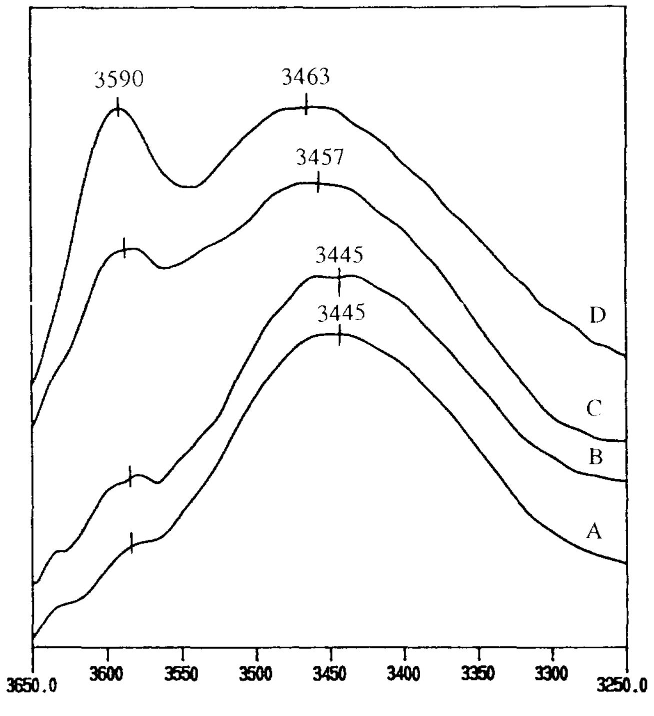

Figure 5 *FT*i.r. spectra, recorded at 140°C, of the hydroxyl stretching region of pure SAA(4.5) and its miscible blends with PMVAc cast from DMF solutions: (A) 50; (B) 25; (C) 10 and; (D) 0 wt% PMVAc

T_gs of both of the component polymers, and, therefore, any previous thermal history of the blends would be eliminated and moisture in the sample could be completely removed. The carbonyl stretching band of pure PMVAc (see curve E) is centred at 1644 cm^{-1}. Upon mixing with SAA(4.5), two additional peaks appear in the carbonyl region of PMVAc. The first, which appears at 1600 cm^{-1}, is attributed to the vibration of the aromatic ring in SAA(4.5), as it can also be clearly observed in the spectra of the pure component. The second peak, at 1629 cm^{-1}, is ascribed to carbonyl groups hydrogen bonding with the hydroxyl groups of SAA(4.5), since it does not appear in either of the spectra of pure SAA(4.5) or pure PMVAc. As shown in *Figure 3*, an increase in the SAA(4.5) content in the blends leads to an increase in the relative intensity of the hydrogen bonded carbonyl peak at 1629 cm^{-1}, when compared with the free carbonyl peak at 1644 cm^{-1}, indicating that further carbonyl groups are involved in hydrogen bonding with hydroxyl groups when the SAA concentration in the blends is increased. The temperature dependence of the carbonyl region, measured for a SAA(4.5)/PMVAc blend which contains 25 wt% PMVAc, is shown in *Figure 4*. This reveals that the contribution of the hydrogen bonded carbonyls at 1629 cm^{-1} decreases, resulting from a dissociation of the intermolecular hydrogen bonding between the carbonyl and the hydroxyl groups as the temperature is increased.

The spectra of the hydroxyl stretching region can also provide evidence of the existence of intermolecular hydrogen bonding between the component polymers. *Figure 5* depicts this region over the range 3650–3250 cm^{-1} for pure SAA(4.5) and its miscible blends with PMVAc, recorded at 140°C. The top spectrum of pure SAA(4.5) (curve D) has a band at 3590 cm^{-1}, which is attributed to free hydroxyl groups, and a broad band centred at 3463 cm^{-1}, representing a wide distribution of hydrogen bonded or self-associated hydroxyl groups. As the PMVAc content in the blend increases, the intensity of the free hydroxyl band at 3590 cm^{-1} decreases, indicating an increasing contribution of these groups to the intermolecular association with the carbonyl groups. This peak almost disappears when the PMVAc content reaches 25 wt% in the blend. Meanwhile, the centre of the broad hydrogen bonded hydroxyl band shifts from 3463 cm^{-1} for pure SAA(4.5) to 3445 cm^{-1} for the blend containing 50 wt% of PMVAc. Since such a frequency shift can be regarded as a measure of the average strength of the intermolecular interactions[14], the above results show that the average strength ($\Delta\nu = 145$ cm^{-1}) of the hydrogen bonding between the tertiary-amide type carbonyl groups in PMVAc and the aliphatic hydroxyl groups in SAA is stronger than that ($\Delta\nu = 127$ cm^{-1}) of the self-associated hydroxyl groups. Thus, we can conclude from these *FT*i.r. studies that the miscibility between SAA and PMVAc arises from the intermolecular hydrogen bonding interactions between the hydroxyl groups in SAA and the carbonyl groups in PMVAc.

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