FT-IR Spectroscopy and Hydrogen Bonding Interactions in Poly(styrene-*co*-methacrylic acid)/Poly(styrene-*co*-4-vinyl pyridine) Blends

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Summary: This contribution reports on a FT-IR study of the hydrogen bonding interactions within blends of different ratios of poly(styrene-*co*-methacrylic acid) containing 15 mol% of methacrylic acid PSMA-15 and poly(styrene-*co*-4-vinylpyridine) containing 15 mol% of 4-vinylpyridine PS4VP-15. Equilibrium constants describing both the self-association K_2 and inter-association K_A in the (75:25) blend of poly(styrene-*co*-methacrylic acid) containing 12 mol% of methacrylic acid PSMA-12 with poly(styrene-*co*-4-vinylpyridine) containing 22 mol% of 4-vinylpyridine PS4VP-22 were experimentally determined using a curve fitting analysis of the infra-red spectra. The FT-IR study at various temperatures confirms the miscibility of this blend up to 175 °C.

Keywords: FT-IR spectroscopy; hydrogen bonding polymer blends; poly(styrene-*co*-methacrylic acid); poly(styrene-*co*-4-vinylpyridine)

Introduction

It is well known that blending two polymers is an important and economical way to prepare a material with predetermined properties. Unfortunately, in most cases, and due to the very low entropy of mixing and the unfavourable enthalpy of mixing, mixtures of non-polar high polymer pairs are immiscible. The introduction of sufficient densities of interacting species that develop specific interactions within the dissimilar components of a blend enhances their miscibility. Many miscible polymer blends are reported in the literature.[1–5]

Poly(methacrylic acid) PMAA is known to form interpolymer complex with poly(4-vinylpyridine) P4VP.[6] We have in previous studies reported that depending on the solvent used, the nature and the densities of the specific groups introduced within the polymeric chains and the chain stiffness, miscibility blends or interpolymer complexes based were obtained.[7–9]

Recently, Coleman et al.[10] carried out a study of blends of poly(styrene-*co*-methacrylic acid) containing 9 mol% of methacrylic acid and poly(styrene-*co*-2-vinylpyridine) containing 17 mol% of 2-vinylpyridine and showed that the specific interactions between the two constituents of the blends are of moderate strength and of hydrogen bonding type.

Fourier transform Infrared Spectroscopy is a powerful tool to explore interactions in a polymer blend. In fact, Hydrogen bonding interactions alter the energy of the covalent bonds on interactive species. For example, perturbations occur in stretching modes as in the carbonyl-hydroxyl interactions or in flexion modes as

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in the pyridine-hydroxyl interactions. FT-IR spectroscopy displays well these modifications in terms of intensity, shift or band width. Curve fitting analysis can be performed to quantitatively characterise these interactions.

The purpose of this work is an attempt to dilute the strong interactions that occurred between PMAA and P4VP, by introduction of high amount of styrene moieties within these two strongly interacting polymers. In a first step, we characterize the hydrogen bonding in a poly(styrene-*co*-methacrylic acid) containing 15 mol% of methacrylic acid PSMA-15 and its blends with poly(styrene-*co*-4-vinylpyridine) containing 15 mol% of 4-vinylpyridine PS4VP-15. In a second step, quantitative analysis of the interactions in a (75:25) PSMA-12/PS4VP-22 blend is performed as a function of temperature. Using the Painter-Coleman association model,[2] self-association and inter-association equilibrium constants K_2, K_A and the enthalpy of hydrogen bonding formation are calculated from the infra-red spectra of this blend.

Experimental

Polymers and Characterizations

Poly(styrene-*co*-methacrylic acid) and poly(styrene-*co*-4-vinylpyridine) of different styrene contents were synthesized by solution free radical polymerization at 60 °C using azobisisobutyronitrile as the initiator and THF as the solvent. The copolymers were purified by several reprecipitation from dilute THF solution into an excess of methanol and dried under vacuum for several days.

The pyridine content in PS4VP copolymers was determined by elemental nitrogen analysis. The methacrylic acid content in PSMA copolymers was determined by standard titration in a benzene/methanol mixture or by UV spectroscopy. The molecular weights of some of these polymers were determined by GPC using a Waters 510 HPLC equipped with three calibrated styragel columns and using THF as the eluent. The glass transition temperatures were determined at a heating rate of 20 K/min, using a DSC-7 Perkin Elmer differential scanning calorimeter. Intrinsic viscosities were determined at room temperature in THF using an Ubbelohde viscometer.

The characteristics of the copolymers used in this study are summarized in Table 1.

TGA Analysis

Coleman et al.[11] reported that copolymers of styrene and methacrylic acid containing less than 10 mol% of methacrylic acid are stable up to temperatures of 240 °C with minimal anhydride formation. In our study, TGA were performed on a TA Instruments Q500 thermogravimetric analyser. As displayed in Figure 1, the TGA curve for the PSMA-29 confirms the stability of not only this copolymer but of copolymers of lower content of methacrylic acid. As the content of methacrylic acid increases within the copolymers as with the PSMA-45, a first degradation step takes place around 180 °C.

Experimental conditions: sample weight = 3.54 mg, method: ramped at 10 °C/min under nitrogen flow.

FT-IR Measurements

Dilute solutions (2% w/v in THF) of these copolymers and their blends were prepared and no precipitation occurs. Thin films were cast from these solutions onto KBr discs

Table 1.
Polymer characteristics.

Copolymers	Styrene content	M_w	T_g	$[\eta]^{THF}$
	%	$kg \cdot mol^{-1}$	K	$dl \cdot g^{-1}$
Poly(styrene-*co*-methacrylic acid)				
PSMA-12	88	–	398	0.840
PSMA-15	85	85,2	393	0.775
PSMA-29	71	–	429	0.925
Poly(styrene-*co*-4-vinylpyridine)				
PS4VP-06	94	7,9	376	–
PS4VP-15	85	5,5	383	–
PS4VP-22	78	–	385	–

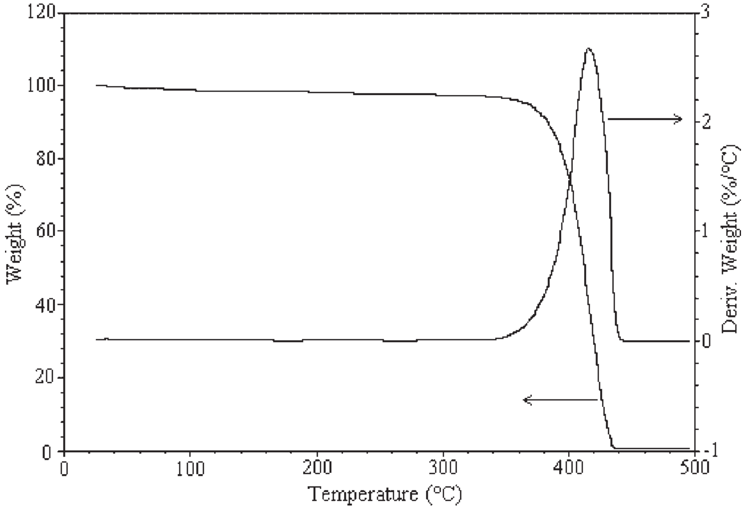


Figure 1.
TGA analysis of PSMA-29. Weight loss (and its derivative) as a function of temperature.

and then dried in a vacuum oven for several days. Infrared spectra of these copolymers and of their blends of different ratios were recorded on a Nicolet 550 Fourier Transform infrared spectrometer with a resolution of 2 cm^{-1} and averaged over 64 scans. The temperature study was carried using a SPECAC high-temperature cell equipped with an automatic controller mounted on the spectrometer. Each spectrum of the (75:25) PSMA-12/PS4VP-22 blend recorded in the considered temperature range (25–175 °C) on heating or on cooling was taken after a stabilization time.

Theoretical Background

The association model approach is described in detail in the monograph of Coleman et al.[2] According to this model, the following interaction schemes describes the competing equilibria in PMAA/P4VP system:

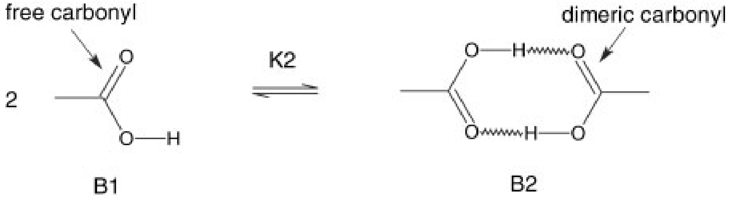
Free carboxylic acid groups (B1) in PMAA self-associate as cyclic dimers (B2) free carboxylic acid (B1) and free pyridine (A1) groups in PMAA/P4VP blend inter-associate to form the (BA) species

Where the self-association equilibrium constant (scheme 1) is given by:

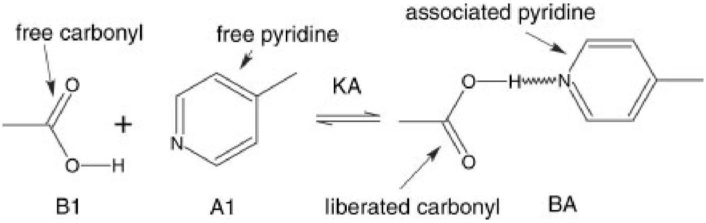
$$K_2 = \frac{\phi_{B_2}}{\phi_{B_1}^2}\left[\frac{1}{2}\right] \qquad (1)$$

and the inter-association equilibrium constant (scheme 2) is given by:

$$K_A = \frac{\phi_{BA}}{\phi_{B_1}\phi_{A_1}}\left[\frac{r}{1+r}\right] \qquad (2)$$



Scheme 1.



Scheme 2.

The stoichiometry of the system is given by

$$\phi_{B_1} + \phi_{B_2} + \phi_{A_1} + \phi_{BA} = 1 \qquad (3)$$

$$\Phi_B = \phi_{B_1}\left[1 + \frac{K_A \phi_{A_1}}{r}\right] + 2K_2\phi_{B_1}^2 \qquad (4)$$

$$\Phi_A = \phi_{A_1}(1 + K_A\phi_{B_1}) \qquad (5)$$

where ϕ_i, Φ_i and r are the volume fraction of the polymer segment containing the i species, volume fraction of interacting polymer in the blend and the ratio of the molar volumes V_A/V_B respectively, while the index B and A relates to self-associated polymer (B) which can interassociates with polymer (A) respectively.

From the above, the fractions of the free and liberated carbonyl ($f_{free}^{C=O}$, $f_{lib}^{C=O}$) and the free and associated pyridine ($f_{free}^{pyr}, f_{ass}^{pyr}$) can be deduced:

$$f_{free}^{C=O} = \frac{\phi_{B_1}}{\Phi_B} \qquad f_{free}^{pyr} = \frac{\phi_{A_1}}{\Phi_A} \qquad (6,7)$$

$$\phi_{BA} = f_{ass}^{pyr}\Phi_A\frac{1+r}{r} \quad \text{or}$$
$$\phi_{BA} = f_{lib}^{C=O}\Phi_B(1+r) \qquad (8,9)$$

As the specific groups are diluted in styrene co-monomer, equilibrium constants can be transferred to a standard value by the relations:

$$K_2^{copolymer}V_B = K_2^{std}100$$
$$K_A^{copolymer}V_A = K_A^{std}100 \qquad (10,11)$$

100 cm^3 is taken as a standard volume.

At various temperatures, equilibrium constants are related to enthalpy and entropy of hydrogen bond formation via the well known Van't Hoff-relationship.

Results and Discussion

Figure 2 shows the scale expanded FT-IR spectra recorded at room temperature of PSMA-15/PS4VP-15 blends of different compositions at different wavenumber ranges. The stretching mode of the hydroxyl in the 3600–3100 cm^{-1} region (Figure 2a) shows two small bands at 3530 and 3445 cm^{-1} attributed to free hydroxyl acid groups and hydroxyl-π electrons interactions respectively.

The 2800–2200 cm^{-1} region is dominated by the band attributed to carboxylic acid dimers satellite band (Figure 2b). A composition effect is observed in this region. As previously reported,[7–9,13] this band centred at 2630 cm^{-1} for PSMA-15, shifts progressively to lower wavenumbers (up to 2515 cm^{-1}) and its intensity increases as PS4VP-15 is added to the blend. This is also an evidence of the presence of carboxyl-pyridine interactions.

The band corresponding to acid carbonyl stretching has a strong absorption in the 1780–1650 cm^{-1} region (Figure 2c). Since there is no significant absorbance of PS4VP-15 in this region, the evolution of acid carbonyl modes is observed without interferences.

Using an adequate spectral curve fitting procedure, performed with Grams 386, three bands are observed with PSMA-15 at 1739 cm^{-1}, 1723 cm^{-1} and 1698 cm^{-1} and are respectively attributed to free, liberated and associated carboxylic groups as cyclic dimers. Similar results were obtained with PSMA-29 with a slightly more intense 1723 cm^{-1} band.

Y. Ozaki et al.[12] observed four bands with poly(acrylic acid) in the carbonyl stretching region at 1742 cm^{-1}, 1723 cm^{-1},

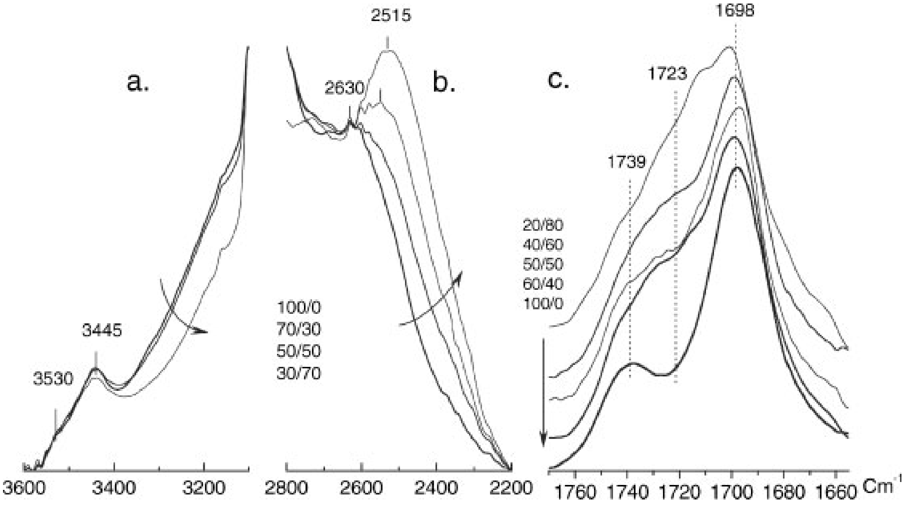


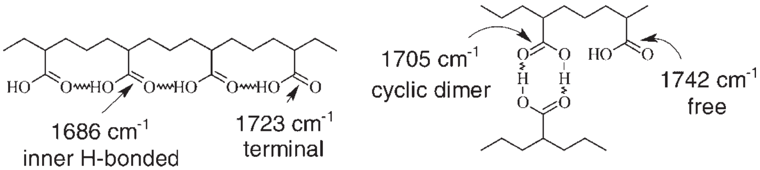
Figure 2.
Scale expanded FT-IR spectra recorded at room temperature obtained on films of as indicated PSMA-15/PS4VP blends.

1705 cm^{-1} and 1686 cm^{-1}. These authors attributed the 1686 cm^{-1} and the 1723 cm^{-1} bands respectively to the inner hydrogen bonded carbonyl groups and to the free terminal carbonyl group of a chain-like self-associated COOH as shown in Scheme 3.

As PS4VP-15 is added to PSMA-15, the intensities of both free and associated carboxylic bands tend to decrease. A new band appears at 1723 cm^{-1} for blends containing an excess of PS4VP-15. This latter band, assigned to carbonyl groups that are liberated as a result of carboxyl-pyridine interactions or a weakening of the cyclic carboxylic dimers, broadens and shifts to a lower frequency as the content of the basic PS4VP-15 copolymer increases.

A quantitative analysis of the interactions that occurred between PSMA-15 and PS4VP-15 was carried out in this carbonyl region. The fractions of the three carbonyl bands as determined using an appropriate spectral curve fitting procedure are summarized in Table 2. The fraction of the liberated carbonyl groups increases with the PS4VP-15 content in the blend.

It has been reported by several authors,[14–16] that the pyridinic flexion mode observed at 1597 cm^{-1} is perturbed as a result of hydrogen bonding interactions in systems involving P4VP and hydroxyl containing polymers. A new spectral contribution appears at higher wavenumbers attributed to associated pyridine. Unfortunately, the phenyl groups absorb in the same region in PSMA-15/PS4VP-15 blends. Although a quantitative analysis is rather difficult in this region, an attempt to determine the fraction of the free pyridine was carried out using a Lorentzian curve



Scheme 3.
Possibilities for the carbonyl groups in relation to hydrogen bonding.

Table 2.
Curve-fitting data from FT-IR carbonyl region of PSMA-15/PS4VP-15 blends.

PSMA-15 weight fraction	% Area			Fraction		
	% A_{free}	% A_{lib}	% A_{dim}	f_{free}	f_{lib}	f_{dim}
1.0	0.220	0.040	0.740	0.236	0.043	0.721
0.8	0.145	0.115	0.740	0.155	0.123	0.721
0.7	0.210	0.165	0.625	0.223	0.175	0.602
0.6	0.185	0.220	0.595	0.196	0.233	0.572
0.5	0.170	0.220	0.605	0.185	0.233	0.582
0.4	0.175	0.225	0.600	0.185	0.238	0.577
0.2	0.175	0.265	0.560	0.184	0.279	0.536

Data obtained by fixing the positions and widths at half-height (ν, $W_{1/2}$ cm^{-1}) of free (1739, 21) and dimeric (1698, 27 cm^{-1}) carbonyls in the 1780–1650 cm^{-1} region. The absorptivity ratio[11 equals to 1.1.

fitting procedure (fixing the positions and widths for the phenyl bands) and using the following equation:[17]

$$f_{\text{free}}^{\text{pyr}} = \frac{A_{1597}}{A_{1597} + A_{1606}} \tag{12}$$

where A_{1597} and A_{1606} are the areas of the bands at 1597 cm^{-1} and 1606 cm^{-1} respectively assuming an absorptivity ratio of unity. Table 3 shows the curve fitting data, while Figure 3 displays the volume fractions of the different species present in this system as a function of the volume fraction of PSMA-15.

The volume fraction of interacting acid-pyridine species (BA) has a bell-shaped curve with a maximum at around 50:50 (v/v) PSMA-15/PS4VP-15 blend composition. As expected, free pyridine volume fraction increases while both free and dimeric acids volume fractions decrease as the volume fraction of PS4VP-15 increases in the blend. The different evolution rate between free and dimeric acids, suggests that the fraction of interacting carboxylic groups is the contribution of breaking dimers rather than of free groups.

Table 3.
Curve-fitting data from FT-IR aromatic band of PSMA-15/PS4VP-15 blends.

PSMA-15 weight fraction	% Area		Mole fraction	
	% A_{free}	% A_{ass}	f_{free}	f_{ass}
0.8	0.275	0.725	0.275	0.725
0.7	0.255	0.745	0.255	0.745
0.6	0.240	0.760	0.240	0.760
0.5	0.310	0.690	0.310	0.690
0.4	0.520	0.480	0.520	0.480
0.2	0.745	0.255	0.745	0.255

Data obtained by fixing the positions and widths at half-height (ν, $W_{1/2}$ cm^{-1}) of phenyl (1601, 10) and (1583, 7) and of free (1597, 10) pyridine in the 1630–1570 cm^{-1} region.

A similar study was carried out with PSMA-15/PS4VP-6 and PSMA-12/PS4VP-6 blends of different ratios at room temperature. The fraction of liberated carbonyl groups using such a basic copolymer, containing only 6 mol% of 4-vinylpyridine, was not sufficient to be analyzed with minimum experimental error in the recommended composition range.[18]

We then carried out a FT-IR study on the (75:25) PSMA-12/PS4VP-22 blend as a function of temperature.

FT-IR Analyses at Different Temperatures

Figure 4 displays the evolution of spectral contributions as a function of temperature of the (75:25) PSMA-12/PS4VP-22 blend in the 1780–1650 cm^{-1} and 1630–1560 cm^{-1} regions. These spectra were recorded at different temperatures, on heating from room temperature to 175 °C and then by cooling the sample with a slow rate to room temperature.

Tables 4 and 5 summarize the curve fitting results in the carbonyl and aromatic regions both on heating and on cooling.

The results show that in the carbonyl (1780–1650 cm^{-1}) region, on heating and cooling to below the glass transition

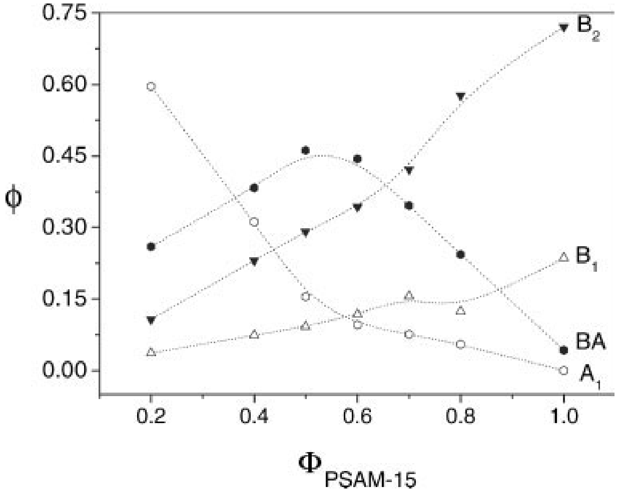


Figure 3.

Plot of experimental volume fraction distributions of B_1, B_2, BA and A_1 species versus the volume fraction of PSMA-15 in the PSMA-15/PS4VP-15 blend. Volume fractions are obtained using equations above and assuming that the constituents of the blend are of the same densities.

temperature, small changes only are observed in the positions, widths and fractions of free, dimeric and liberated carbonyls.

However above the glass transition temperatures: from 125 °C to 175 °C, the position of the band characteristic of liberated carbonyl groups shifts to lower wavenumbers and its width broadens as the temperature is raised. This may be explained by a new spectral contribution from weakened dimers that may exist as open chains at high temperature. The

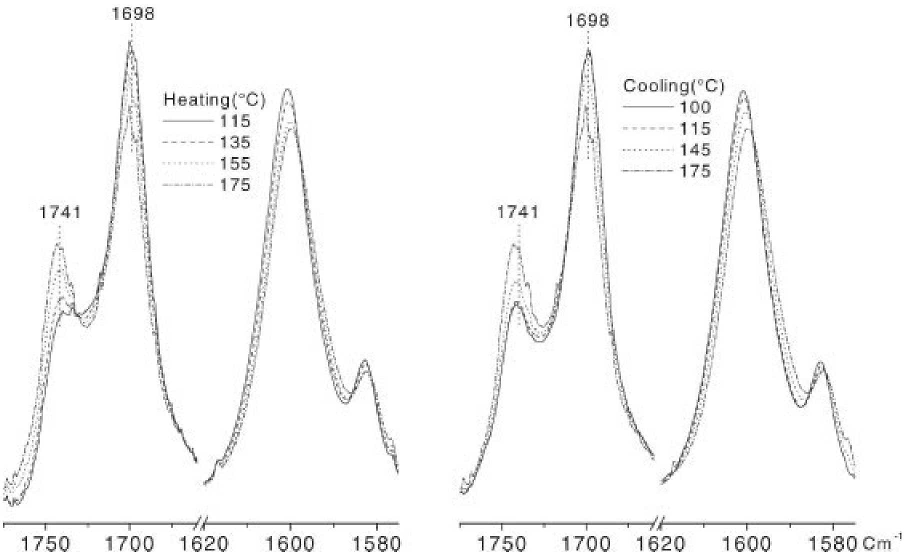


Figure 4.

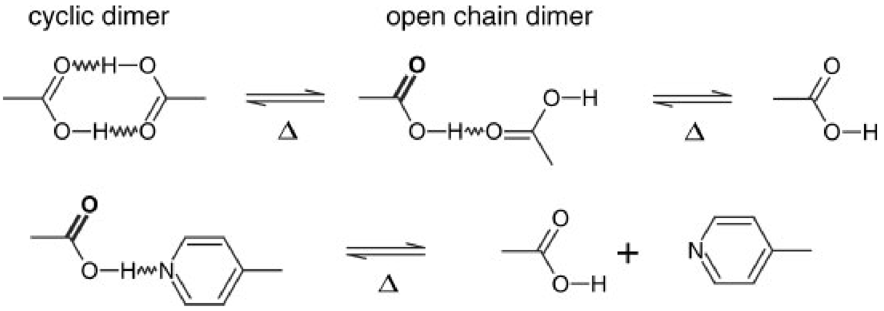
Scale-expanded FT-IR spectra obtained on a film of a (75:25) PSMA-12/PS4VP-22 blend recorded as a function of as indicated heating or cooling temperatures.

Table 4.
Curve-fitting data from the carbonyl band of 75/25 PSMA-12/PS4VP-22 blend on heating from 25 to 175 °C and cooling to room temperature.

T	ν			Width at ½ height			Mole fraction		
°C	cm^{-1}			cm^{-1}			f_{free}	f_{lib}	f_{dim}
	ν_{free}	ν_{lib}	ν_{dim}	w_{free}	w_{lib}	w_{dim}			
25	1742.8	1724.2	1698.1	17.3	33.8	21.6	0.135	0.210	0.656
115	1742.6	1726.5	1699.3	17.3	33.5	24.7	0.139	0.235	0.626
125	1742.7	1726.7	1699.5	17.6	33.7	24.8	0.148	0.225	0.627
135	1742.7	1725.7	1699.6	18.6	35.6	24.7	0.180	0.218	0.603
145	1743.1	1726.9	1699.9	18.6	35.8	25.3	0.195	0.208	0.598
155	1743.0	1724.4	1700.0	20.0	39.4	25.1	0.240	0.193	0.566
165	1742.9	1717.1	1699.8	21.4	46.1	23.9	0.289	0.230	0.481
175	1743.5	1712.5	1699.8	21.8	48.7	22.6	0.307	0.300	0.392
145	1742.8	1715.2	1699.5	22.3	47.4	23.5	0.263	0.228	0.509
125	1742.8	1721.2	1699.3	22.2	46.5	24.3	0.225	0.183	0.592
115	1742.7	1720.5	1699.2	22.1	48.5	24.0	0.221	0.193	0.586
100	1742.8	1720.7	1699.0	22.2	47.2	23.9	0.223	0.179	0.598
25	1742.7	1726.1	1698.0	21.0	42.6	21.4	0.205	0.134	0.661

Table 5.
Curve-fitting data from the aromatic band of 75/25 PSMA-12/PS4VP-22 blend on heating from 25 to 175 °C and cooling to room temperature.

T	ν				Width at ½ height				Mole Fraction	
°C	cm^{-1}				cm^{-1}				f_{ass}	f_{free}
	ν_{ass}	$\nu_{styrene}$	ν_{free}	$\nu_{styrene}$	w_{ass}	w_{1600}	w_{free}	w_{1583}		
25	1606.4	1601.5	1595.3	1583.2	8.85	9.5	7.7	5.5	0.788	0.212
115	1605.5	1600.5	1594.2	1582.5	10.4	11.7	9.1	6.8	0.723	0.277
125	1605.4	1600.4	1594.3	1582.4	10.3	11.7	9.7	7.0	0.654	0.346
135	1605.4	1600.4	1594.7	1582.3	10.0	11.7	10.9	7.2	0.527	0.473
145	1604.9	1600.2	1594.7	1582.2	10.3	11.6	11.1	7.3	0.510	0.490
155	1605.0	1600.2	1594.7	1582.1	10.0	11.6	11.4	7.5	0.429	0.571
165	1604.7	1600.1	1594.7	1581.9	9.9	11.3	11.9	7.9	0.394	0.606
175	1604.4	1599.8	1594.9	1581.8	9.3	11.1	12.4	8.2	0.364	0.636
145	1605.0	1600.2	1594.5	1582.2	10.4	11.6	11.1	7.2	0.519	0.481
125	1605.2	1600.4	1594.2	1582.4	11.0	11.5	10.0	6.9	0.673	0.327
115	1605.7	1600.6	1594.1	1582.6	10.4	11.9	9.4	6.7	0.683	0.317
100	1605.8	1600.7	1594.4	1582.7	10.6	11.5	9.5	6.5	0.702	0.298
25	1606.9	1601.6	1594.2	1583.3	9.5	10.7	7.0	5.9	0.754	0.246



Scheme 4.
Dimerization possibilities.

Table 6.
Experimental volume fractions of different species and calculated equilibrium constants of the (75:25) PSAM-15/PS4VP blend at different temperatures.

T °C	f_{B1}	f_{B2}	f_{A1}	$f_{BA\ C{=}O}$	$f_{BA\ Pyr}$	K_2	$K_A^{C{=}O}$	K_A^{pyr}
25	0.101	0.492	0.212	0.243	0.560	24.1	15.9	36.7
115	0.104	0.470	0.069	0.272	0.514	21.6	13.2	25.1
125	0.111	0.471	0.087	0.260	0.465	19.1	9.5	17.0
135	0.135	0.452	0.118	0.252	0.374	12.4	5.5	8.3
145	0.144	0.450	0.123	0.241	0.362	10.9	4.8	7.2
155	0.180	0.427	0.143	0.220	0.305	6.6	3.0	4.2
165	0.219	0.369	0.152	0.251	0.280	3.8	2.7	3.0
175	0.231	0.294	0.143	0.347	0.258	2.8	3.3	2.5
145	0.197	0.380	0.120	0.266	0.369	4.9	3.9	5.5
125	0.169	0.444	0.082	0.211	0.478	7.8	5.4	12.2
115	0.165	0.441	0.079	0.222	0.485	8.0	5.9	13.0
100	0.167	0.449	0.075	0.206	0.499	8.0	5.8	14.0
25	0.154	0.496	0.061	0.155	0.536	10.5	5.8	20.0

modes of liberated carbonyl (bolded style in Scheme 4) are overlapped resulting in a broad band.

It is also observed that the fraction of the free carbonyl increases with temperature at the expense of the carboxylic dimers and the liberated carbonyl. As can be seen from Table 4 the positions and widths of the three bands remain practically constant below the glass transition temperatures on cooling from 175 °C to room temperature.

As shown in Table 5, curve fitting data obtained from infra-red spectra in the pyridine 1630–1560 cm^{-1} region showed that the fraction of the hydrogen bonded pyridine ring decreases as the temperature increases and varied slightly on heating or cooling to room temperature. These results

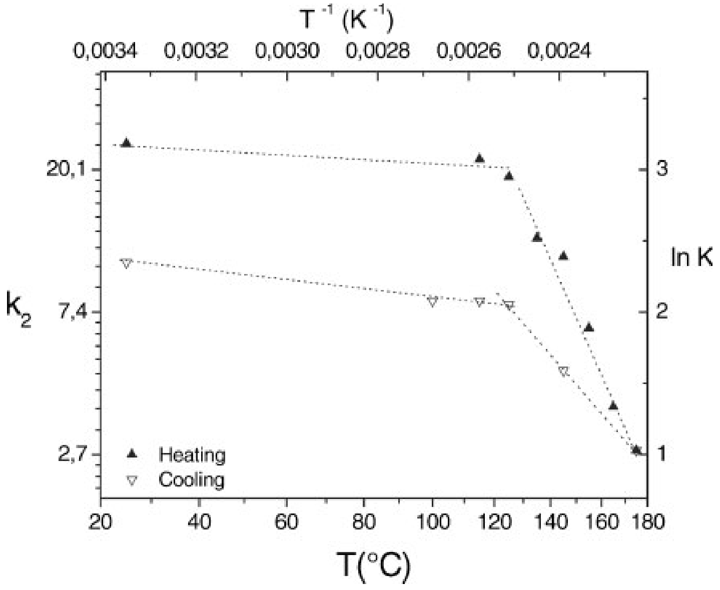


Figure 5.
Van't Hoff plot of K_2 (logarithmic scale) versus temperature (reciprocal scale) of 75/25 PSMA-12/PS4VP-22 blend. The slope differs on either different thermal treatment (heating or cooling) or temperature range (below or above T_g).

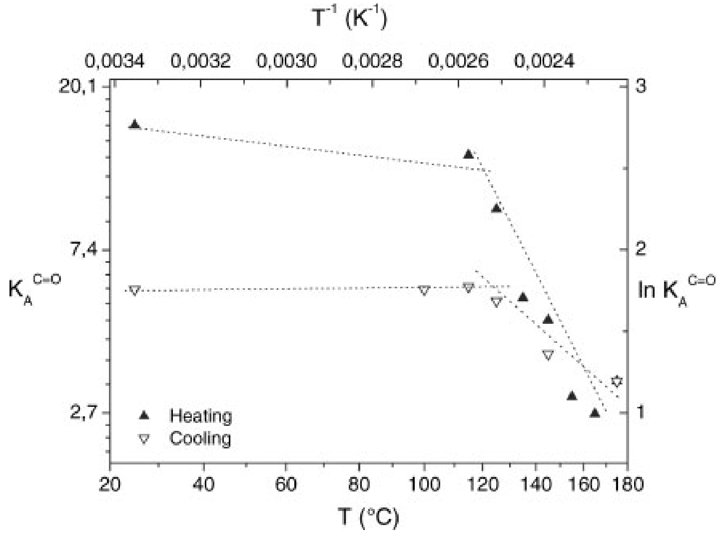


Figure 6.
Van't Hoff plot of K_A (logarithmic scale) versus temperature (reciprocal scale) of 75/25 PSMA-12/PS4VP-22 blend. The slope differs on either different thermal treatment (heating or cooling) or temperature range (below or above T_g).

confirm the miscibility of this blend and that phase separation does not occur even at 175 °C.

The interactions between the constituents of the blend are defined by the self-association and inter-association equilibrium constants K_2, K_A and the enthalpy of hydrogen bonding formation. These are calculated from the infra-red spectra of the (75:25) PSMA-12/PS4VP-22 blend using

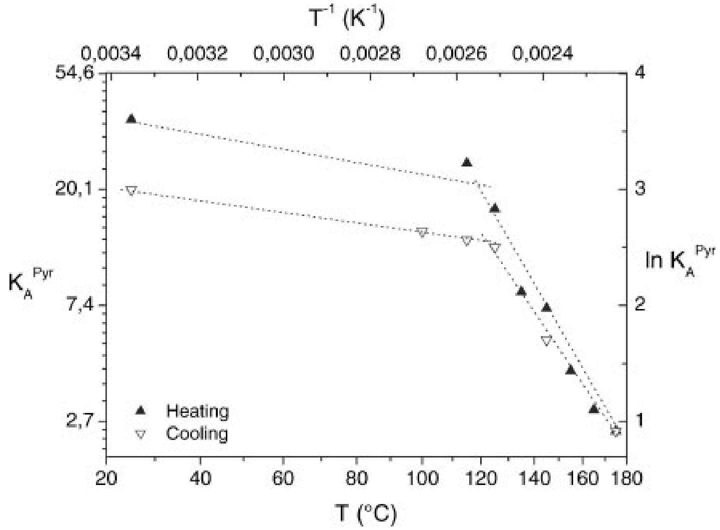


Figure 7.
Van't Hoff plots of K_A (logarithmic scale) versus temperature (reciprocal scale) of 75/25 PSMA-12/PS4VP-22 blend. The slope differs on either different thermal treatment (heating or cooling) or temperature range (below or above T_g).

Table 7.
Thermodynamic data obtained on cooling in the 175–125 °C temperature range.

	Linear fit	$-h$ (kcal · mol^{-1})	K_{eq}(25 °C)	K_{eq}^{std}
K_2	$-07.11 + 3.64\ 10^3\ T^{-1}$	07.20	163	$1.26\ 10^3$
K_A^{pyr}	$-11.65 + 5.61\ 10^3\ T^{-1}$	11.12	$1.3\ 10^3$	$5.40\ 10^3$

The molar volumes of PSMA-12 and PS4VP-22 are calculated by group contributions as 770.8 and 418.2 cm^3 mol^{-1}. K(25 °C) are extrapolated to room temperature using the van't Hoff equation. K^{std} are calculated using equations (10,11).

the appropriate equations derived from the Painter-Coleman association model.[2]

The self-association constant was calculated from equation (1). The inter-association constant K_A was calculated from equation (2) using the volume fraction ϕ_{BA} deduced from equations (8) and (9) and noted as K_A^{pyr} and $K_A^{C=O}$ respectively. Table 6 shows the obtained results for this (75:25) particular blend. As it can be seen from these results, both K_2 and K_A decrease with an increase of temperature.

Figures 5–7 display plots of lnK versus the reciprocal of temperature. As expected, important differences are observed in the behavior of these constants above or below 125 °C attributed to glass transition temperature, both on heating or on cooling of the blend.

Table 7 summarizes the thermodynamic data for the PSMA-12/PS4VP-22 on cooling in the 175–125 °C temperature range.

The calculated values of standard self-association equilibrium constant and enthalpy of hydrogen bonding formation ($K_2^{std} = 1.26\,10^3, h = -7.2\,\text{kcal} \cdot \text{mol}^{-1}$) using data on cooling above T_g are in agreement with that reported by Coleman et al.[11] for poly(styrene-*co*-methacrylic acid) containing 9 mol% of methacrylic acid.

As shown above, the spectral contribution of liberated carbonyl is rather a wide distribution of overlapping species. For this reason, the interassociation equilibrium constant K_A^{pyr} seems to interpret well the carboxyl-4-vinylpyridine interaction.

The distribution of the volume fractions of the different species as a function of

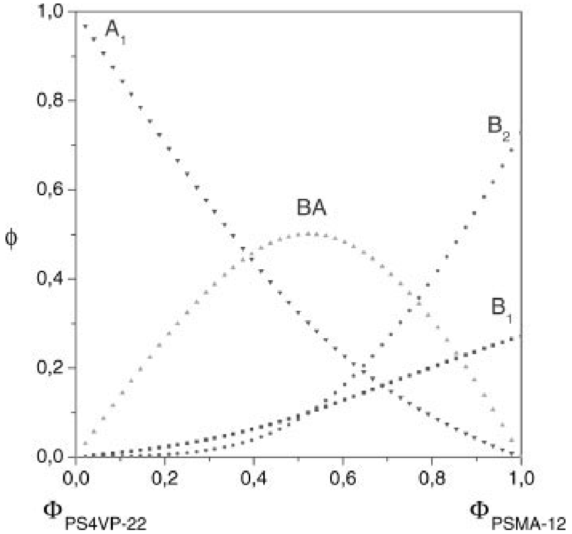


Figure 8.
Plot of theoretical volume fraction distributions of B_1, B_2, BA and A_1 species versus the volume fraction of PSMA-12 in the PSMA-12/PS4VP-22 blend at 145 °C (on cooling).

blend composition at 145 °C (on cooling) is calculated using the appropriate values of the molar volumes and the obtained equilibrium constants and is shown in Figure 8.

Conclusion

The miscibility of PSMA/PS4VP blends (containing high amounts of styrene) and due to the presence of specific interactions of hydrogen bonding type was confirmed qualitatively and quantitatively by FTIR spectroscopy. The temperature study carried out on the (75:25) PSMA-12/PS4VP-22 blend showed that this system is miscible up to 175 °C. Using the Painter-Coleman association model, quantitative analysis of the interactions in this blend can be performed. Self-association and inter-association equilibrium constants K_2, K_A and the enthalpy of hydrogen bonding formation are calculated from the infra-red spectra of this blend.

The obtained results showed that both of K_2 and K_A decrease with increasing temperature, as expected. The inter association carboxyl-4-vinylpyridine interaction constant, determined from the fraction of associated pyridine confirms the miscibility of the PSMA-12/PS4VP-22 even at 175 °C.

The values of standard K_2 and h, calculated on cooling above T_g are in agreement with that reported.[11]

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