Hydrogen-Bonding Interactions Between Poly(styrene-*co*-methacrylic acid) and Poly(styrene-*co*-4-vinylpyridine)

Sadjia Bennour, Farid Metref, Said Djadoun

Laboratoire des Matériaux Polymères, Faculty of Chemistry, University of Sciences and Technology, Houari Boumediene, BP 32, El Alia, Algiers, 16111, Algeria

ABSTRACT: The complexation behavior between poly-(styrene-*co*-methacrylic acid) of different compositions (SMA-12 or SMA-29) and poly(styrene-*co*-4-vinylpyridine) (S4VP-6 or S4VP-15) was studied by viscometry and differential scanning calorimetry using tetrahydrofuran (THF) and butan-2-one as solvents. This complexation is attributed to the presence of strong intermolecular interactions between the different polymer chains by hydrogen bonding. A single glass-transition temperature, intermediate between those of the two pure copolymers SMA-29 and S4VP-15, was obtained with each composition of the mixture when THF or butan-2-one is used as a common solvent. The obtained results showed that the formation of such complexes depends strongly on the nature of the solvent and the contents of the interacting species. The complex formation is inhibited in THF because of the important ability of this latter to interact with the SMA. A quantitative analysis of the interactions between the constituents of these blends was carried out by FTIR spectroscopy. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 806–811, 2005

Key words: specific interactions; glass transition; interpolymer complexes; blends; FTIR

INTRODUCTION

The introduction of small proportions of groups capable of developing hydrogen-bonding interactions between the polymers in a blend is known as a miscibility enhancement method.[1–4] It has also been reported[5–9] that under certain conditions, interpolymer complexes are formed as the contents of interacting species within the polymers are increased. The complexation of polymers has been extensively studied recently. Several polymer–polymer complexes such as poly(vinylpyridine)/poly (*n*-alkylitaconates),[10] poly(2-hydroxypropyl methacrylate)/poly(*N,N*-dimethylacrylamide),[11] poly(styrene-*co*-vinylphenol)/poly(styrene-*co*-4-vinylpyridine),[12] and poly (vinylphenol)/poly(*N,N*-dimethylacrylamide)[13] were reported. The polymer–polymer complexation was studied by different techniques such as nonradiative energy transfer fluorospectroscopy,[12,14] laser light scattering,[8,15] viscometry[7,8,16] and FTIR.[17–19] Many factors, particularly the nature of the solvent, the temperature, the feed composition, and the concentration were found to affect the formation of polymer complexes. Depending on the type of interactions, other classes of polymer complexation such as stereocomplexation, polyelectrolyte complexation, or charge-transfer complexation were also reported in the literature.[8,20,21]

In this article, we present some of the results of a viscometry, DSC, and FTIR study of mixtures of different compositions of poly(styrene-*co*-methacrylic acid) containing 12 or 29 mol % of methacrylic acid with poly(styrene-*co*-4-vinylpyridine) containing 6 or 15 mol % of 4-vinylpyridine.

EXPERIMENTAL

Poly(styrene-*co*-4-vinylpyridine) (S4VP-6 or S4VP-15) containing 6 or 15 mol % of 4-vinylpyridine, respectively, and poly(styrene-*co*-methacrylic acid) (SMA-12 or SMA-29) containing 12 or 29 mol % of methacrylic acid were prepared by free-radical polymerization at 60°C, using azobisisobutyronitrile (AIBN) as initiator. Styrene contents in these copolymers were determined by UV spectroscopy and elemental analysis. The methacrylic acid content in the SMA copolymers was also determined by standard titration technique in a mixture of benzene/methanol.

Viscosity measurements of these copolymers or of their mixtures were carried out manually using a capillary Ubbelohde viscometer in butan-2-one and in tetrahydrofuran (THF) at 25°C.

The intrinsic viscosities in THF were of 0.840, 0.925, and 0.495 dL/g for SMA-12, SMA-29, and S4VP-6, respectively.

Blends of different ratios of SMA-29/S4VP-15 were prepared by codissolution of the polymers in a com-

Correspondence to: S. Djadoun (djadounsaid@hotmail.com).

mon solvent (THF). Films were generated from polymeric solutions with evaporation of solvent with pure polymers or in the case of formation of blends. The same operation was carried out in a common solvent butan-2-one. The precipitates (complexes) were separated. All the samples (films and precipitates) were dried in a vacuum oven for several days. A DSC-7 differential scanning calorimeter (Perkin–Elmer Cetus Instruments, Norwalk, CT) was used to determine the glass-transition temperature of the copolymers and of their mixtures. All measurements were carried out at a heating rate of 20 K/min under a nitrogen blanket.

Thin films of these copolymers and of their blends were cast from THF solutions with a concentration of 2% w/v onto KBr discs and then dried in a vacuum oven at 70°C for several days. FTIR spectra of these copolymers and of their blends of different ratios were recorded on a model 550 Fourier transform infrared spectrometer (Nicolet Instrument Technologies, Madison, WI) at room temperature with a resolution of 2 cm^{-1} and were averaged over 60 scans.

RESULTS AND DISCUSSION

Viscometry

Viscometry is a widely used technique to study not only miscibility of polymer blends but also interpolymer complexation arising from the presence of hydrogen-bonding interactions of different amounts between the constituents of the mixtures. Several studies were carried out and showed that the formation of interpolymer complexes in dilute solution accompanies a contraction of the component polymer chains. This implies a decrease in the reduced viscosity.[5,12]

Before measurements of the reduced viscosities of the polymer mixtures, qualitative compatibility tests were carried out using THF or butan-2-one as a common solvent. When THF was the common solvent, homogeneous solutions were obtained. The precipitation was obtained with all binary mixtures of copolymers when butan-2-one was used as the solvent. The total concentration of the two constituents of these blends used in the reduced viscosity measurements was kept at 0.1 g/dL below the critical concentration.

The reduced viscosity of the binary blends of SMA-12/S4VP-6 or SMA-29/S4VP-6 varied linearly with the weight fraction of SMA-12 or SMA-29, respectively, when THF was used as a solvent. This may be considered as evidence of weak specific interpolymer associations, given that the solvent THF has an important ability to form hydrogen bonding and interacts with the acidic SMA and inhibits the complex formation. Copolymers containing higher amounts of interacting species are expected to form interpolymer complexes in this solvent.

A different behavior was observed when butan-2-one was used as the solvent; that is, the ability of
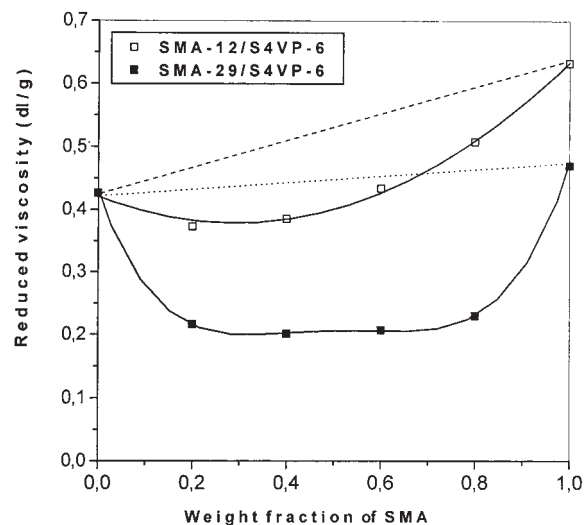

Figure 1 Reduced viscosity versus the weight fraction of SMA of SMA/S4VP-6 blends in butan-2-one at 25°C.

butan-2-one to form hydrogen bonds is lower than that of THF. As shown in Figure 1, negative deviations of the reduced viscosity of the SMA-12/S4VP-6 or SMA-29/S4VP-6 solutions from those calculated by the additivity rule, more pronounced with solutions containing higher methacrylic acid content, were observed.

Such behavior is attributed to the formation of interpolymer complexes. A minimum that depends on the contents of the interacting species is observed at an approximately 1 : 1 ratio for SMA-12/S4VP-6 and SMA-29/S4VP-6 mixtures.

Differential scanning calorimetry

One glass-transition temperature (T_g), intermediate between the glass-transition temperatures of the two pure copolymers SMA-29 and S4VP-15, was observed from the DSC thermograms of the blends of the different compositions prepared in THF. This confirms the miscibility of this pair of polymers. SMA-29, however, was found to form interpolymer complexes with S4VP-15, as shown by the formation of precipitates just after mixing the two polymers in butan-2-one, a common solvent. The miscibility and the complexation of the SMA-29/S4VP-15 system were analyzed from the T_g composition in THF and butan-2-one. As shown in Figure 2, the T_g values of the blends or the complexes are all above the linear average line when butan-2-one and THF are used as solvents. The positive deviation of the T_g from the weight average of the glass-transition temperatures of the pure components is attributed mainly to specific polymer–polymer interactions (carboxylic acid–pyridine) that occurred between the components of the blends.
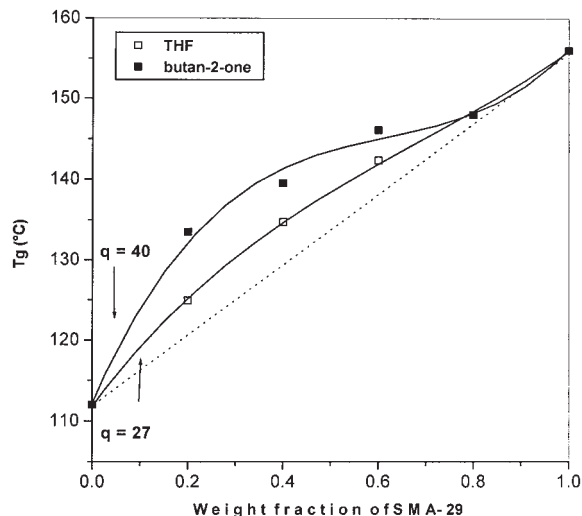
Figure 2 Glass-transition temperature versus the weight fraction of SMA-29 of SMA-29/S4VP-15 mixtures.

These specific interactions were estimated from the Kwei constant q obtained from the following equation[22]:

$$T_{gM} = w_1 T_{g1} + w_2 T_{g2} + q w_1 w_2 \qquad (1)$$

where w_1 and w_2 are the weight fractions of the components of the blend and T_{g1}, T_{g2}, and T_{gM} are the glass-transition temperatures.

According to Painter et al.,[23] the q parameter depends on the balance between the process of self-association and interassociations in the blend. We note that the q value for the SMA-29/S4VP-15 system in butan-2-one ($q = 40$) is higher than that obtained in THF ($q = 27$). These results confirm that hydrogen-bonding–specific interactions are stronger in butan-2-one than in THF, which provides evidence of inter-polymer complexation in the former case. The DSC results are in agreement with those obtained from the viscometry study.

Infrared spectroscopy

We have in a first step carried out a qualitative analysis of the specific interactions arising from hydrogen bonding between the carboxylic groups of the SMA and the pyridine groups of the S4VP in the most interesting regions.

Figure 3 shows the scale-expanded infrared spectra of SMA-29 and of its blends with S4VP-15 in the 2700–2200 cm^{-1} region. As we have previously reported with poly(α-methyl styrene-*co*-methacrylic acid)/poly(butyl methacrylate-*co*-4-vinylpyridine) blends,[24] in addition to the broad band centered at around 2630 cm^{-1}, characteristic of COOH dimers observed with the acidic copolymer, a new band of
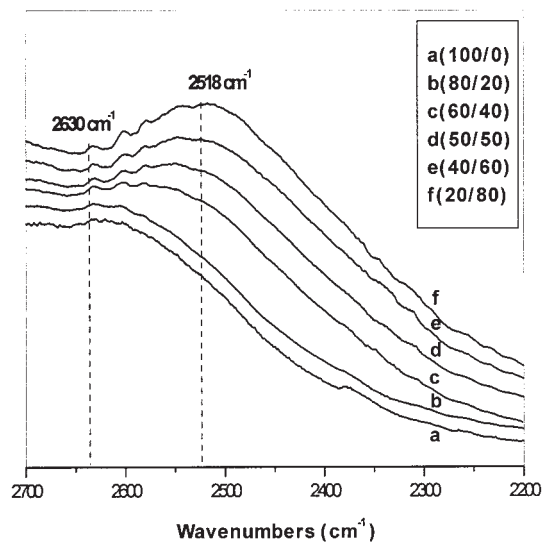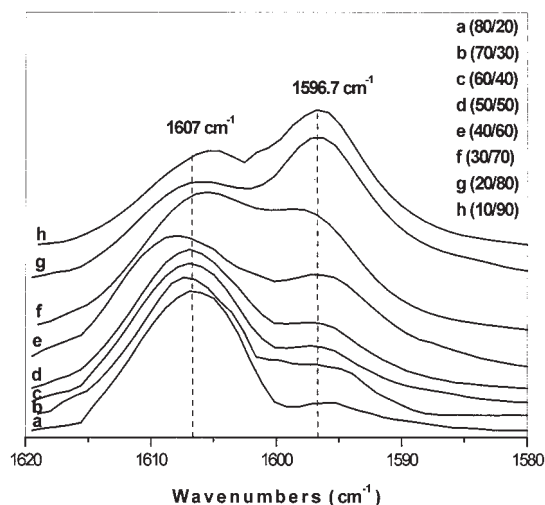

Figure 3 Scale-expanded FTIR spectra of SMA-29/S4VP-15 blends in the 2700–2200 cm^{-1} region recorded at room temperature.

increasing intensity appears at 2518 cm^{-1} as the basic S4VP copolymer is added to the blend, which is characteristic of carboxyl–pyridine interactions.

In the carbonyl-stretching 1780–1630 cm^{-1} region, the infrared spectrum of pure SMA-12 recorded at room temperature showed two peaks at 1740 and 1698 cm^{-1}, attributed to free and associated carboxylic groups, respectively. Similarly, SMA-29 shows also two peaks at 1737 and 1699 cm^{-1}. Qualitatively, as S4VP is added to SMA, the intensities of both bands are affected and a new band of increasing intensity appears at around 1723 cm^{-1}, as shown in Figure 4. This latter is attributed to carbonyl groups that are
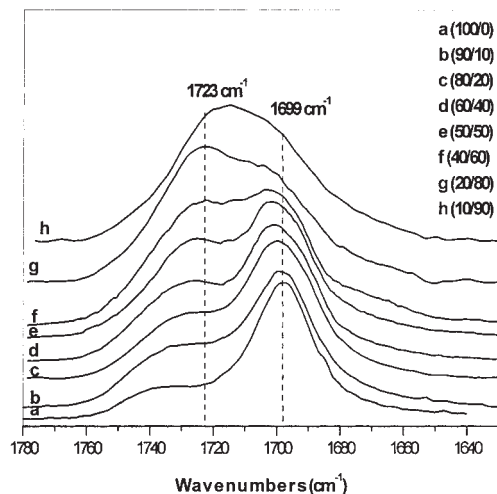
Figure 4 Scale-expanded FTIR spectra of SMA-29/S4VP-15 blends in the 1780–1630 cm^{-1} region recorded at room temperature.

Figure 5 Scale-expanded FTIR difference spectra (substraction of PS) bands of SMA-29/S4VP-15 blends in the 1620–1580 cm^{-1} region recorded at room temperature.

liberated as a result of hydroxyl–pyridine associations. As the content of pyridine groups within the S4VP increases, as in the SMA-29/S4VP-15 blends, the intensity of the liberated carbonyl groups increases compared to that in SMA-29/S4VP-6 blends.

It has been reported[25,26] in the 1620–1580 cm^{-1} region that the pyridinic ring mode, observed at 1597 cm^{-1} with poly(4-vinyl-pyridine) and attributed to free groups, is perturbed as a result of hydrogen-bonding interactions. Upon blending poly(4-vinyl-pyridine) with a polymer containing hydroxyl groups, a new band appears at higher wavenumbers. Qualitatively, as the content of S4VP-6 or S4VP-15 is added to SMA-29, the main band shifts to 1602 cm^{-1}. The substraction spectrum of polystyrene (PS) from those of the blends shows, in Figure 5, a band at 1596.7 cm^{-1} attributed to the free pyridine groups and a new band

at 1607 cm^{-1} characteristic of the associated pyridine groups.

In the second step an attempted quantitative analysis of the interactions that occurred between the SMA and S4VP was carried out in the carbonyl region in which the S4VP is transparent. The fractions of the relative areas related to the three carbonyl bands were determined by using Lorentzian and Gaussian spectral curve-fitting procedures after substraction of the PS spectrum. The wavenumbers of the three bands were fixed at 1737, 1723, and 1699 cm^{-1} for free, liberated, and associated carboxylic groups, respectively. The best results obtained with a Lorentzian spectral curve fitting are summarized in Table I. The fraction of the liberated carbonyl groups, arising from the hydroxyl–pyridine interassociations, increases with the S4VP content. The interpolymer associations that occurred with the SMA/S4VP blends mainly result from the decrease observed with the carboxylic dimers, depending strongly on the content of S4VP-15 in the blend, given that the fraction of the free carboxylic remains practically unchanged for blends containing an excess of the acidic copolymer.

As the content of pyridine groups within the S4VP increases as in the SMA-29/S4VP-15 blends, the fraction of the liberated carbonyl groups increases compared to that in the SMA-29/S4VP-6 blends. In the former case, the fraction of free carbonyl groups decreases as the S4VP-15 in the blend increases.

As the content of pyridine groups within the S4VP increases as in the SMA-29/S4VP-15 blends, the broadening of the dimeric and liberated carbonyl bands is significant.

A quantitative analysis of the interactions that occurred between the S4VP and the SMA in the 1620–1580 cm^{-1} region is rather difficult because the styrene groups absorb in the same region, and thus an attempt to determine the fraction of associated pyridine was

TABLE I
Curve-Fitting Data from Infrared Spectra of Substraction of PS from SMA-29/S4VP-15 Blends in the Carbonyl Region 1780–1630 cm^{-1} at Room Temperature

Weight %	Free C=O ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	Area fraction	Dimeric C=O ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	Area fraction	Liberated C=O ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	Area fraction
				(SMA-29/S4VP-15)–PS					
100/0	1737	23	0.17	1699	23	0.83	—	—	—
90/10	1737	21	0.18	1699	25	0.71	1723	20	0.11
80/20	1737	20	0.14	1699	25	0.71	1723	23	0.15
70/30	1737	19	0.12	1699	25	0.64	1723	22	0.24
60/40	1737	19	0.16	1699	25	0.62	1723	23	0.22
50/50	1737	16	0.09	1699	25	0.58	1723	25	0.33
40/60	1737	15	0.08	1699	27	0.54	1723	26	0.42
30/70	1737	13	0.02	1699	27	0.47	1723	28	0.51
20/80	1737	13	0.02	1699	28	0.40	1723	32	0.58
10/90	—	—	—	1699	28	0.43	1723	32	0.57

TABLE II
Curve-Fitting Data from Infrared Spectra of SMA-29/S4VP-15 Blends in the Pyridine Region 1620–1580 cm^{-1}
at Room Temperature

	Styrene				Free pyridine			Associated pyridine		
Weight %	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	Area fraction	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	Area fraction
					(SMA-29/S4VP-15)					
90/10	1583.0	6.10	1601.4	9.80	1596.7	10.00	0.188	1606.2	10.00	0.812
80/20	1583.0	5.90	1601.4	9.50	1596.7	10.33	0.208	1606.8	10.89	0.792
70/30	1583.0	6.30	1601.4	9.70	1596.7	11.00	0.249	1606.8	11.70	0.751
60/40	1583.0	5.85	1601.4	9.00	1596.7	10.00	0.255	1606.8	11.42	0.745
50/50	1583.0	5.75	1601.4	8.80	1596.7	10.50	0.282	1606.9	11.88	0.718
40/60	1583.0	6.00	1601.4	9.10	1596.6	11.73	0.438	1607.2	13.19	0.562
30/70	1583.0	5.50	1601.5	9.00	1597.0	10.50	0.480	1606.8	10.50	0.520
20/80	1583.1	6.05	1601.4	8.75	1596.7	10.13	0.614	1606.7	11.65	0.386
10/90	1583.0	6.40	1601.4	9.50	1596.7	10.12	0.667	1606.6	11.00	0.333
					(SMA-29/S4VP-15)–PS					
90/10	—	—	—	—	1596.0	10.00	0.102	1606.7	11.00	0.898
70/30	—	—	—	—	1596.0	10.00	0.173	1607.1	11.00	0.827
60/40	—	—	—	—	1596.0	10.00	0.181	1607.0	11.00	0.819
50/50	—	—	—	—	1596.0	10.00	0.211	1607.1	11.70	0.789
40/60	—	—	—	—	1596.0	10.00	0.363	1608.0	11.14	0.637
30/70	—	—	—	—	1596.5	11.00	0.384	1607.5	10.50	0.616
20/80	—	—	—	—	1596.3	10.00	0.590	1607.2	11.00	0.410
10/90	—	—	—	—	1596.7	12.00	0.632	1607.2	11.00	0.368

carried out using a Lorentzian curve-fitting procedure. The results of this analysis indicate three bands for S4VP at 1601, 1597, and 1583 cm^{-1} and two bands for SMA at 1601 and 1583 cm^{-1}. The fraction of free pyridine groups was calculated from the following relation[27]:

$$F_F^N = \frac{A_{1597}}{A_{1597} + \dfrac{a_{1597}}{a_{1607}}A_{1607}} \qquad (2)$$

where A_{1597} and A_{1607} are the areas of the bands at 1597 and 1607 cm^{-1}, respectively, and a_{1597} and a_{1607} are the absorptivities of the two bands, assuming an absorptivity ratio of unity.

The styrene ring-stretching bands were eliminated from the spectra of these copolymers and their blends of different ratios. In a similar way the fraction of free pyridine groups was calculated in this region.

Table II summarizes the curve-fitting data, whereas Figure 6 shows the fraction of the associated pyridine groups in the SMA-29/S4VP-15 blends as a function of SMA-29. As it can be observed, the fraction of associated pyridine groups to the hydroxyl groups of the SMA increases as the SMA content increases in the blend.

CONCLUSIONS

As a contribution to the study of miscibility–complexation transitions in polymer blend systems in-

duced by hydrogen bonding, SMA-12/S4VP-6, SMA-29/S4VP-6, and SMA-29/S4VP-15 blends were studied by viscometry, differential scanning calorimetry, and FTIR.

- Viscometry study revealed that in butan-2-one solution, SMA-12/S4VP-6 and SMA-29/S4VP-6 systems formed interpolymer hydrogen-bonding complexes, whereas these systems did not form complexes in THF. This study showed that the
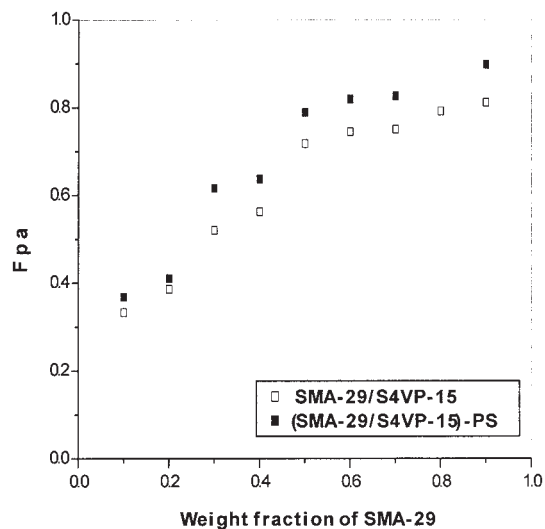
Figure 6 Fraction of associated pyridine groups (Fpa) versus the weight fraction of SMA-29.

formation of these complexes depends strongly on the nature of the solvent and the contents of the interacting species.

- The DSC results are in agreement with those obtained from the viscometry study.
- The qualitative analysis carried out by FTIR confirms the presence of the hydrogen-bonding interactions that occurred between the carboxylic and pyridine groups in the different regions.
- The quantitative analysis showed an increase of the fraction of the associated pyridine groups as the content of the SMA in the blend increases.

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