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Interactions in Miscible Blends of Poly(styrene-*co*-methacrylic acid) with Copolymers Containing Vinylpyrrolidone and Vinylpyridine Groups

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In this paper we report the results of infrared spectroscopic studies of styrene-*co*-methacrylic acid (STMAA) copolymer blends with styrene copolymers containing the complementary functional groups vinylpyrrolidone (VPr) and 2-vinylpyridine (VPy). The nature of the MAA/VPy interaction has been previously studied by several other research groups who were all in agreement that the interassociation between MAA and VPy groups is strong.[1−4] However, whether or not the interaction should be classified as ionic (complex) in nature or a strong hydrogen bond has been a subject of some debate. Zhou et al. compared complexes of poly(acrylic acid) (PAA) and poly(vinylpyridine) (PVPy) with those of poly(methacylic acid) (PMAA) and PVPy.[1] In essence, these researchers used a combination of FTIR and X-ray photoelectron spectroscopy (XPS) to study the nature of the interaction. Their results showed that hydrogen bonding is the principal interaction involving MAA and VPy groups in PMAA blends with PVPy, while in analogous PAA blends ionic interactions dominated. This they attributed to the higher acidity of PAA vis-à-vis PMAA.[2]

The work presented here involves the mixing of *copolymers* containing MAA with those containing VPr or VPy segments. The MAA and VPr (or VPy) segments are substantially “diluted” by copolymerization with “inert” styrene segments. Such mixtures do not precipitate from solution in a common solvent, and the formation of miscible blends is feasible. The styrene-*co*-vinylpyrrolidone (STVPr), styrene-*co*-2-vinylpyridine (STVPy), and styrene-*co*-methacrylic acid (STMAA) copolymers used in this study were synthesized in our laboratories, and details are contained in the theses of Motzer,[5] Zhang,[6] and Cleveland,[7] respectively. Blends of these copolymers were prepared by casting films onto KBr windows at room temperature from a 1% (w/v) solution in THF. Following air-drying at room temperature, the windows were placed in a vacuum oven overnight at 60 °C to completely remove the solvent. All films were thin enough to be within an absorbance range where the Beer−Lambert law is obeyed. Infrared spectra were recorded on a Digilab model FTS-45 Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm^{-1}. Thermal analysis was performed on a Seiko DSC-U220 differential scanning calorimeter. A heating rate of 20 °C min^{-1} was used, and glass transition temperatures were calculated as the midpoint of the heat capacity change.

We will commence with an examination of blends of STMAA{9} (a styrene-*co*-methacrylic acid copolymer containing 9 mol % MAA) with STVPr{13} (a styrene-*co*-2-vinylpyrrolidone copolymer containing 13 mol % VPr). We should point out that we deliberately chose to make blends of these two styrene-rich copolymers for the following main reasons. First, by “diluting” the MAA and VPr segments with essentially “inert” styrene segments, we reduce the possibility of phase separation during film formation as the solvent is evaporating. Second, the presence of significant amounts of styrene tends to minimize the difference in the average nonassociative solubility parameters of the two different copolymers, which, in turn, increases the probability of the formation of a miscible blend.[8] In fact, the solubility parameter difference between STMAA{9} and STVPr{13} is estimated at ≈0.1 (cal cm^{-3})$^{0.5}$, which, together with the obvious possibility of a strong intermolecular hydrogen-bonding interaction involving the VPr carbonyl group and the acidic proton of the MAA group, leads us to confidently predict a miscible system.[8] Blends of STMAA{9} and STVPr{13} are optically transparent, and DSC studies of 20:80; 50:50, and 80:20 wt % compositions exhibit single glass transition temperatures at 86, 84, and 79 °C—strong evidence for a single-phase system.[5] In common with a number of polymer blends that involve strong intermolecular interactions, there is a strong deviation from the Fox equation, and in fact, the T_g’s of the blends lie below both those of the pure materials (91 and 106 °C, respectively).

Since we have previously examined the infrared spectra of STMAA{9}[9] and recently discussed the ramifications of self-association on the infrared spectra of copolymers containing VPr segments,[10] we are in a position to summarize what we might expect to observe in the carbonyl stretching region of STMAA{9} blends with STVPr{13}. There are numerous possible interactions, and the most important are summarized in Scheme 1.

In the spectrum of pure STMAA{9} we should observe two bands in the carbonyl stretching region: a “free” (non-hydrogen-bonded) MAA carbonyl band, $\nu_{\mathrm{F(MAA)}}^{\mathrm{C=O}}$, at ≈1742 cm^{-1} and a hydrogen-bonded cyclic dimer band, $\nu_{\mathrm{HB(Dimer)}}^{\mathrm{C=O}}$, at ≈1700 cm^{-1}. On the other hand, in the spectrum of pure STVPr{13} only one carbonyl band should be present at ≈1684 cm^{-1}, which is attributed to “free” VPr groups, $\nu_{\mathrm{F(VPr)}}^{\mathrm{C=O}}$. In a miscible blend of STMAA{9} and STVPr{13} two additional bands are present. The first, at ≈1640 cm^{-1} is assigned to the VPr carbonyl group that is directly hydrogen bonded to the MAA hydroxyl group, $\nu_{\mathrm{HB(MAA/VPr)}}^{\mathrm{C=O}}$. This is a relatively strong hydrogen bond as evidenced by a large frequency shift of ≈44 cm^{-1} (from that of the $\nu_{\mathrm{F(VPr)}}^{\mathrm{C=O}}$). The second carbonyl band associated with the MAA/VPr interaction is a “free” carbonyl band, $\nu_{\mathrm{F(MAA/VPr)}}^{\mathrm{C=O}}$, at ≈1720 cm^{-1}, which is caused by the liberation of the MAA carbonyl group when the MAA hydroxyl group forms a hydrogen bond with the VPr carbonyl. Hence, at equilibrium in the spectrum of STMAA{9} and STVPr{13} blends we can anticipate at least five carbonyl bands that vary in relative intensity with composition and temperature.

All these bands are clearly observed in Figure 1, which summarizes the infrared spectral data recorded at room temperature, 150 °C, and 200 °C in the carbonyl stretching region (1600−1800 cm^{-1}) of pure STMAA-

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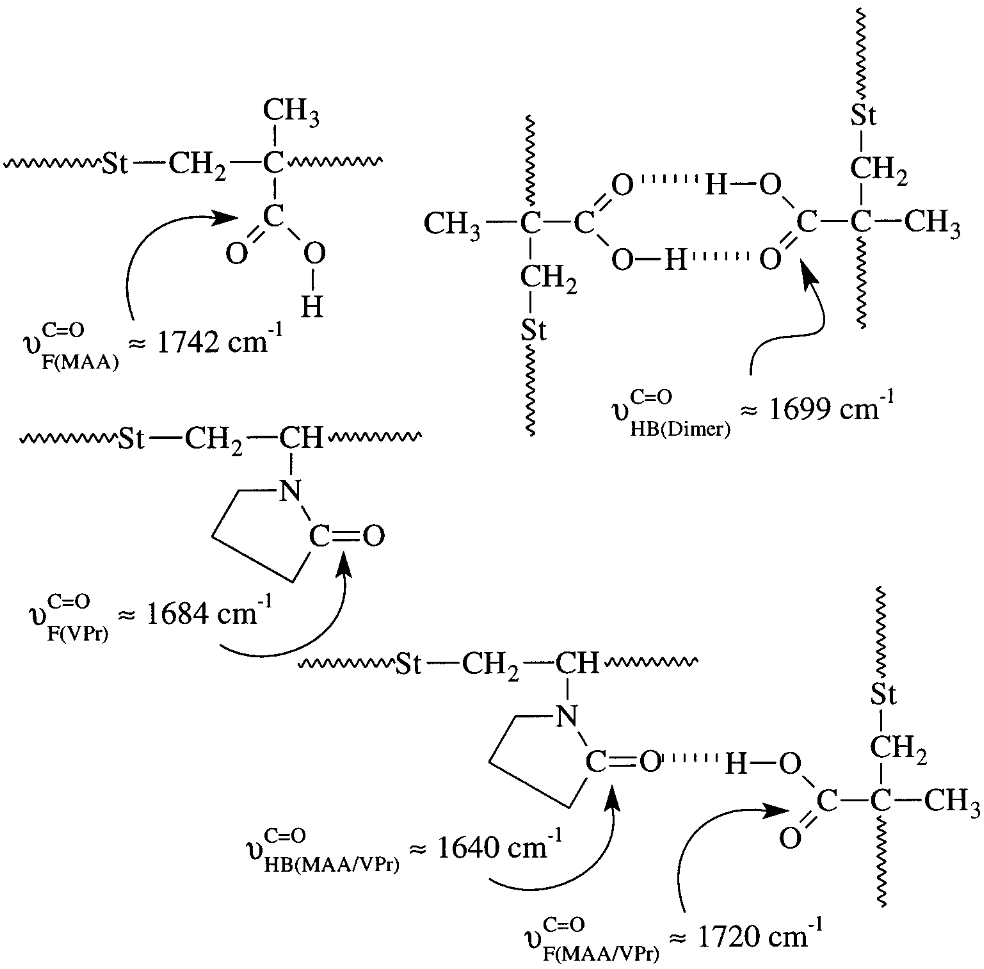
Scheme 1



{9}, pure STVPr{13}, and three blends of the two copolymers containing 80:20; 50:50, and 20:80 wt %. Note that as we increase temperature, the "free" $\upsilon^{C=O}_{F(MAA)}$ band in pure STMAA{9} increases in intensity at the expense of the hydrogen-bonded dimer $\upsilon^{C=O}_{HB(Dimer)}$ band (top spectra moving to the right). This is simply a reflection of an equilibrium process that dictates the fraction of hydrogen-bonded MAA groups should decrease with increasing thermal motion.[9] The "free" VPr group band, $\upsilon^{C=O}_{F(VPr)}$, on the other hand, just appears to broaden somewhat as the temperature is increased to 200 °C (bottom spectra moving to the right). This is more complicated than it looks. As we have pointed out previously, the VPr segment strongly self-associates through transition dipole coupling.[10] While "dilution" with the styrene comonomer reduces the magnitude of the transition dipole coupling, some of the inherent breadth of the $\upsilon^{C=O}_{F(VPr)}$ band is caused by this phenomenon. Raising the temperature should reduce the effect of transition dipole coupling resulting in a narrowing of the band, but this is offset somewhat by a slight broadening of isolated infrared bands with temperature. The bands associated with the intermolecular hydrogen-bonded interaction between the MAA and VPr segments, $\upsilon^{C=O}_{HB(MAA/VPr)}$ and $\upsilon^{C=O}_{F(MAA/VPr)}$, are clearly observed in the spectra of the blends (note particularly the room temperature spectra of the 80:20 and 50:50 blends). Looking at the spectra of the blends as a whole, they represent an excellent example of how the distribution of "free" and hydrogen-bonded species varies with composition and temperature. Given the complexity of these infrared spectra, one must exercise caution when attempting to characterize the carbonyl stretching region of the spectra of polymer blends containing the MAA and VPr segments.

Finally, we should briefly consider infrared frequency shifts and their relationship to the enthalpy of hydrogen bond formation.[8,11,12] Essentially, all other things being equal, the larger the shift of the hydrogen-bonded band from that of the "free" band ($\Delta\upsilon$), the greater the strength of the between the donor and acceptor groups. From the spectra of the STMAA{9}blends with STVPr{13}, the difference between the frequency of the $\upsilon^{C=O}_{F(MAA)}$ and $\upsilon^{C=O}_{HB(MAA/VPr)}$ bands is $\Delta\upsilon \approx 37$ cm^{-1}. This indicates that the strength of the hydrogen bond between MAA and VPr is substantial. If we compare this shift with that of the self-association of MAA ($\Delta\upsilon \approx 42$ cm^{-1}), where we have determined[9] the enthalpy of the individual hydrogen bond in the dimer to be $\approx$8.3 kcal/mol, it is apparent that the MAA/VPr hydrogen bond is $>$5 kcal/mol and most probably in the neighborhood of 6$-$7 kcal/mol.

Let us now turn our attention to STMAA{9} blends with a styrene-*co*-vinylpyridine STVPy{17}. Again, the choice of the common "diluent" styrene was deliberate as the solubility parameter difference between STMAA{9} and STVPy{17} is estimated at $\approx$0.2 (cal cm^{-3})$^{0.5}$, which, together with the obvious possibility of a strong intermolecular hydrogen-bonding interaction involving the lone pair of electrons of the VPy nitrogen atom and

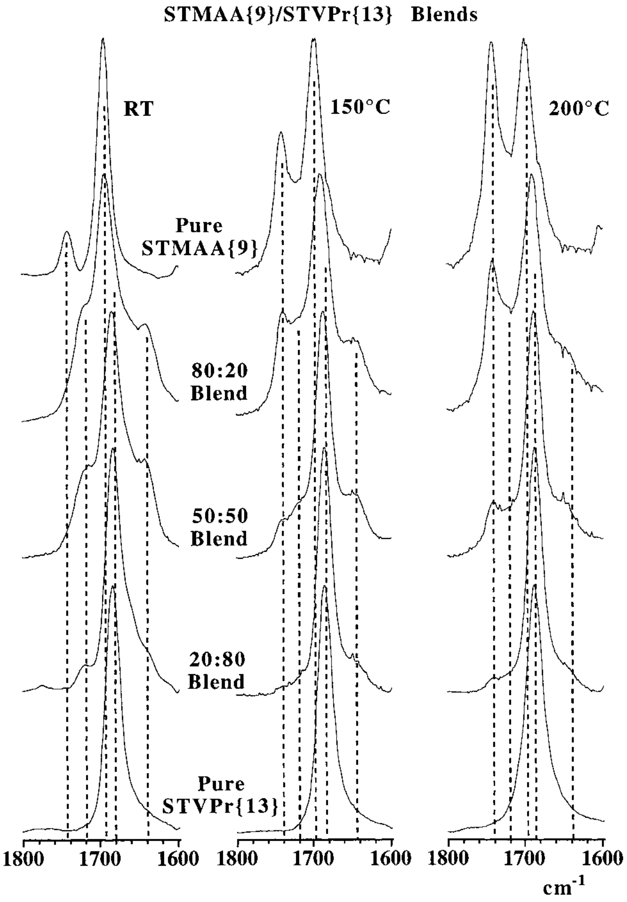


Figure 1. Infrared difference spectra of STMAA{9}/STVPr{13} blends (with the two phonon bands of the monosubstituted phenyl ring eliminated) recorded in the carbonyl stretching region at 25, 150, and 200 °C.

the acidic proton of the MAA group, leads us to confidently predict a miscible system.[8] Blends of STMAA{9} and STVPr{17} and are optically transparent, and DSC studies of 20:80; 50:50, and 80:20 wt % compositions exhibit single glass transition temperatures at 75, 79, and 84 °C—strong evidence for a single-phase system.[5] The T_g's of pure STMAA{9} and STVPy{17} are 78 and 99 °C, respectively, and as in the case of the STVPr blends, there is a strong deviation from the Fox equation.

Figure 2 shows a comparison of scale expanded room temperature FTIR spectra in the carbonyl stretching region (1650–1800 cm^{-1}) of pure STMAA{9}and films of 80:20, 50:50, and 20:80 wt % STMAA{9}:STVPy{17} blends.

Three major bands are clearly identified in the carbonyl stretching region (see Scheme 2): two we have described before, $\upsilon^{C=O}_{F(MAA)}$ at ≈1742 cm^{-1} and $\upsilon^{C=O}_{HB(Dimer)}$ at ≈1700 cm^{-1}, and a third at ≈1726 cm^{-1}, $\upsilon^{C=O}_{F(MAA/VPy)}$, which is attributed to "free" carbonyl groups formed when an interaction is formed between the VPy nitrogen atom and the hydroxyl group of MAA (interassociation). This is an equilibrium process, and with increasing concentration of STVPy{17} in the blend, the relative intensity of the VPy/MAA interassociation band at 1726 cm^{-1} increases at the expense of the "free" MAA (1742 cm^{-1}) and the hydrogen-bonded MAA dimers (1700 cm^{-1}).

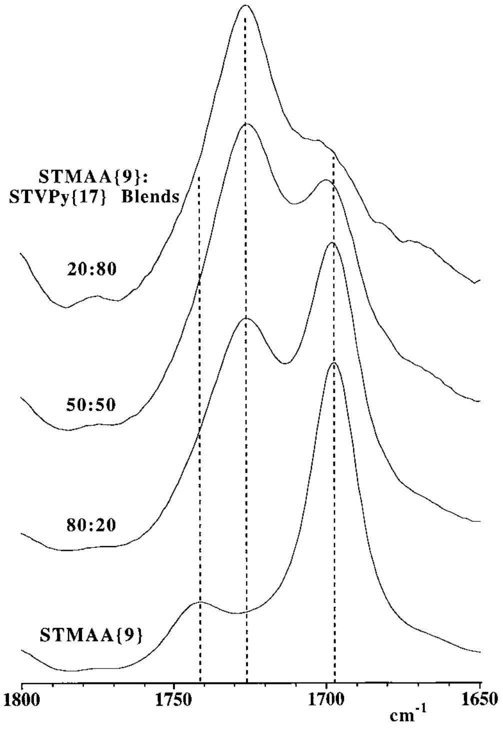
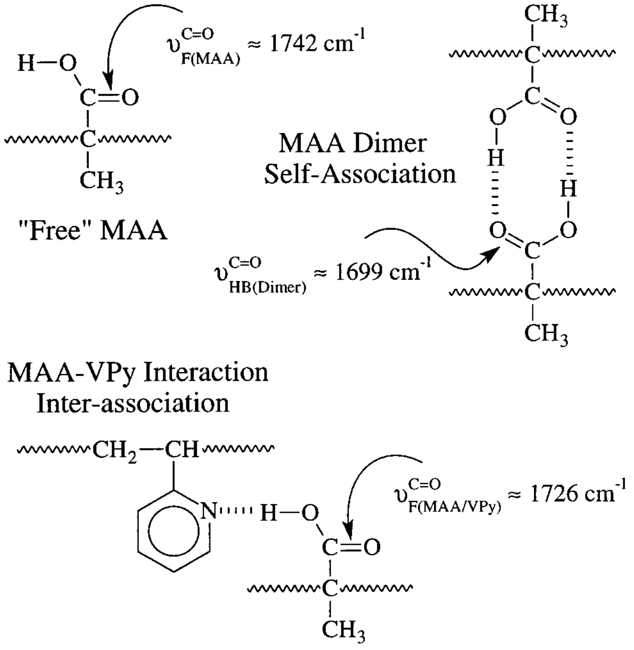


Figure 2. Infrared difference spectra of STMAA{9} and its blends with STVPy{17} (with the two phonon bands of the monosubstituted phenyl ring eliminated) recorded in the carbonyl stretching region at room temperature.

Scheme 2



It should be emphasized that we cannot directly compare frequency shifts (relative to that of the true "free" MAA carbonyl band at 1742 cm^{-1}) of the VPy/MAA interassociation band ($\Delta\upsilon$ = 16 cm^{-1}) to that of say MAA self-association ($\Delta\upsilon$ = 42 cm^{-1}) and make judgments about the relative strength of the VPy/MAA hydrogen bond. At first glance, one might be tempted to think that the VPy/MAA hydrogen bond is only of moderate strength, but remember (Scheme 2), the carbonyl group is not directly hydrogen bonded in the VPy/MAA interaction, whereas it is in the MAA dimer. Accordingly, comparing these two frequency shifts is not appropriate.

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