# Notes

## Infrared Spectroscopic Studies of Poly(styrene-*co*-methacrylic acid) Blends with Polytetrahydrofuran

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We recently reported the results of a comprehensive infrared study of the self-association of methacrylic acid copolymers.[1] Values of equilibrium constants that describe the number of hydrogen-bonded carboxylic acid dimers formed at equilibrium were determined and found to be a strong function of chain stiffness. In this note, we present some further spectroscopic results involving miscible blends of poly(tetrahydrofuran) (PTHF) with one of these random styrene-*co*-methacrylic acid copolymers that contains 9 mol % methacrylic acid (denoted STMAA{9}).

At a given temperature, above the glass transition temperature and below the onset of anhydride formation, the carbonyl groups of STMAA{9} exist in a state of dynamic equilibrium, oscillating between isolated "free" (non-hydrogen-bonded) and hydrogen-bonded carboxylic acid dimers (there is also a transient "open-dimer" intermediate state that has been detected in dilute solution studies, but not in polymer work[1]). This equilibrium may be simply depicted as

$$B + B \overset{K_D}{\rightleftharpoons} B_2 \qquad (1)$$

In the infrared spectrum of STMAA{9} at 140 °C we observe two major carbonyl stretching bands at ≈1740 and 1700 $cm^{-1}$ that are attributed to the "true" isolated "free", $\upsilon^{C=O}_{F(true)}$, and hydrogen-bonded, $\upsilon^{C=O}_{HB}$, carbonyl groups, respectively (see Scheme 1, parts A and B, and the bottom spectrum of Figure 1). In what has now become a routine process, the overtone and combination bands of the monosubstituted phenyl ring have been eliminated from the spectra shown in Figure 1 by spectral subtraction using the spectrum of atatic polystyrene recorded at the same temperature.[1] From quantitative measurement of the areas of these bands and knowledge of the absorptivity ratio of the hydrogen bonded to free bands, we can determine the fraction of "free" carbonyls and, in turn, a dimensionless equilibrium constant that describes the self-association of STMAA copolymers.[1]

The free energy of mixing of hydrogen-bonded polymer blends is dominated by the balance of two major opposing forces, often (in the older literature) referred to as "physical" and "chemical" forces.[2] The contribution

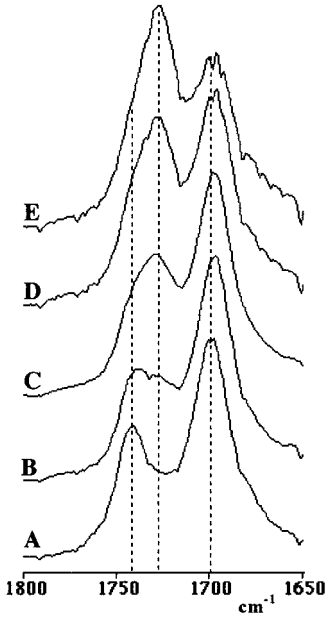
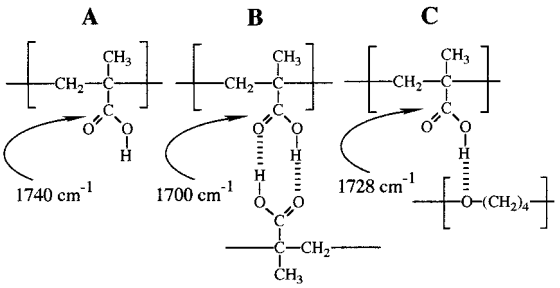



**Figure 1.** Infrared difference spectra of STMAA{9}/PTHF blends (with the two phonon bands of the monosubstituted phenyl ring eliminated) recorded in the carbonyl stretching region at 140 °C. Key: (A) 0, (B) 5, (C) 10, (D) 20, and (E) 30 wt % PTHF.

**Scheme 1**




to the former may be expressed in terms of a nonassociative $\chi$ parameter (or equivalent solubility parameter difference), while the "chemical" force contribution to the free energy emanates from the changing pattern of hydrogen bonding in the mixture vis-à-vis the pure components. Specifically, when STMAA{9} forms a miscible blend (or an intimately mixed two-phase blend, for that matter) with another polymer that contains a proton acceptor, such as the ether group of PTHF, a competition to form a hydrogen bond to the carboxylic acid −OH group occurs between another carboxylic acid −OH group (self-association, see eq 1) and the ether −O− atom of PTHF (interassociation—denoted C in Scheme 1). The appropriate equilibrium scheme for the interassociation is

$$A + B \overset{K_A}{\rightleftharpoons} AB \qquad (2)$$

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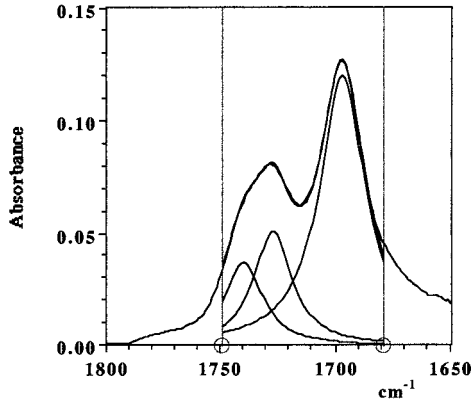


**Figure 2.** Curve-fitting results of the infrared difference spectrum of the 90:10 wt % STMAA{9}/PTHF blend.

It is important to recognize that when a hydrogen bond is formed between the carboxylic acid −OH and ether −O− groups, a "free" (non-hydrogen-bonded) carbonyl group is generated. Note, however, that there is a subtle difference between this "free" carbonyl group and the "true" isolated "free" carbonyl group mentioned above, in that the −OH group is now hydrogen bonded to an ether group of PTHF. The question arises, does this subtle difference in structure result in two separate "free" infrared bands that have significantly different frequencies (and presumably different absorptivities)? In our past studies on ethylene-*co*-methacrylic acid (EMAA)/polyether blends,[3] we made no distinction between these two "free" bands, but in this case we were using EMAA copolymers that were rich in methacrylic acid (MAA) and any contribution from the "true" isolated "free" band, $\upsilon^{C=O}_{F(true)}$, was negligible. In this present study, however, we are dealing with a more "dilute" STMAA{9} copolymer that has a relatively stiff chain and where there is a major contribution from the $\upsilon^{C=O}_{F(true)}$ band (see the bottom spectrum of Figure 1 in this work at 140 °C and Figure 10 in ref 1 for other temperatures).

We will refer to the "free" carbonyl stretching band where the carboxylic acid −OH group is hydrogen bonded to an ether group as $\upsilon^{C=O}_{F(OH\cdots O)}$. Infrared spectra of the 95:5, 90:10, 80:20, and 70:30 wt % STMAA{9}/PTHF blends recorded at 140 °C in the region from 1650 to 1800 $cm^{-1}$ are displayed in Figure 1. It is readily apparent to the eye that the carbonyl band envelope consists of three separate bands that vary in a consistent fashion with composition, $\upsilon^{C=O}_{HB}$ at ≈1700, $\upsilon^{C=O}_{F(OH\cdots O)}$ at ≈1728, and $\upsilon^{C=O}_{F(true)}$ at ≈1740 $cm^{-1}$. Unsurprisingly, with increasing concentration of PTHF ether groups in the blends, the relative intensity of the $\upsilon^{C=O}_{HB}$ and $\upsilon^{C=O}_{F(true)}$ bands decrease while that of the $\upsilon^{C=O}_{F(OH\cdots O)}$ band increases.

To determine the fraction of each of the carbonyl species present in the respective blends, the carbonyl band envelope was resolved into the three peaks, as illustrated in Figure 2. The methodology has been discussed in detail in previous publications,[1,2] and we will not dwell upon it here. Suffice it to say that a baseline was set by drawing a straight line from approximately 3600 to 2000 $cm^{-1}$ and the curve-fitting limits set to 1680−1750 $cm^{-1}$ (at approximately the half-widths of the two outside bands). The 90:10 wt % STMAA{9}/PTHF difference spectrum recorded at 140 °C has appreciable intensity contributions from all three bands, where the determination of band shapes, frequencies, $\upsilon$, and width at half-heights, $w_{1/2}$, can be determined with the greatest accuracy. Lorenzian band shapes were fixed, and the frequencies of the three bands determined to be $\upsilon$ = 1698, 1728, and 1740 ± 1 $cm^{-1}$ with $w_{1/2}$ = 24, 19, and 20 ± 1 $cm^{-1}$, respectively. Areas for each of these three bands were measured and determined to be 4.60, 1.28, and 1.42 arbitrary units, respectively.

**Table 1. Distribution of "Free" and Hydrogen-Bonded Carbonyl Groups**

| wt % STMAA{9}:PTHF | $f^{C=O}_{F(true)}$ | $f^{C=O}_{F(OH\cdots O)}$ | $f^{C=O}_{HB}$ |
|---|---|---|---|
| 95:5 | 0.22 | 0.13 | 0.65 |
| 90:10 | 0.17 | 0.23 | 0.60 |
| 80:20 | 0.16 | 0.33 | 0.51 |
| 70:30 | 0.14 | 0.45 | 0.41 |
| 60:40 | 0.14 | 0.51 | 0.33 |

To calculate the corresponding fractions of carbonyl groups that are hydrogen bonded, $f^{C=O}_{HB}$; "free", but in which the carboxylic acid −OH group is hydrogen bonded to an ether group, $f^{C=O}_{F(OH\cdots O)}$, and truly "free", $f^{C=O}_{F(true)}$, we must take into account the differences in the infrared absorptivities of the "free" and hydrogen-bonded carbonyl bands.[1−3] We recently determined[1] an appropriate absorptivity ratio based upon the *areas of Lorenzian bands* for the "free" and hydrogen-bonded MAA carbonyl bands, $a_R = a_{HB}/a_F = 1.1$, where $a_{HB}$ and $a_F$ are the absorptivities of the hydrogen-bonded and "free" carbonyl bands. Accordingly, the respective fractions for the 90:10 wt % STMAA{9}/PTHF are, $f^{C=O}_{HB}$ = 0.61, $f^{C=O}_{F(OH\cdots O)}$ = 0.18, and $f^{C=O}_{F(true)}$ = 0.21. The remaining spectra shown in Figure 1 were curve resolved in a similar manner using Lorenzian bands in the frequency and width at half-height ranges mentioned above and the results are summarized in Table 1. Note that the $f^{C=O}_{HB}$ decreases from about 0.66 to 0.35 while that of the $f^{C=O}_{F(true)}$ remains fairly constant within a range from 0.23 to 0.18 as the concentration of PTHF is increased in the blend from 5 to 40 wt %. Concomitantly, the $f^{C=O}_{F(OH\cdots O)}$ increases from 0.11 to 0.45.

We recently modified Dr. J. F. Graf's "Phase Calculator" program that accompanies our monograph,[2a] to include affects of chain connectivity.[4] After choosing the appropriate equilibrium scheme (in this case that based on eqs 1 and 2) and inputting appropriate values of the molar volume ($V_i$), molar mass ($M_i$), solubility parameter ($\delta_i$), self-association and interassociation equilibrium constants ($K_D$, $K_A$), enthalpies of hydrogen bond formation ($h_D$, $h_A$), and the intramolecular screening factor ($\gamma$), the program calculates the fraction of hydrogen-bonded functional groups, the individual contributions to the free energy of mixing, phase diagrams, miscibility windows and miscibility maps, etc., as a function of temperature and composition. In this work, the following values of the various parameters were used. For the specific repeat of the STMAA{9} copolymer, $V_B$ = 1030 $cm^3$/mol, $M_B$ = 1150 g/mol and $\delta_B$ = 9.6 (cal. $cm^{-3})^{0.5}$. The value of the self-association equilibrium constant, $K_D$ = 50 dimensionless units (at 140 °C based upon a reference volume, $V_B$ = 100 $cm^3$/mol), was determined previously (see ref 1 for details), and the value of $\gamma$ was assumed to be 0.30.[4] For PTHF values of $V_A$ = 71.1 $cm^3$/mol, $M_A$ = 72.1 g/mol and $\delta_A$ = 8.8 (cal. $cm^{-3})^{0.5}$ were used. What we do not know is the corresponding value of the interassociation equilibrium constant, $K_A$. How-

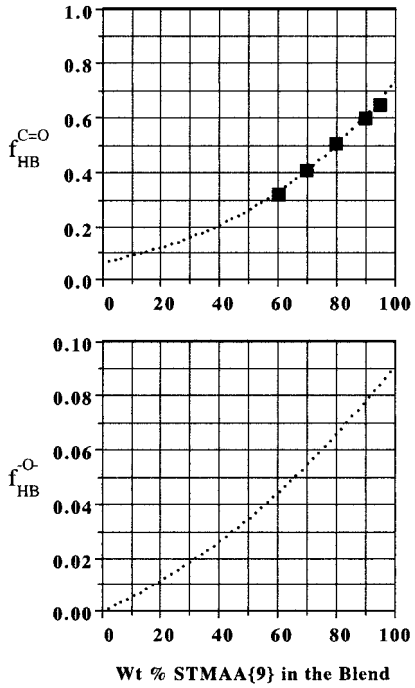


**Figure 3.** Calculated values (small dots) of the fraction of hydrogen-bonded carbonyl groups (top) and the fraction of hydrogen-bonded ether groups (bottom) as a function of STMAA{9}/PTHF blend composition at 140 °C. Values of $K_D = 50$ and $K_A = 5.3$ dimensionless units were assumed. The larger black squares denote the experimental results.

ever, we can assume values for $K_A$ and calculate the $f_{HB}^{C=O}$ as a function of blend composition and compare the results to the experimentally determined values given in the second column of Table 1.

At the top of Figure 3, we show a comparison of the predicted values (small dots) for $f_{HB}^{C=O}$ as a function of blend composition to the experimental data (larger filled squares). Here a value of $K_A = 5.3$ dimensionless units was found to best fit of the data. Note that this is approximately an order of magnitude less than that of $K_D$. At the bottom of Figure 3 is the corresponding calculation of the fraction of hydrogen-bonded ethers, $f_{HB}^{-O-}$. Knowing the composition of the STMAA{9}/PTHF blend, we can readily calculate the molar equivalents of ether oxygens that are hydrogen-bonded, $meq_{HB}^{-O-}$ (i.e., $f_{HB}^{-O-} \times mequiv_{total}^{-O-}$). This must be equal to the molar equivalents of MAA groups that are hydrogen-bonded to ether moieties, or, in other words, the molar equivalents of the "free" carbonyl groups where the carboxylic acid −OH is hydrogen-bonded to an ether, $mequiv_{F(OH\cdots O)}^{C=O}$. Now, the molar equivalents of all the "free" carbonyl groups, $mequiv_{F(total)}^{C=O}$, must equal $(1 - f_{HB}^{C=O})$ *x* $mequiv_{total}^{C=O}$. Thus, we can calculate $f_{F(true)}^{C=O}$ and $f_{F(OH\cdots O)}^{C=O}$ for the STMAA{9}/PTHF blends using values of $K_D = 50$ and $K_A = 5.3$ dimensionless units and compare them to the experimental data. While not perfect, the calculated values of $f_{F(true)}^{C=O}$ and $f_{F(OH\cdots O)}^{C=O}$ match the experimental data reasonably well.

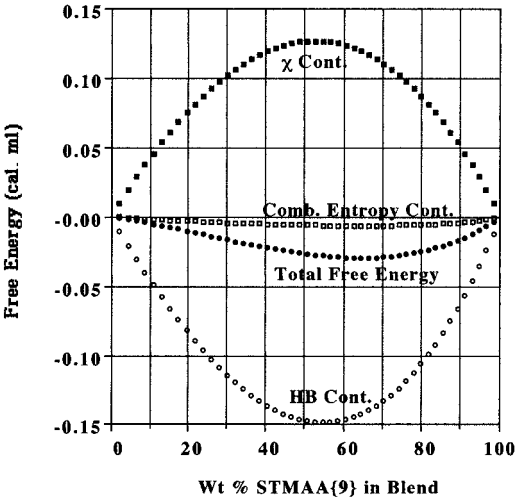


**Figure 4.** Calculated values of the total free energy and the relative contributions arising from combinatorial entropy, "physical" forces (the $\chi\Phi_A\Phi_B$ term) and "chemical" forces (the hydrogen-bonding term) as a function of STMAA{9}/PTHF blend composition at 140 °C using values of $K_D = 50$ and $K_A = 5.3$ dimensionless units.

Finally, using the values of the parameters mentioned above along with the values of the self- and interassociation equilibrium constants, $K_D = 50$ and $K_A = 5.3$ dimensionless units, we can calculate the total free energy of mixing ($\Delta G_m$) as well as the contributions from the "physical" and "chemical" forces over the entire composition range for the STMAA{9}:PTHF blends at 140 °C. The results are displayed graphically in Figure 4. The value of $\Delta G_m$ is negative, and the second derivative with respect to composition is positive over the entire blend composition range, characteristic of a miscible (single phase) system. The negative values of the combinatorial entropy and hydrogen bonding contributions offset the positive $\chi$ parameter ("physical" forces) contribution.

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## References and Notes

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