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Theoretical and Experimental Studies of Styrene-*co*-2-vinylpyridine Blends with 2,3-Dimethylbutadiene-*co*-4-vinylphenol

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Recently, we have been particularly interested in our ability to predict phase behavior of hydrogen-bonded polymer blends from equilibrium constants derived from low molecular weight analogues.[1,2] To achieve this, one must take into account chain connectivity effects including intramolecular screening, functional group accessibility, and polymer chain architecture.[3−5] In this note we present the theoretical predictions of the miscibility map and some experimental results designed to test the predictions for styrene-*co*-2-vinylpyridine (ST2VPy) blends with dimethylbutadiene-*co*-4-vinylphenol (DMBVPh).

To predict a miscibility map for the DMBVPh:ST2VPy system, we first require standard equilibrium constant values that describe the self-association of vinylphenol segments. These are well established and were obtained from the model compound 4-ethylphenol (EPh). $K_2^{\mathrm{Std}} =$ 21 and $K_2^{\mathrm{Std}} = 66.8$ dimensionless units describe respectively the formation of hydrogen-bonded phenolic dimers and chainlike multimers (at 25 °C, based upon a molar volume of 100 g/mol).[4,5] Next we require the standard interassociation equilibrium constant (K_A^{Std}) that describes the formation of hydrogen bonds between the hydroxyl group of the VPh segment and the nitrogen atom of the VPy segment. This was not available, and we now briefly turn our attention to how we obtained the value of K_A^{Std}.

The VPy/VPh interassociation equilibrium constant can be determined from dilute solution infrared studies of the low molecular weight analogues, EPh and 2-ethylpyridine (EPy). We have previously discussed in detail the infrared spectroscopic methodology used in the determination of interassociation equilibrium constants from model analogues and emphasized the importance of performing measurements in an appropriate concentration range to minimize errors.[6,7] EPy/EPh/cyclohexane mixtures were injected into sealed KBr liquid cells, which varied in path length from 0.5 to 1 mm. Infrared spectra were recorded at room temperature, and care was taken to ensure that the absorbances were in accordance with the limitations of the Beer−Lambert law. Digital subtraction of a pure cyclohexane (CHEX) spectrum was performed using the same liquid cell. The difference spectrum is essentially that of the "pure" EPy/EPh interacting species at a given dilution, in a noninteracting solvent. Prior EPh solution studies[6,7] revealed that an EPh concentration of 0.02 M in CHEX was the minimum concentration necessary to ensure that the vast majority of the phenolic groups were "free" (non-hydrogen-bonded). This was evidenced by the presence of only a sharp, free OH band at 3619 cm^{-1}, and the absence of a broad, hydrogen-bonded OH absorbance centered around 3300 cm^{-1}. Accordingly, the EPh concentration in the mixtures was maintained at a constant value of 0.02 M. Dimensionless interassociation equilibrium constant values (K_A^{Std}) for numerous EPy/EPh/CHEX mixtures were calculated using the method attributed to Coggeshall and Saier.[8] After preliminary studies to determine the appropriate range over which the equilibrium constant could be accurately determined, six different solutions at concentrations between 0.05 and 0.10 M EPy and 0.02 M EPh in cyclohexane were prepared in 500 mL volumetric flasks. The value of K_A^{Std} was determined to be 1200 ± 100 dimensionless units.[6,7] For purposes of comparison, this value is considerably larger than that determined for EPh/EIB interactions ($K_A^{\mathrm{Std}} = 170$ dimensionless units) and significantly smaller than the corresponding EPh/ethylpyrrolidone interaction ($K_A^{\mathrm{Std}} = 6000$ dimensionless units). Additional details can be found in the thesis of Motzer.[9]

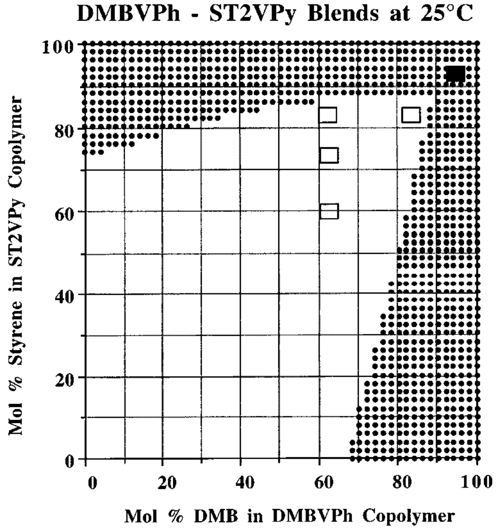

Figure 1. Theoretical miscibility map calculated for the DMBVPh−ST2VPy blend system at 25 °C. A miscible system is defined as having a single phase across the entire composition range. The area enclosed by the small black dots represents the predicted two-phase region. Experimental results are represented by larger black (immiscible) and white squares (miscible).

Armed with appropriate values of both the self- and interassociation equilibrium constants derived from model low molar mass analogues, we are now in a position to use Guigley's modification[2] of the original Phase Calculator program written by Graf[4] to calculate a theoretical miscibility map for the DMBVPh:ST2VPy blend system. Thus, standard equilibrium constant values of $K_A^{\mathrm{Std}} = 21$, $K_B^{\mathrm{Std}} = 66.8$, and $K_A^{\mathrm{Std}} = 1200$ dimensionless units were used together with a value of $\gamma = 0.3$ for the intramolecular screening factor.[1,2,10] The molar volumes, solubility parameters, and molecular weights of each repeat unit for the four monomers were calculated using group contributions.[4,5] The predicted miscibility map is shown in Figure 1, where the black dots represent the two-phase region. From this map, it is clear that blends made from copolymers that have roughly greater than 25 mol % VPy and VPh are predicted to be miscible. The validity of this map was

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tested using DMBVPh:ST2VPy experimental optical, thermal, and infrared data, which is discussed next.

Blends of the homopolymers poly(2-vinylpyridine) (P2VPy) and poly(4-vinylphenol) (PVPh) precipitate when mixed together in a common solvent to form single-phase complexes.[11] In the blends examined in this work, however, the VPh and VPy segments are substantially “diluted” by copolymerization with “inert” styrene or dimethylbutadiene segments. Such mixtures do not precipitate from solution in a common solvent, and formation of miscible blend films from common solvents is feasible. The ST2VPy and 2,3-dimethylbutadiene-*co*-4-vinylphenol (DMBVPh) copolymers used in this study were synthesized in our laboratories, and details are contained in the theses of Zhang[12] and Pehlert,[13] 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 calculated as the midpoint of the heat capacity change.

Five different blend systems were examined, of which four are predicted to be single-phase by the theoretical miscibility map shown in Figure 1. The first was a DMBVPh{6} blend with ST2VPy{8} (the number {*x*} refers to the mol % of VPh or VPy). The blend film was cloudy, and thermal analysis of this blend revealed the obvious presence of two glass transition temperatures (T_g's) at 5 and 63 °C. This is consistent with a two-phase system and in concert with theoretical prediction. The second blend system was prepared from DMBVPh{18} and ST2VPy{17}. Films of these blends were transparent, and single T_g's were observed in 80:20; 50:50, and 20:80 wt % blends at 39, 54, and 76 °C, intermediate between the T_g's of the pure components (11 and 99 °C). This is good evidence for single-phase systems. Note that this is very close to the boundary between single- and two-phase in the theoretical miscibility map (Figure 1). Nonetheless, the prediction of a single-phase system is entirely consistent with experiment. The other three other blends were prepared with DMBVPh{38}. Blends with ST2VPy{17}, ST2VPy{26}, or ST2VPy{40} were all transparent, and thermal analyses revealed that they each had single T_g's. There was appreciable deviation from the normal Fox equation, however, with increasing concentration of VPh and VPy segments. In any event, the experimental results were consistent with the prediction of the theoretical miscibility map.

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