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On the Glass Transition Temperature of Copolymers of 4-Vinylphenol with *n*-Alkyl Methacrylates

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As part of our continuing studies of polymer blends involving strong specific interactions (hydrogen bonds), we have recently synthesized a series of essentially random copolymers containing 4-vinylphenol (VPh) with *n*-ethyl methacrylate (EMAVPh), *n*-butyl methacrylate (BMAVPh), and *n*-decyl methacrylate (DMAVPh). The copolymers all have number-average molecular weights in the range of 10 000–20 000 and polydispersities close to 2. Details of the synthesis and characterization of these copolymers, which are similar to those previously described for the analogous styrene-*co*-vinylphenol copolymers,[1] will be reported at a later date.

Glass transition temperatures (T_g) of the various EMAVPh, BMAVPh, and DMAVPh copolymers were experimentally determined using differential scanning calorimetry. In addition, experimental T_g's were obtained for pure poly(vinylphenol) (PVPh; M_n = 14 000; synthesized under the same conditions as the copolymers) and PEMA, PBMA, and PDMA (M_n = 13 000, 55 000, and 28 000, respectively; synthesized by group-transfer polymerization). Figures 1–3 show the experimental T_g's plotted as a function of the weight fraction of VPh in the EMAVPh, BMAVPh, and DMAVPh copolymers, respectively. Not unexpectedly, we observe a large deviation from the T_g values calculated using the simple Fox relationship.[2]

It has long been recognized that the presence of strong specific interactions, such as hydrogen bonds, play a significant role in determining the T_g's of copolymers and miscible polymer blends (see ref 3 and citations therein). Recently, we derived an equation for the compositional dependence of the T_g for miscible polymer mixtures (i.e., single-phase materials across the entire blend composition range) that involve strong specific interactions[3]

$$T_{g_m} = \frac{X_A T_{g_A} + k X_B T_{g_B}}{X_A + k X_B} + X_A X_B(q'_m(X) + q'_B(T)) \qquad (1)$$

where T_{g_m}, T_{g_A}, and T_{g_B} are the glass transition temperatures of the mixture and the pure A and B components, respectively. X_A and X_B are the mole fractions, k is the ratio of the specific heat increments ($\Delta C_{p_B}/\Delta C_{p_A}$), $q'_m(X)$ is a composition-dependent term that depends on the contribution of hydrogen-bonding interactions to the liquid-state heat of mixing, and $q'_B(T)$ represents the contribution from the change in the liquid-state specific heat of the self-associating polymer (B) on going from T_{g_B} to T_{g_m}. This last term is significant in polymers that hydrogen bond.

Although this equation was originally derived specifically for miscible binary blends, e.g., PVPh with PBMA, it is entirely applicable to copolymers containing the same type of functional groups, e.g., BMAVPh copolymers. Conceptually, there is no difference, and the same assumptions made in the original derivation still apply.[3] To employ this equation for, say, a *copolymer* of VPh with BMA, we require a knowledge of the molar volumes of the "specific repeats" of the two polymer segments; equilibrium constants that describe self-association of phenolic hydroxyl groups (two in the case of VPh, K_2 and K_B, for the formation of hydroxyl dimers and multimers, respectively); an equilibrium constant that describes interassociation between phenolic hydroxyl and methacrylate carbonyl groups (K_A) and corresponding enthalpies of hydrogen bond formation (h_2, h_B, and h_A).[4] Values of these parameters have all been determined from spectroscopic measurements.[4] In addition, we require the T_g's of the pure polymers, PVPh and PBMA, and the difference in heat capacity (ΔC_p), liquid minus glass, of these pure polymers, which may be obtained experimentally or calculated by a heat capacity group contribution method.[5] Table I summarizes the values of these parameters used in this work.

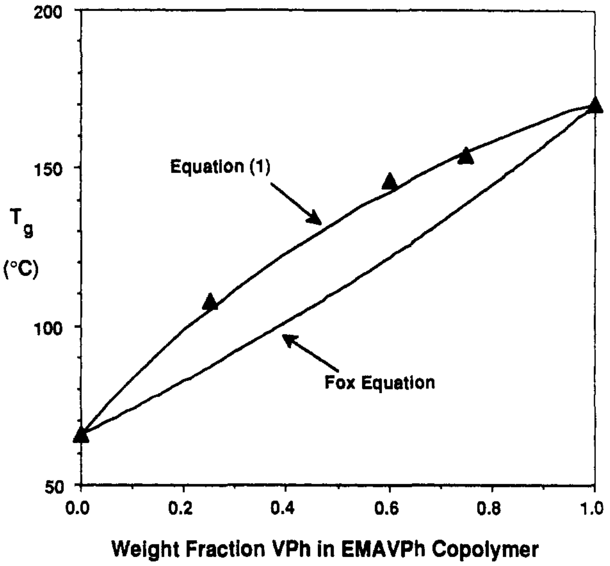

Figure 1. Comparison of the experimental glass transition temperatures to the theoretical values calculated from eq 1 and the Fox relationship[2] for the EMAVPh copolymers.

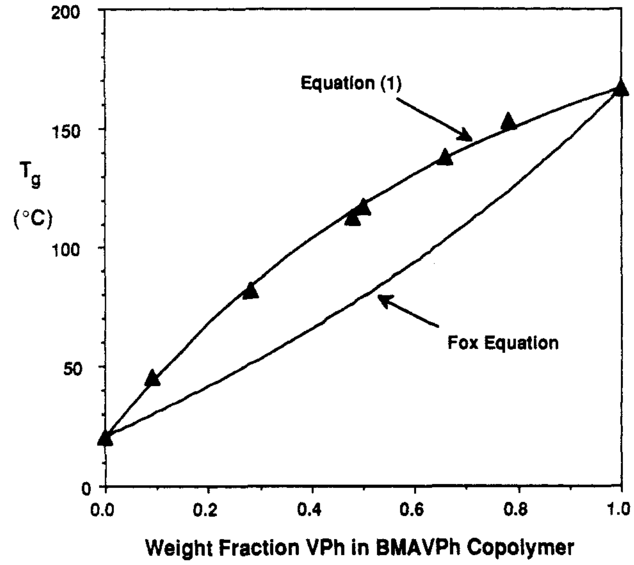

Figure 2. Comparison of the experimental glass transition temperatures to the theoretical values calculated from eq 1 and the Fox relationship[2] for the BMAVPh copolymers.

The results of the calculations for the compositional dependence of the T_g for the EMAVPh, BMAVPh, and DMAVPh copolymers, which we stress are performed

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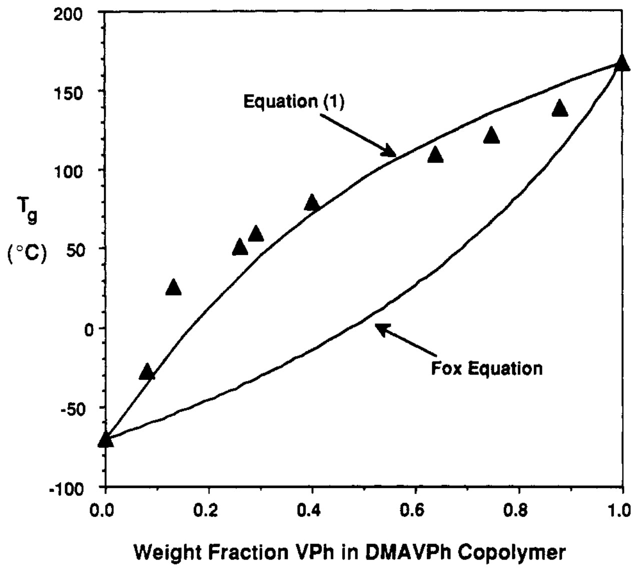

Figure 3. Comparison of the experimental glass transition temperatures to the theoretical values calculated from eq 1 and the Fox relationship[2] for the DMAVPh copolymers.

without using any adjustable parameters, are included in Figures 1–3, respectively. (Details of the calculation procedure are given in refs 3 and 4.) There is excellent agreement between experimental and predicted T_g's as a function of VPh concentration, and, more importantly, the observed positive deviation from the Fox equation is matched.

Table I
Parameters Employed

polymer segment	VPh	EMA	BMA	DMA
V (cm^3/mol)[a]	100	101	134	233
ΔCp (cal/g·K)[b]	0.145	0.0888	0.0883	0.0875
K_2 (dimensionless)	21.0			
K_B (dimensionless)	66.8			
K_A (dimensionless)		37.1	37.1	37.1
h_2 (cal/mol)	−5600			
h_B (cal/mol)	−5200			
h_A (cal/mol)		−3750	−3750	−3750

[a] Calculated from our molar volume group contributions.[4] [b] Calculated from van Krevelen's heat capacity group contributions.[5]

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References and Notes

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