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A counterintuitive observation concerning hydrogen bonding in polymer blends

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It has been determined from an infrared analysis of miscible blends of *n*-butyl methacrylate-co-4-vinylphenol and styrene-co-2-vinyl pyridine copolymers that the fraction of hydrogen-bonded carbonyl groups actually increases with temperature. At first glance, this is counterintuitive, but it is entirely consistent behaviour for a multicomponent hydrogen-bonding system containing competing acceptor groups that have disparate enthalpies of hydrogen bond formation. © 1998 Elsevier Science Ltd. All rights reserved.

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We recently reported the results[1] of an infrared spectroscopic study of a miscible binary polymer blend system consisting of a *n*-butyl methacrylate-*stat*-4-vinyl phenol copolymer containing 54 wt.% 4-vinyl phenol (denoted BMAVPh[54]) and a styrene-*stat*-2-vinyl pyridine copolymer containing 27 wt.% 2-vinyl pyridine (denoted STVPy[27]). The primary focus of the study was intramolecular screening[2], a direct consequence of chain connectivity and a significant factor that limits the fraction of intermolecular interactions that are formed between complementary (co)polymers in polymer blends. However, during these studies we had occasion to measure the fraction of hydrogen-bonded carbonyl groups (details of the methodology are given in Refs. [3–5]) that are formed in blends of BMAVPh[54] with STVPy[27] as a function of temperature over the range from 150 to 200°C (data that were not used in Ref. [1]). As summarized in *Table 1*, the fraction of hydrogen-bonded carbonyl groups, $f_{HB}^{C=O}$, is observed to *increase* with temperature—a result that is, at first glance, counterintuitive. In general one would expect the $f_{HB}^{C=O}$ to decrease with temperature, as it surely does in the case of pure BMAVPh[54] (see *Table 1*), numerous other homopolymers (such as polyamides, polyurethanes etc.) and miscible amorphous binary polymer blend systems[1,4]. As hydrogen bonds are dynamic, simultaneously breaking and reforming at the whim of thermal motion, this decrease in $f_{HB}^{C=O}$ simply reflects a reduction in the average number of hydrogen bonds present at equilibrium as the temperature is increased. In fact, the enthalpy of hydrogen bond formation, h_A, is routinely determined from $f_{HB}^{C=O}$ data obtained as a function of temperature, via the appropriate equilibrium constants and a van't Hoff plot[4]. Why then do we see an increase in $f_{HB}^{C=O}$ with temperature in the case of the BMAVPh[54] blends with STVPy[27]? This is the major question addressed here.

To adequately describe the equilibrium distribution of hydrogen-bonded structures that are formed in pure BMAVPh[54] at a given temperature, a minimum of three self-association equilibrium constants, K_2, K_B and K_C, are required together with their corresponding enthalpies of hydrogen bond formation, h_2, h_B and h_C, as depicted by the following equilibria (1):

$$B_1 + B_1 \overset{K_2}{\rightleftharpoons} B_2 \quad K_2 = 2.10 \text{ dimensionless units;}$$

$$h_2 = -5.6 \text{ kcal/mol}$$

$$B_h + B_1 \overset{K_B}{\rightleftharpoons} B_{h+1} \quad K_B = 66.8 \text{ dimensionless units;}$$

$$h_B = -5.2 \text{ kcal/mol}$$

$$B_h + C \overset{K_C}{\rightleftharpoons} B_hC \quad K_C = 37.0 \text{ dimensionless units;}$$

$$h_C = -3.8 \text{ kcal/mol}$$

These are standard equilibrium constant values based on a reference volume for the VPh segment ($V_B = 100$ cm^3/mol at 25°C) and describe the formation of hydrogen-bonded phenolic hydroxyl/hydroxyl dimers (B_2), phenolic hydroxyl/hydroxyl 'chain-like' multimers (B_{h+1}) and phenolic hydroxyl/BMA carbonyl interactions (B_hC), respectively (see *Figure 1* for a schematic representation of these various hydrogen-bonded structures).

In the BMAVPh[54] blends with STVPy[27] an additional inter-association equilibrium constant and corresponding enthalpy of hydrogen bond formation are required that describe the competing hydrogen-bonding interaction between phenolic hydroxyls and pyridine groups (B_hC);

$$B_h + A \overset{K_A}{\rightleftharpoons} B_hA \quad K_A = 233 \text{ dimensionless units;}$$

$$h_A = -7.0 \text{ kcal/mol}$$

Note that the value of K_A is much larger than K_C at room temperature (233 *versus* 37 dimensionless units—a factor > 6) which implies that in blends containing comparable concentrations of VPy and BMA segments, VPh hydroxyl/VPy pyridine interactions will be strongly favoured over VPh hydroxyl/BMA carbonyl interactions. The relative strengths of these two interactions is also very different (−7.0 *versus* − 3.8 kcal/mol, respectively) which, as we will see, markedly affects the rate that the equilibrium

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constants change with temperature—the key to the apparent anomalous observation that the fraction of hydrogen-bonded carbonyl groups increases with temperature.

Figure 2 shows the values of the different equilibrium constants (calculated via the van't Hoff relationship, $\ln K = -\Delta h/RT + C$), plotted as a function of temperature from 25 to 200°C. The dissimilar rate of change of the equilibrium constant values with temperature is striking, especially if one compares the curves pertaining to K_A and K_C, which describe the competition of the VPy pyridine and the BMA carbonyl groups in forming a hydrogen bond to VPh hydroxyls. In the insert of *Figure 2* is presented a scale expanded region from 150 to 200°C. Here we can see that K_A and K_C have the same value at $\approx$ 178°C. Above this temperature the value of K_A is actually less than K_C (implying that for equivalent numbers of VPy and BMA segments, the latter are now favoured to form hydrogen bonds with VPh hydroxyls—the opposite of that observed at temperatures below 178°C).

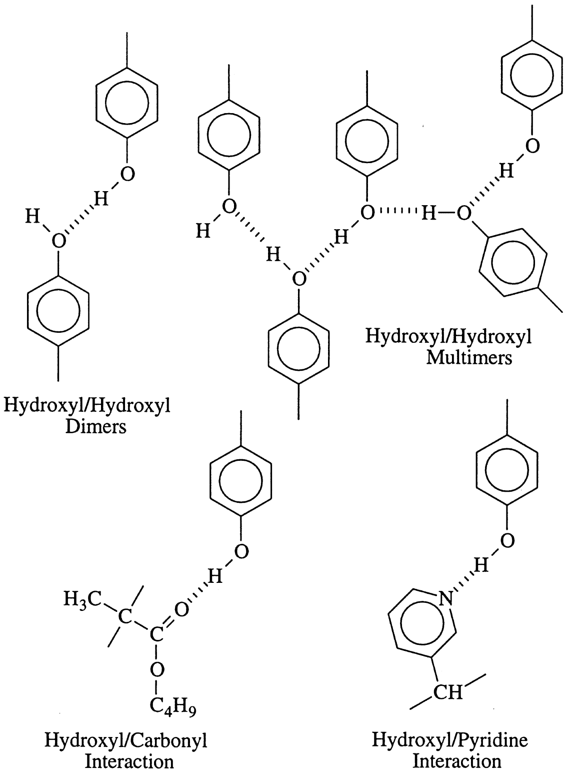

Figure 1 Schematic representation of the hydrogen-bonded structures formed between phenolic hydroxyl groups (dimers and 'chain-like' multimers) and those formed between hydroxyl and carbonyl and hydroxyl and pyridine groups

It is a relatively straightforward task to calculate, from the equations describing the stoichiometry of the system, the fraction of BMA and VPy segments that are hydrogen bonded in a BMAVPh[54]/STVPy[27] blend as a function of composition and at a specific temperature[4]. One requires values of the equilibrium constants K_2, K_B, K_C (self-association) and K_A (inter-association), the molar volumes of the segments VPh ($V_B = 100\ \mathrm{cm^3/mol}$), BMA ($V_C = 134\ \mathrm{cm^3/mol}$) and STVPy ($V_A = 339\ \mathrm{cm^3/mol}$) together with the volume fraction of BMA in the BMAVPh[54] copolymer ($\Phi_C = 0.508$). *Figure 3* shows the results of such calculations performed at 200°C (top), 150°C (middle) and 25°C (bottom) obtained using a modified version of the computer program (written by Dr J. F. Graf) that accompanies our monograph[4]. At 25°C, when $K_A \gg K_C$ (233 *versus* 37 dimensionless units), the fraction of hydrogen-bonded BMA carbonyls, $f_{HB}^{C=O}$, is markedly less than the fraction of hydrogen-bonded VPy pyridines, $f_{HB}^{C=O}$,

Table 1 Fraction of hydrogen-bonded carbonyl groups, $f_{HB}^{C=O}$

Temp. (°C)	BMAVPh[54]:STVPy[27] blend composition (wt.%)				
	100:0	40:60	30:70	20:80	10:90
150	0.46_5	0.34_3	0.32_4	0.28_9	0.28_0
160	0.45_9	0.34_9	0.33_5	0.30_6	0.28_0
170	0.45_4	0.35_4	0.35_1	0.31_7	0.29_8
180	0.44_9	0.36_8	0.35_3	0.33_4	0.30_0
190	0.44_3	0.36_8	0.35_3	0.33_6	0.30_0
200	0.43_7	0.36_9	0.35_7	0.33_7	0.30_9

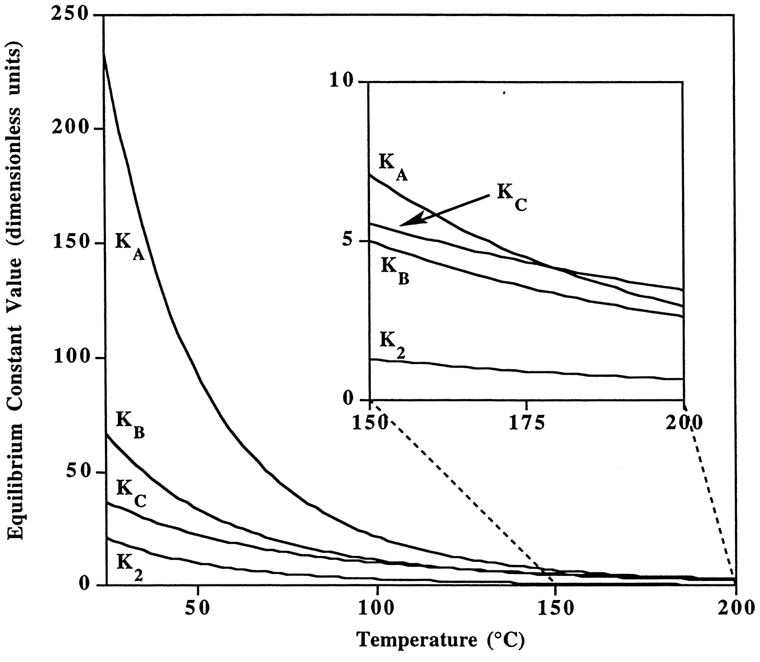

Figure 2 Equilibrium constant values as a function of temperature from 25 to 200°C. Insert: scale expanded range from 150 to 200°C

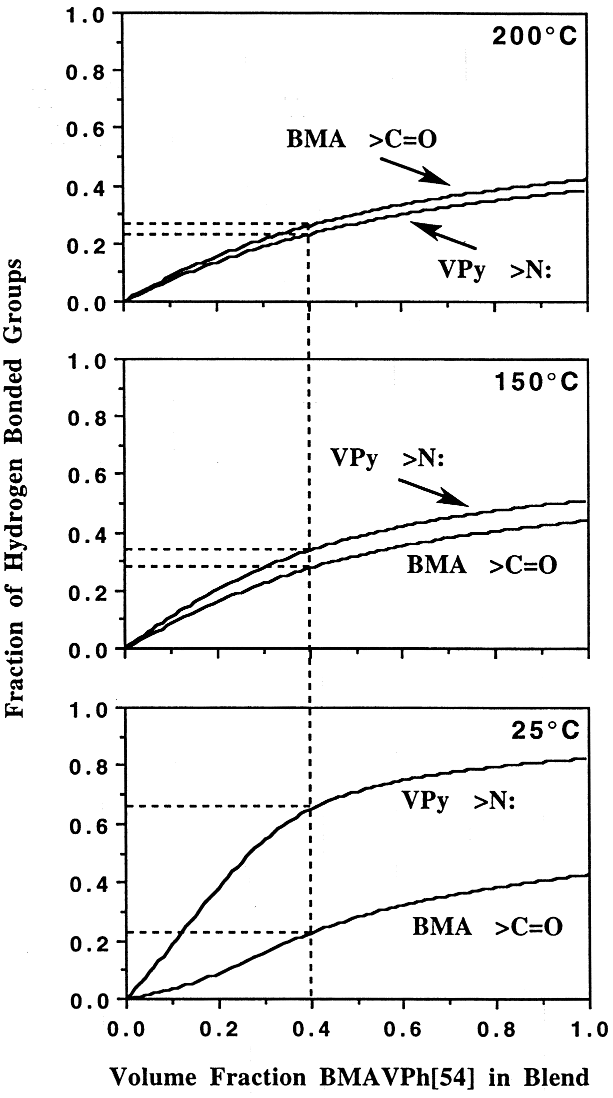

Figure 3 Theoretical calculation of the fraction of hydrogen-bonded BMA carbonyl and VPy pyridine groups for BMAVPh[54]/STVPy[27] blends. Top, 200°C; middle, 150°C; and bottom, 25°C

over the entire blend composition range. If we focus our attention on the blend containing 40 vol.% BMAVPh[54] (which is close to one of the compositions listed in *Table 1*), only 22% of the BMA carbonyls are hydrogen bonded, while for the VPy pyridines the number is 65%. On the other hand, at 150°C, when $K_C \approx K_A$ (7.0 *versus* 5.3 dimensionless units), $f_{\mathrm{HB}}^{\mathrm{C=O}}$ is still somewhat less than $f_{\mathrm{HB}}^{>\mathrm{N}}$, but now, in comparison, at 40 vol.% BMAVPh[54] *more* BMA carbonyls are hydrogen bonded (28% *versus* 22% at 25°C), while there is a large decrease in the fraction of hydrogen-bonded VPy pyridines (34% *versus* 65% at 25°C). At 200°C, when $K_{\mathrm{C}} > K_{\mathrm{A}}$ (3.4 *versus* 2.9 dimensionless units), $f_{\mathrm{HB}}^{\mathrm{C=O}}$, is now greater than $f_{\mathrm{HB}}^{>\mathrm{N}}$. It is important to recognize that the *total* number of hydrogen-bonded acceptor groups (i.e., hydrogen-bonded BMA carbonyls plus hydrogen-bonded VPy pyridines), is less at 200°C than at 150°C, and in turn considerably less than at 25°C. It is just that the distribution between hydrogen-bonded BMA carbonyls to hydrogen-bonded VPy pyridines changes in favour of the former as the temperature is raised.

In conclusion, since only the $f_{\mathrm{HB}}^{\mathrm{C=O}}$ is amenable to quantitative analysis by infrared spectroscopy, the observation that the fraction of $f_{\mathrm{HB}}^{\mathrm{C=O}}$ increases with temperature in BMAVPh[54]/STVPy[27] blends (*Table 1*) is entirely consistent with a multicomponent hydrogen-bonding system containing competing acceptor groups with disparate enthalpies of hydrogen bond formation.

Acknowledgements

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References

1. Coleman, M. M., Narvett, L. A., Park, Y. H. and Painter, P. C., *J. Macromol. Sci. Phys.*, 1998, **B37**, 283.
2. Painter, P. C., Veytsman, B., Kumar, S., Shenoy, S., Graf, J. F., Xu, Y. and Coleman, M. M., *Macromolecules*, 1997, **30**, 932.
3. Narvett, L. A., M.S. Thesis. The Pennsylvania State University, 1997.
4. Coleman, M. M., Graf, J. F. and Painter, P. C., *Specific Interactions and the Miscibility of Polymer Blends*. Technomic Publishing, Inc., Lancaster, PA, 1991.
5. Coleman, M. M. and Painter, P. C., *Prog. Polym. Sci.*, 1995, **20**, 1.