gas-phase chromatograph using the same conditions employed previously[9] to isolate the isomers of 2,4-dichloropentane. The Kerr effect and dielectric apparatus along with the experimental techniques have been previously described.[6] Carbon tetrachloride at 25 °C was employed as the solvent for all measurements reported here.

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(12) Note that the $\langle\mu^2\rangle$ and ${}_mK$ observed for the 58:42 r:m mixture (5.06, 10.8) are nearly identical with the additive sum of the $\langle\mu^2\rangle$'s and ${}_mK$'s observed for the separated isomers [(0.58)(5.00) + (0.42)(5.29) = 5.12 and (0.58)(13.6) + (0.42)(8.46) = 11.4]. There do not appear to be any specific interactions between isomers in solution which are reflected in the observed dipole moment or molar Kerr constant of their mixture.
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Effect of Hydrogen Bonding on the Lower Critical Solution Temperature of a Polymer Mixture

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The free energy of mixing of two polymers, according to recent theories,[1,2] can be analyzed in terms of three contributions: combinational entropy of mixing, an interactional energy term, and a "free volume" term. To achieve miscibility of two polymers of high molecular weight, a negative interaction energy is required. Phase separation takes place on raising the temperature to the lower critical solution temperature (LCST) because the free volume term becomes more positive and the interactional energy term less negative at elevated temperatures. A simplified version of the Prigogine–Flory theory has been given by Patterson and Robard[3,4] in an approximate equation that describes the essential features of the theory

$$\frac{\chi^{12}}{V_1^*} = \frac{P_1^*}{RT_1^*}\left[\frac{\tilde{V}_1^{1/3}}{\tilde{V}_1^{1/3}-1}\left(\frac{X_{12}}{P_1^*}\right) + \frac{\tilde{V}_1^{1/3}}{2(\frac{4}{3}-\tilde{V}_1^{1/3})}\tau^2\right] \quad (1)$$

The first term on the right-hand side of eq 1 is the interactional contribution and the second, the free volume contribution. In eq 1, χ is the Flory–Huggins interaction parameter, $\tilde{V}$ is the reduced volume, the starred symbols are calculated from equation-of-state properties, and X_{12} is the exchange (or contact) interaction parameter. The interaction and free volume terms are characterized by molecular parameters X_{12}/P^* and τ^2, respectively, where $\tau = 1 - T_1^*/T_2^*$. Equation 1 was used successfully by Patterson and Robard to describe the various features of polystyrene–poly(vinyl methyl ether) blends.[3,4]

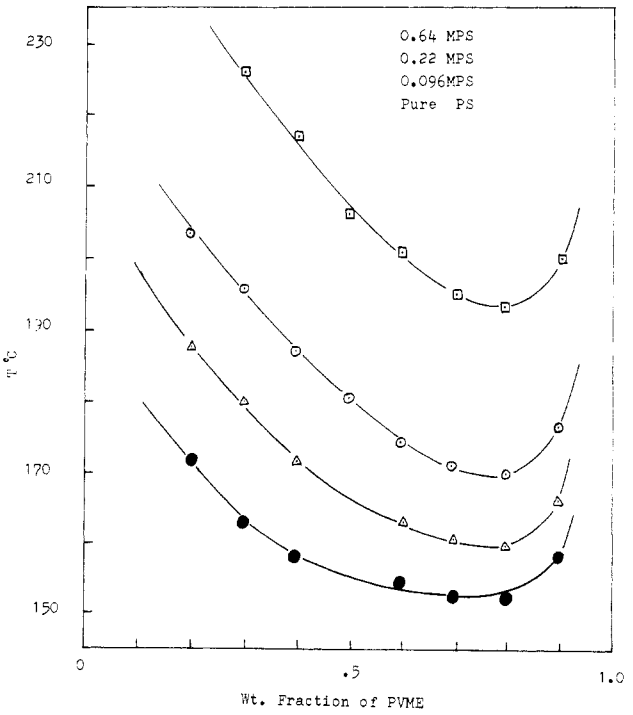

Figure 1. LCST phenomena of the various modified PS's and PVME systems at the heating rate of 2 °C min^{-1}: (□) 0.64MPS; (○) 0.22MPS; (△) 0.096MPS; (●) pure PS.

An increase in the strength of interaction (more negative) leads to a higher temperature for phase separation. This was verified experimentally when polystyrene was modified to contain a small amount of vinylphenylbis(trifluoromethyl)carbinol as comonomer units.[5] The bis(trifluoromethyl)carbinol group, a strong hydrogen bond donor, interacts with the ether group of PVME and, as a result, the LCST is raised. The purpose of the present note is to demonstrate that the increase in interaction due to hydrogen bonding indeed balances the increase in the free volume term when phase separation takes place at a higher temperature for the blend containing modified polystyrene (MPS) and PVME.

The relevant LCST data are shown in Figure 1. Note that the nomimal concentration of the $C_6H_4C(CF_3)_2OH$ group in the modified polystyrenes reported as 0.1, 0.2, and 0.4% in ref 5 should be amended to become 0.096, 0.22 (both calculated from reactivity ratios), and 0.64% (from fluorine analysis). The LCST values for mixtures containing 80% by weight of PVME are 425 K for PS and 433, 442, and 446 K respectively for the three modified polystyrenes. At each LCST, the free volume term can be calculated from equation-of-state properties, with the approximation that the parameters for PS can be used for MPS because the degree of modification is very small. Since $\chi = 0$ at LCST for high molecular weight polymers, X_{12} can be calculated from the free volume term. If the change in the dispersion forces in the temperature range of interest is ignored, the *increase* in X_{12} upon the incorporation of the $C_6H_4C(CF_3)_2OH$ group in MPS is then a direct measure of the number of hydrogen bonds, C_b, remaining at the phase separation temperature because the enthalpy of hydrogen bonding can be estimated independently for this system. The fraction of hydrogen bonds remaining at LCST calculated by this procedure should be consistent with a reasonable value of the equilibrium constant of hydrogen bonding at room temperature and the Arrhenius temperature dependence of hydrogen bonding (from ΔH).

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Table I
Fraction of Hydrogen Bonds Remaining at LCST in MPS–PVME Blends[a]

$C_0 \times 10^6$, (mol of OH) cm^{-3}	LCST, K	X_{12}, J cm^{-3}	$X_H \times 10^2$, J cm^{-3}	$C_b \times 10^7$, mol cm^{-3}	$C_b/C_0 \times 10^2$	$C_b/C_0 \times 10^2$ [b]
0	425	−1.166				
9.2	433	−1.188	−2.2	6.58	7.2	8.1
21.1	442	−1.212	−4.6	13.8	6.5	6.7
61.4	466	−1.277	−11.1	33.2	5.4	4.5

[a] C_0 = moles of hydroxyl group per cm^3 of MPS, $X_H = X_{12}(T) - X_{12}$ (425 K), and C_b = number of bonded hydroxyl groups (calculated from $X_H/\Delta H$; ΔH of hydroxyl bond formation = −8.0 kcal mol^{-1} (−33.5 kJ mol^{-1}). [b] C_b/C_0 calculated by using a value of 0.4 mol^{-1} L as the equilibrium constant, $K_{eq} = C_b/[C_{PVME}(C_0 - C_b)]$, at 300 K.

Table II
Fraction of Hydrogen Bonds Remaining at LCST in MPS–PMMA Blends[a]

$C_0 \times 10^4$ (mol of OH) cm^{-3}	LCST, K	X_{12}, J cm^{-3}	X_δ, J cm^{-3}	X_H, J cm^{-3}	$C_b \times 10^5$, mol cm^{-3}	$C_b/C_0 \times 10^2$	$C_b/C_0 \times 10^2$ [b]
3.75	477	−0.425	0.060	−0.485	1.97	5.3	5.8
4.18	515	−0.450	0.059	−0.509	2.07	5.0	3.7

[a] ΔH = −5.9 kcal mol^{-1}. Blend composition is 80% by weight of PMMA. [b] Calculated by using a value of 0.3 mol^{-1} L as K_{eq} at 300 K.

In the context of this calculation, X_{12} is used as the enthalpic parameter. The corresponding entropic parameter, Q_{12}, is not considered.[1,6,7] If X_{12} is interpreted as a free energy parameter, then the fraction of hydrogen bonds should be calculated from the free energy of hydrogen bond formation rather than the enthalpy. This would increase the value of C_b. However, the main thesis of our argument is not affected.

The pertinent parameters used in our calculation are $T_1^*/T_2^* = 1.137$, $\alpha_1 = 5.80 \times 10^{-4}$ K^{-1}, and $P_1^* = 500$ J cm^{-3}, all three values having been used by Patterson and Robard in their calculations. The enthalpy of hydrogen bonding is estimated to be −8.0 kcal mol^{-1} of H bond from the infrared shift in the hydroxyl absorption of the $C_6H_4C(CF_3)_2OH$ group in the blend[5] and the enthalpy–frequency shift correlation established for hydrogen bond formation between hexafluoro-2-propanol and basic molecules.[8] The results of our calculation are self-explanatory and are listed in Table I. The last column gives the fraction of hydrogen bond remaining at LCST if the equilibrium constant of hydrogen bond formation is assumed to be 0.4 mol^{-1} L at 300 K and the temperature dependence of hydrogen bonding is to obey the Arrhenius equation. The agreement between C_b/C_0 values calculated with the use of eq 1 and the ones from simple equilibrium considerations is deemed satisfactory when allowance is made for the various approximations made. If a different set of equation-of-state parameters is used, $T_1^*/T_2^* = 1.137$ as before but $\alpha_1 = 5.2 \times 10^{-4}$ K^{-1} and $P_1^* = 755$ J cm^{-3} from Olabisi and Simha,[9] the C_b/C_0 values in column 6 become 0.091, 0.085, and 0.073, consistent with K_{eq} of 0.5 at 300 K, which gives C_b/C_0 values of 0.099, 0.082, and 0.055, respectively, at phase separation temperatures.

The LCST data for blends containing 60% by weight of PVME yield C_b/C_0 values of 0.12, 0.11, and 0.08 for the three mixtures, using the parameters from ref 3. These values are to be compared with 0.15, 0.11, and 0.07, respectively, obtained from equilibrium constant considerations, using $K_{eq} = 1.0$ mol^{-1} L at 300 K.

We note that the equilibrium constant of hydrogen bond formation between hexafluoro-2-propanol and diethyl ether in carbon tetrachloride is about 30 mol^{-1} L at room temperature.[8] The value of 0.4–1.0 mol^{-1} L for the equilibrium constant between MPS and PVME used in our calculation is much smaller in comparison. It is possible that the apparent equilibrium constant is smaller in a viscous medium of polymer mixture in the solid state. Alternatively, if a slightly larger value of τ is assumed, the calculated values of C_b/C_0 and K_{eq} would be much larger.

The above procedure can also be used, with slight modification, to calculate the fraction of hydrogen bonding in mixtures of modified polystyrene and poly(methyl methacrylate). However, PS and PMMA are immiscible and the exchange interaction parameter for MPS–PMMA consists of a dispersion force contribution (positive) due to PS–PMMA and a hydrogen-bonding contribution (negative). The former contribution can be estimated from the solubility parameters of PS and PMMA,[10] with $\Delta\delta = 0.2$. Again, X_{12} can be calculated from the free volume term, and $X_{H\,bond}$ is equal to the difference between X_{12} and X_δ. The equation-of-state parameters are $T_1^*/T_2^* = 1.067$, $P = 755$ J cm^{-3}, and $\alpha_1 = 5.2 \times 10$ K^{-1} from ref 9. In this case, since the hydroxyl content is higher in the MPS, about 4%, the use of the same parameters for MPS and PS is a gross approximation. Nonetheless, the results of our calculation are given in Table II. The fractions of hydrogen bond remaining at LCST, listed in the last column, are consistent with a K_{eq} value of 0.3 at 300 K.

We believe that the above calculation gives a reasonable account of the contribution of hydrogen bonding to the increase of LCST. Quantitative measurement of C_b/C_0 by infrared spectroscopy near LCST remains to be carried out to confirm the above calculations.

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Registry No. PVME (homopolymer), 9003-09-2; (vinylphenylbis(trifluoromethyl)carbinol)·(styrene) (copolymer), 95859-13-5; PMMA (homopolymer), 9011-14-7.

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