and there is no basis for expecting the right-hand side of this expression to vanish at the limit.

For concreteness we suppose that

$$\Psi = \chi_1\phi^2 + \chi_2\phi^3 + O(\phi^4) \tag{21}$$

where the coefficients χ_i are functions of temperature alone. This is equivalent to assuming the validity of a virial expansion of the chemical potential

$$-(\mu_1 - \mu_1^0)/RT = \frac{\phi}{m} + (\tfrac{1}{2} - \chi_1)\phi^2 + (\tfrac{1}{3} - \chi_2)\phi^3 + \ldots \tag{22}$$

where the coefficients of ϕ^2 and ϕ^3 are the second and third virial coefficients. Then as $\phi \rightarrow 0$, eq 17 and 18 are satisfied if

$$\chi_1 = \tfrac{1}{2} \tag{23}$$

$$\chi_2 < \tfrac{1}{3} \tag{24}$$

and eq 20 becomes

$$\lim_{\phi_c \rightarrow 0}\left(\frac{dT_c}{d\phi_c}\right) = (1 - 3\chi_2)\bigg/\frac{d\chi_1}{dT} \tag{25}$$

We remark that the simple form of the Flory–Huggins theory[2] corresponds to a special case of eq 21 with $\chi_i = 0$ for $i \geq 2$. Assuming a temperature dependence

$$\chi_1 = \beta_0 + \beta_1/T \tag{26}$$

with β_0 and β_1 positive constants, which implies merely the resolution of the free energy quantity $RT\chi_1$ into entropic and enthalpic components in the region of an upper critical separation, we have for this case a result

$$\lim_{\phi_c \rightarrow 0}(dT_c/d\phi_c) = -T^2/\beta_1 \tag{27}$$

that unequivocally contradicts eq 2. Furthermore, if eq 16 to 18 and the succeeding development are beyond question, eq 27 effectively refutes the corollary of eq 2 that would deem the classical Flory–Huggins model thermodynamically inadmissible.

Continuing with Ψ described by the single χ parameter, we can easily see what is needed to resolve the discrepancy. We have

$$\Gamma = \chi_1\phi(1 - \phi) \tag{28}$$

whence

$$\Gamma'' = -2\chi_1 \tag{29}$$

$$\Gamma''' = \Gamma'''' = 0 \tag{30}$$

and the critical conditions of eq 7 to 9 reduce to

$$(1 - \phi)^{-1} + (m\phi)^{-1} - 2\chi_1 = 0 \tag{31}$$

$$(1 - \phi)^{-2} - (m\phi^2)^{-1} = 0 \tag{32}$$

$$(1 - \phi)^{-3} + (m\phi^3)^{-1} > 0 \tag{33}$$

At $\phi = 0$, eq 32 can only be satisfied if

$$\lim_{\phi \rightarrow 0}(1/m\phi^2) = 1 \tag{34}$$

which means that $(m\phi^3)^{-1}$ must simultaneously pass to infinity. Now eq 31 to 34 are in complete accord with eq 16 to 18, and we conclude finally that the condition on G'''', eq 9, must be amended to include

$$\lim_{\phi \rightarrow 0}(G'''') = \infty \tag{35}$$

The same conclusion is reached if Γ contains terms of higher order than quadratic in ϕ.

In support of eq 2 Kennedy cites an analysis[6] of phase-separation data of Koningsveld, Kleintjens, and Shultz[7] on the system polystyrene + cyclohexane, to give a Θ temperature near 30°, at least 3° below fairly concordant values found in a number of earlier studies. We cannot fault the data of Koningsveld, *et al.*, but we think two remarks are pertinent. (A) There is no reason to suppose, but rather the converse, that phase-separation measurements lead to values of the Θ temperature more reliable than those established by the vanishing of the second virial coefficient,[2] and measurements of the latter kind[8] on polystyrene + cyclohexane have usually yielded values between 34° and 35°. (B) Conventional extrapolations of critical temperatures to infinite molecular weight are based on the premise that a plot of T_c^{-1} *vs.* $m^{-1/2}$ becomes linear as $m \rightarrow \infty$, and not on direct use of $dT_c/d\phi_c$. This dependence is easily shown to obtain for a system obeying eq 26, 31, and 32. More significantly perhaps, it is also confirmed by a less specific derivation[9] requiring only that a virial expansion be applicable in the neighborhood of a critical point in dilute solution.

The support of the National Science Foundation under Grant DMR74-14953 is gratefully acknowledged.

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Glass Transition of the Polymer Microphase

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Received October 16, 1974

Studies of block copolymer behavior showed that the properties of the finely dispersed microphase are not the same as those of the polymer in bulk. Hendus, Illers, and Ropte[1] observed that the glass transition temperature of the styrene component in SBS systems is lowered for more finely dispersed microphase. The decrease of the glass transition temperature of the hard component with decreasing concentration of its blocks was also observed by Cooper and Tobolsky.[2] Ductility of the polystyrene microphase was observed at lower temperatures than predictable[3-5] from the values of the bulk material. Fischer and Henderson[6] found the T_g of polystyrene blocks in the SBS system at about 70° which is a low limit compared to bulk polystyrene for which $T_g \approx$ 90–100° at reasonably high molecular weights. The two-phase system poly[(ethylene-*co*-propylene)-*g*-vinyl chloride] was found by us to exhibit a lower glass transition temperature of the PVC microphase according to both dilatometric and stress relaxation measurements.[7] Fischer and coworkers[8,9] did not find any significant decrease of the glass transition temperatures of the amorphous microphase in semicrystalline polybutene and polyethylene. It follows from these experimental data[1-9]

Table I
Styrene–Butadiene–Styrene Block Copolymer (Unadjusted Data from ref 1)[e]

Polystyrene Wt %	Polystyrene Vol %	Morphology	Thickness or diameter of microdomains, Å	S/V × 10^{-6}, cm^{-1}	T_g (°C) from G_i'[a]	T_g (°C) from G_{max}''	ΔT_g (°C)[b] G_i'	ΔT_g (°C)[b] G_{max}''
84	81	Spheres[c]	200–250	0.8				
66				1.0[d]	110	102		
55	50	Plates	150	1.3				
50				1.5[d]	105	95	5	7
38		Cylinders	150–200	2.2	102	90	8	12
32				2.9[d]	100	80	10	22
31	26	Cylinders	100 0	4.0				
26				4.0[d]		70		32
24				4.1[d]		75		27
12	10	Spheres	80–90	7.0				

[a] Inflex point at G'. [b] Relative shift with respect to the sample containing 66 wt % of polystyrene; *i.e.*, $\Delta T_{gx} = T_{g66} - T_{gx}$. [c] Spheres of butadiene blocks. [d] Interpolated values. [e] $K_S = (8.4 \pm 1.0) \times 10^{-6}$ cm deg.

that the T_g of the plastic phase is lowered if it is dispersed in a phase with *lower* T_g. To explain the depression of the glass transition temperature one immediately suspects partial mixing of the phases. Arguments for the existence of an intermixed zone were presented[12,13] and the experimental data show that a certain amount of the mixed phase really exists; there is an intermediate loss peak below that corresponding to the polystyrene glass transition[3] or at least a pronounced low temperature shoulder of the loss peak corresponding to the glass transition of the polystyrene phase.[1] The existence of the intermixed zones had to be assumed also in the interpretation of viscoelastic data.[14] On the contrary, Lim, *et al.*,[15] do not assume any appreciable mixing in Kraton 102 styrene–butadiene–styrene copolymer. Obviously, the existence of the intermixed zone depends not only on the properties of components, but also on the method of preparation, *e.g.*, casting solvent,[3] etc. In case one assumes that the mixing is homogeneous, the concentrations of components within each phase can be easily estimated using either specific volumes of the pure components or their thermal expansion coefficients and the Gordon–Taylor equation.[7] In the actual case, the mixing is inhomogeneous and the concentration profile has generally sigmoidal shape.[16–19]

In order to understand the T_g lowering data in terms of the free value concept we expect that mixing increases the average free volume available to the glassy microphase. Though mixing is not homogeneous, the size of the microphase domains may be considered small enough to yield an average, lower, T_g rather than the unchanged glass transition temperature of the microphase and an intermediate, well separated transition of the intermixed zone. To make a simple approximation, it seems reasonable to assume that the amount of mixing, and, consequently, the amount of the additional free volume, is proportional to the interface area. It immediately follows from the standard free volume calculations[11] that the term expressing the T_g lowering should have the form $-K_s(S/V)$, where K_s is a constant, and S/V is the surface (interface)-to-volume ratio of the plastic phase. The well-known formula[10,11] expressing the

$$T_g = T_{g\infty} - K_M/M \qquad (1)$$

dependence of the T_g on molecular weight M, can then be expanded for this purpose by including one more term on the right-hand side.

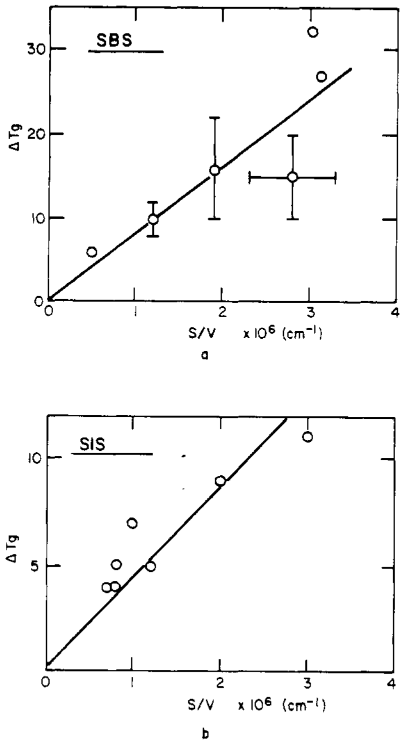

Figure 1. The depression of the glass transition temperature ΔT_g *vs.* the surface-to-volume ratio of the polystyrene microphase (S/V); (a) styrene–butadiene–styrene triblock, vertical bar shows the variation in the T_g estimate (Tables I and II), horizontal bar reflects the variation in the S/V results (Table II), $K_s = (8.4 \pm 1) \times 10^{-6}$ cm deg; (b) styrene–isoprene–styrene copolymer (Table III), $K_s = (4.3 \pm 0.5) \times 10^{-6}$ cm deg.

$$T_g = T_{g\infty} - K_M/M - K_s(S/V) \qquad (2)$$

The T_g is the transition temperature of the plastic phase and the $T_{g\infty}$ and K_M are constants, respectively.

An attempt has been made to check the validity of eq 2 using relevant experimental data available in the literature. Only a few papers bring information concerning both morphologies and some estimates of corresponding glass transition temperatures. Estimates based on the relations between molecular weights of blocks and morphology[13,16,19–22] have sometimes been made to complete the morphological data. In order to make the data concerning T_g applicable to eq 2, determinations from various methods have been corrected as customary to make possible the comparison of the glass transition temperatures to eq 2. For styrene–butadiene–styrene copolymers listed in Table I, T_g temperatures and their shifts were determined from the temperatures of the loss peaks obtained by torsion pendulum.[1] Because the frequencies of these experiments may vary, possible $T_g \sim T(G_{max}'')$ variation has been estimated using the WLF equation. Though the WLF coefficients for bulk polymer and polymer component in a two-phase system are somewhat different,[7,15,23] the difference is unimportant in this estimate. The variation of the peak frequency from 0.5 to 5 Hz results in the temperature variation of about 5°. Empirical correction[24] of about −10 to −20° had been taken for the value $T_g \sim 95°$ obtained by the vibrating reed method[3] (frequency ~50 Hz) for Kraton 101 (Table II). The T_g shifts with respect to the highest T_g morphology were used in the case where a reference reading for the bulk polystyrene was not available (Table I).

Table II
Kraton 101 (Styrene–Butadiene–Styrene Block Copolymer)[3]

Styrene wt %	Mol wt × 10^{-3}	Mol wt of one S block × 10^{-3}	Diameter of micro-domains, Å	S/V × 10^{-6}, cm^{-1}	K_m/M,[a] deg	T_g measured, °C	ΔT_g,[c] °C
28	76	11	120	~3.3 (2.3[d])	5	75–85[b]	10–20

[a] Correction for molecular weight of styrene blocks. [b] From G_{max}'' temperature ~95°;[3] 10–20° is subtracted to account for the frequency [~50 Hz] effect of vibrating reed method.[24] [c] According to eq 1. [d] From the small angle X-ray scattering data.[27]

Table III
Styrene–Isoprene–Styrene Block Copolymer (Unadjusted Data from ref 5)[b]

Code of author[5]	Polystyrene		Mol wt of one PS block × 10^{-3}	Morphology	Thickness or diameter micro-domains, Å	S/V × 10^{-6}, cm^{-1}	T_g from DSC,[5] °C	ΔT_g,[a] °C
	Wt %	Vol %						
SIS 4	95.9	92	49	Spheres[c]	80[d]	0.7	98	4
SIS 10	90.7	89	46	Spheres[c]	100[d]	0.7	98	4
SIS 15	85.1	83	42	Spheres[c]	100[d]	1.2	97	5
SIS 20	79.0	76	41	Rods[c]	150[d]	0.8	97	5
SIS 40	57.9	54	32	Plates	200	1.0	95	7
SIS 60	41.5	38	22	Rods	200	2.0	92	9
SIS 80	18.6	16.5	9	Spheres	200[d]	3.0	87	11
Polystyrene	100	100	100				102	0

[a] Difference: T_g (bulk polystyrene) − T_g (microphase) including the correction K_m/M for the molecular weight of the polystyrene block. [b] $K_s = (4.3 \pm 0.5) \times 10^{-6}$ cm deg. [c] Of polyisoprene. [d] Estimates according to ref 13, 16, and 20–22.

Actually, it only reduces the number of available results from n to $n - 1$. The maximum variation of the T_g data (Table I) due to various lengths of the polystyrene blocks has been estimated at ±2°. Where more complete data were avilable,[3,5] corrections for styrene block length K_M/M have been calculated (Tables II and III). $T_{g\infty} = 100$ and $K_M = 10^5$ were taken for polystyrene.[10,25] The properly adjusted experimental results (Figure 1) indeed show a clear trend suggesting the linear dependence $\Delta T_g = K_s(S/V)$ where $\Delta T_g = T_g - T_{g\infty} + (K_M/M)$. Scatter observed on the figures is most probably caused by inaccuracy in morphology determination.

To get an idea how much free volume is involved in the T_g depression of the microphase, we assume volume additivity of the mixing. Using then the published values of the free volume expansion coefficients, T_g's, and specific volumes for polystyrene,[1,10,25,26] polyisoprene,[1,5,26] and polybutadiene,[1,26] we find out from the Gordon–Taylor equation that the equivalent T_g depressions can be reached if the polystyrene microphase is homogeneously mixed with roughly one adjacent monolayer (~10 Å) of the elastomer.

Acknowledgment. Valuable comments of Professor Bernhard Wunderlich are gratefully acknowledged.

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