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# Thermodynamics of Polymer Compatibility

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ABSTRACT: A simple form of the Prigogine–Flory solution thermodynamics has been used to discuss the thermodynamics of compatible polymer mixtures which are contrasted with polymer–solvent systems and mixtures of oligomers. The treatment is similar to, but simpler than, that of McMaster (*Macromolecules*, **6**, 760, 1973), facilitating estimation of the trends the $\chi$ parameter may be expected to show as a function of temperature and pressure. The free volume contribution, depending on a difference in thermal expansion coefficients of the components, is positive, i.e., unfavorable to mixing. For a compatible high molecular weight system, this is balanced at low $T$ by a small favorable interactional or contact energy term ($X_{12} < 0$) due to hydrogen bonding or charge transfer which decreases with increase of $T$ bringing about phase separation. This LCST has, typically, a considerable positive dependence on pressure (~0.2 K atm$^{-1}$) which may become negative for a mixture of a cohesive (high $P^*$) but flexible (low $T^*$) polymer of lower cohesion and flexibility.

Recent reviews[1,2] testify to increasing interest in the thermodynamics of polymer–polymer interactions and the causes of polymer compatibility or incompatibility. The basic treatment by Scott[3] and Tompa[4] applied the Flory–Huggins theory of polymer solution thermodynamics which is mainly concerned with the positional or combinatorial entropy of mixing the two components. More recently, the Flory–Huggins theory has been extended through the introduction of free volume or equation of state effects giving the Prigogine–Flory theory,[5] and this has proved very useful for polymer–solvent systems. McMaster[6] has now applied the Prigogine–Flory theory to the thermodynamics of polymer mixtures and finds that free volume effects are of importance in polymer–polymer as well as in polymer–solvent systems. However, the equations developed by McMaster are extremely complex, partly because he has generalized the Prigogine–Flory theory at the same time as applying it to polymer mixtures.

We believe it is useful to apply the original Prigogine–Flory theory in a simple but adequate approximation which has been extensively used to treat phase diagrams in polymer–solvent systems at ordinary pressure[7] and at higher pressure.[8] Our aim is to review and give an intuitive understanding of some of the main effects in polymer–polymer thermodynamics. Numerical predictions are similar to those of McMaster, but our general impression is that free volume is less important in these systems than one might infer from his paper. For instance, he made the important and correct prediction that phase separation in a compatible polymer–polymer system normally takes place on raising the temperature at a Lower Critical Solution Temperature (LCST). We believe that the primary cause of this LCST does not lie in an increasingly unfavorable free volume effect, as in the usual polymer–solvent system, as suggested by McMaster. We prefer to place the emphasis on the favorable interaction between the polymers which stabilize the mixtures at low $T$ but which fall off at higher $T$.

We do not believe that the Prigogine–Flory theory is capable of explaining the detailed shape of binodals such as the double peaks recently found by Koningsveld[1] and others. Koningsveld and Stepto have suggested[9] that these may reflect a new interaction between the polymers which would be outside the scope of the present Prigogine–Flory theory. It should also be noted that Sanchez and Lacombe[10] have recently developed a new theory of liquid mixtures which allows for free volume effects, and they have applied it to polymer mixtures. Predictions should be similar to those of the Prigogine–Flory theory, and a detailed comparison could be of interest at a later date.

## Review of Thermodynamic Contributions in the Prigorine–Flory Theory

**The Interactional or Contact Energy Term.**[11] This arises from the weakness or strength of unlike 1–2 contacts in the mixture relative to the like 1–1 and 2–2 contacts in the pure components. In the usual case of dispersion forces, the unlike contacts are relatively weak and there is a positive, endothermic contribution in $\Delta H_M$, or in the Flory nomenclature, $X_{12}$ is positive. Although in principle there is an accompanying positive contribution in $\Delta S_M$, this is small and the net effect in $\Delta G_M$ and the $\chi$ parameter is positive, i.e., unfavorable to mixing. However, in the rare case of a specific interaction between the components, i.e., a hydrogen bond or a weak charge transfer complex, it is possible to have a negative or exothermic contribution in $\Delta H_M$ and $X_{12}$ is negative. This is important here since only through such specific interactions can a stable mixture of high polymers be obtained. Various groups are known which should interact in this way, e.g., an aromatic with an ether. Unfortunately, an exothermic contribution in $\Delta H_M$ may be overcome by an unfavorable negative contribution in $\Delta S_M$ making difficult the prediction of compatible pairs of polymers.

**The Free Volume Term.**[11] Two liquid components will generally have different free volumes or degrees of thermal expansion. A liquid polymer has extremely low free volume because of chain connectivity. The chain segments are linked by strong covalent bonds which decrease the number of "external", expansion-promoting degrees of freedom/segment. Thus the difference in free volume between a polymer and a typical solvent will be large. However, even two polymeric

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liquids will have a free volume difference because of differing flexibilities of the chain backbones and/or different pendant groups. According to the Prigogine–Flory theory, two liquids of differing free volume will experience a net contraction on mixing and, as a result of this, negative contributions appear in both $\Delta H_M$ and $\Delta S_M$. The *net* contribution to the free energy of mixing, $\Delta G_M$, is predicted to be positive, i.e., unfavorable to mixing. It is usual to add the free volume and contact energy contributions to give a total $\chi$ parameter.

**The Combinatorial Entropy of Mixing.** It is obvious that a mixture is more "disordered" than the pure components. Thus, the positional or combinatorial $\Delta S_M$, as evaluated by the Flory–Huggins or another approximation, is positive and this is the main reason for the stability of mixtures of small-molecule liquids. However, both the interactional and free volume contributions are proportional to the *volume* of the system whereas the combinatorial entropy depends on the *number of molecules* in the system. Thus, when high molecular weight polymers are mixed, the combinatorial entropy becomes relatively unimportant, and the main cause of stability for small-molecule mixtures is no longer available. According to theory, for high molecular weights, compatibility can only be achieved through counterbalancing the unfavorable free volume contribution with a favorable interactional contribution due to specific interactions.

## The Flory–Huggins Critical Value of $\chi$

In the Flory–Huggins theory,[3,4] $\chi_{12}$ refers to the free energy increase associated with a whole molecule of component 1 forming contacts of the 1–2 type. This free energy and $\chi_{12}$ are thus normalized to the volume of a molecule 1 which is usually the solvent in a polymer (2)–solvent (1) system. The critical value of $\chi_{12}$ beyond which phase separation occurs is the well-known value[12]

$$\chi_{12,c} = {}^1\!/_2[1 + r^{-1/2}]^2 \tag{1}$$

where $r$ is the number of polymer "segments" defined as the ratio, $V_2/V_1$, of the molar volumes of the components. More recently, $r$ has been expressed using the core volumes of the component molecules, quantities emerging from the Prigogine–Flory theroy, i.e.

$$r = \frac{V_2^*}{V_1^*} = \frac{M_2 v_2^*}{M_1 v_1^*} \tag{2}$$

where the $M_i$ are molecular weights and $v_i^*$ the specific core volumes of the components. Expression 1 is valid in the case of a polymer–polymer system as well as the usual polymer–solvent system.[13] However, the normalization to the volume of component molecule 1 is inconvenient since molecule 1 may now be extremely large and may indeed tend to infinite size. Thus, other normalization volumes have been used, e.g., the volume of a repeat unit or segment of component 1, or for two polymers present in a solvent, the volume of the solvent molecule. Perhaps the most direct form of eq 1 uses $\chi_{12}$ per unit core volume of the interacting molecules, i.e., $\chi_{12}$ is divided by $M_1 v_1^*$ expressing $\chi_{12}$ per cm$^3$. The resulting quantity also has the advantage of being symmetrical in 1 and 2, whereas $\chi_{12}$ itself is not, i.e., $\chi_{12} \neq \chi_{21}$. Equation 1 becomes

$$\frac{\chi_{12,c}}{M_1 v_1^*} = \frac{1}{2}\left[\frac{1}{(M_1 v_1^*)^{1/2}} + \frac{1}{(M_2 v_2^*)^{1/2}}\right]^2 \tag{3}$$

For most components, $v_1^* \simeq v_2^* \simeq 1$ cm$^3$/g, so that

$$\frac{\chi_{12,c}}{M_1 v_1^*} \simeq \frac{2}{\overline{M}}$$

where

$$\frac{1}{\overline{M}^{1/2}} = \frac{1}{2}\left(\frac{1}{\overline{M}_1^{1/2}} + \frac{1}{\overline{M}_2^{1/2}}\right) \tag{4}$$

As $\overline{M} \to \infty$, $\chi_{12,c}/M_1 v_1^*$ tends rapidly to zero, so that the total of interactional and free volume contributions must be negative to achieve compatibility.

**Table I**
**Free Volume Quantities**

| | $t$, °C | $\alpha \times 10^4$,[a] K$^{-1}$ | $T^*$,[b] K | $\tilde{V}^{1/3}$ 200 °C | $\tau_{PS}$ |
|---|---|---|---|---|---|
| Polymer | | | | | |
| Polystyrene | 135 | 5.80 | 8191 | 1.07 | |
| Polybutadiene | 25 | 6.85 | 6571 | 1.11 | 0.20 |
| Polyisobutylene | 25 | 5.55 | 7577 | 1.08 | 0.07 |
| PMMA | 120 | 5.75 | 8119 | 1.07 | 0.00 |
| PVME | 135 | 7.23 | 7201 | 1.09 | 0.12 |
| Solvent | | | | | |
| Heptane | 25 | 12.4 | 4645 | 1.25 | 0.43 |
| Butyl acetate | 55 | 12.1 | 4974 | 1.19 | 0.39 |
| Carbon tetrachloride | 20 | 12.7 | 4582 | 1.27 | 0.44 |
| Benzene | 25 | 13.8 | 4445 | 1.32 | 0.46 |

[a] Obtained at $t$ °C. [b] From eq 5–7.

## The Prigogine–Flory Theory

**Parameters for Polymers.** In the Prigogine theory,[5a,11] the basic quantities characterizing a liquid are the reduced temperature ($\tilde{T}$), volume ($\tilde{V}$), and pressure ($\tilde{P}$) defined by

$$\tilde{T} = T/T^*; \quad \tilde{V} = V/V^* = v/v^*; \quad \tilde{P} = P/P^* \tag{5}$$

Here the starred quantities are constant reduction parameters and $V^*$ and $v^*$ also have the significance of being the molar and specific volumes at 0 K, i.e., the "core volumes". At ordinary temperature $\tilde{P} = 0$ and $\tilde{V}$ and $\tilde{T}$ are linked by an equation of state. Both are measures of the free volume of the liquid and of the temperature. A theoretical model, e.g., that of Flory,[5b] allows $\tilde{V}$ and $\tilde{T}$ to be calculated from an experimental value of the thermal expansion coefficient, $\alpha$:

$$\tilde{V}^{1/3} - 1 = \alpha T/3(1 + \alpha T) \tag{6}$$

$$\tilde{T} = (\tilde{V}^{1/3} - 1)/\tilde{V}^{4/3} \tag{7}$$

Equation 6 shows that for $\alpha = 0$, $\tilde{V}^{1/3} = 1$, i.e., the system is at 0 K whereas as $\alpha \to \infty$, $\tilde{V}^{1/3} \to {}^4\!/_3$, a point which corresponds to the vapor–liquid critical point.[14] All $\tilde{V}^{1/3}$ values are found between the extremes of 1 and ${}^4\!/_3$. Table I shows values of $\alpha$, $\tilde{V}^{1/3}$, and $T^*$ for some common polymers and solvents. It will be noted that polymers are characterized by small values of $\tilde{V}^{1/3}$ even at an elevated temperature, 200 °C. At the same temperature common solvents have very large values, $\sim{}^4\!/_3$, corresponding to proximity to the vapor–liquid critical point. Because of degradation, it is impossible for polymers to reach such a large value of $\tilde{V}^{1/3}$.

The *free volume difference* between two components in a system is characterized by

$$\tau = 1 - \frac{T_1^*}{T_2^*} \tag{8}$$

Values of $\tau$ are listed in Table I for systems composed of a typical polymer, polystyrene, with other polymers and also polystyrene with common solvents. It is clear that the $\tau$ parameter for two polymers is relatively small, ~0.15 or less, whereas for a polymer–solvent system $\tau \sim 0.4$. The $\tau$ parameter may be related to the difference of thermal expansion coefficients ($\Delta\alpha$) of the two polymers. If $\Delta\alpha$ is small compared with $\alpha$ of either polymer, then an expansion from the Prigogine–Flory theory may be used to give $\tau$

$$\tau = 9\tilde{V}^{-1/3}\left(\frac{4}{3} - \tilde{V}^{1/3}\right)\left(\frac{\Delta\alpha}{\alpha}\right) \simeq 0.6\,\frac{\Delta\alpha}{\alpha} \tag{9}$$

where $\tilde{V}$ is the reduced volume of either polymer.

The *interactional term* is characterized in the Flory nomenclature by the $X_{12}$ parameter having the dimensions of pressure. The ratio $X_{12}/P_1{}^*$ is a fundamental dimensionless quantity ($\nu^2$ was used for this in ref 11). Values of the $X_{12}$ parameter for various dispersion force interactions are given by Flory[5b] and are positive. However, many systems are known where the heat of mixing is negative, showing that $X_{12} < 0$. Thus, benzene + dioxane[15] and $CCl_4$ + dioxane[15] have equimolar heats of mixing of $-150$ and $-250$ J mol$^{-1}$, while $CCl_4$[15] and $CHCl_3$[15] + $n$-propyl ether have heats of $-300$ and $-2000$ J mol$^{-1}$ at 25 °C. These heats would correspond to very large negative values of $X_{12}$. Nevertheless they do not necessarily give favorable interactions between the components from the stand point of the free energy. The systems with dioxane have positive values of the excess free energy while those with $n$-propyl ether have negative values considerably less than the excess heats, indicating that these specific interactions cause not only a negative heat effect but also a negative effect in the entropy of mixing. Flory and collaborators[16] have introduced another empirical parameter, $Q_{12}$, having an entropic significance. In the case of specific interactions between polymers, we may expect that $Q_{12}$ should be negative, corresponding to an ordering of the component molecules by the interaction.

**The Prigogine–Flory Expression for $\chi$.** Previous reviews[11,17] have discussed an approximate relation from the Prigogine theory for the $\chi_{12}$ parameter (normalized to the molecular volume of component 1):

$$\chi_{12} = \underbrace{\frac{(-U)_1}{RT}\left(\frac{X_{12}}{P_1{}^*}\right)}_{\substack{\text{interactional}\\ \text{or contact}\\ \text{energy}}} + \underbrace{\frac{C_{\text{p},1}}{2R}\tau^2}_{\substack{\text{free}\\ \text{volume}}} \tag{10}$$

Here $U_1$ is the molar configurational energy of component 1, taken to be the reference liquid, $-U_1$ being the energy of vaporization, and $C_{\text{p},1}$ is the configurational heat capacity. In the case of a dilute polymer solution, the solvent is the reference liquid 1, while for two polymers either may be taken as the reference. Only the first order of the small quantity $X_{12}/P_1{}^*$ and second order of $\tau$ have been retained.[17] Furthermore we ignore the concentration dependence of $\chi_{12}$ predicted by the Prigogine–Flory theory, keeping $\chi_{12}$ constant as in the original Flory–Huggins theory. However, eq 10 proved useful[7,8] for dilute polymer–solvent systems where $\tau$ and usually $X_{12}$ are much larger than in polymer–polymer systems, and hence we expect eq 10 to be useful here. As in previous work, we shall use a model to predict $-U_1$ and $C_{\text{p},1}$ in eq 10. The Flory model[5b] assumes a van der Waals liquid giving

$$-U_1 = P_1{}^*V_1{}^*\tilde{V}_1{}^{-1} \tag{11}$$

$$C_{\text{p},1} = \frac{P_1{}^*M_1v_1{}^*\tilde{V}_1{}^{1/3}}{T_1{}^*}\Big/\left(\frac{4}{3} - \tilde{V}_1{}^{1/3}\right) \tag{12}$$

Using these together with eq 7 for $\tilde{T}$, we have

$$\frac{\chi_{12}}{M_1v_1{}^*} = \frac{c_1}{M_1v_1{}^*}\left[\underbrace{\frac{\tilde{V}_1{}^{1/3}}{\tilde{V}_1{}^{1/3} - 1}\left(\frac{X_{12}}{P_1{}^*}\right)}_{\text{interactional}} + \underbrace{\frac{\tilde{V}_1{}^{1/3}}{2(4/3 - \tilde{V}_1{}^{1/3})}\tau^2}_{\text{free volume}}\right] \tag{13}$$

$$\frac{c_1}{M_1v_1{}^*} = \frac{P_1{}^*}{RT_1{}^*} \tag{14}$$

On the right-hand side $c_1$ is the number of "segments" in the component 1 molecule, each segment chosen to have three external degrees of freedom like a monomer. In practise, only the ratio $c_1/M_1v_1{}^*$ is required, given in eq 14.

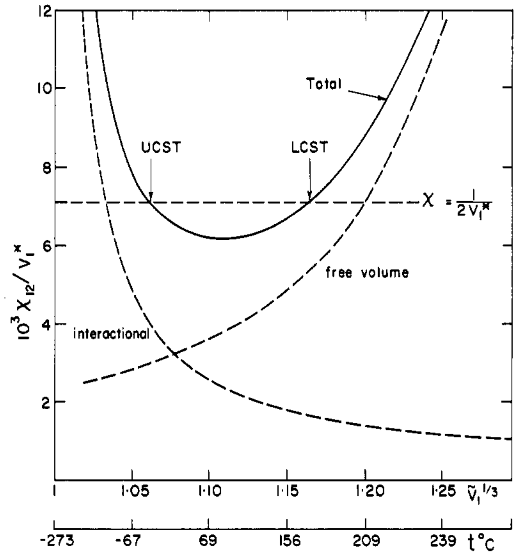

**Figure 1.** Polymer–solvent system. The $\chi_{12}$ parameter expressed per unit volume of interacting molecules, i.e., $\chi_{12}$, divided by $V_1{}^* = M_1v_1{}^*$ for a polymer (2)–solvent (1) system against $\tilde{V}_1{}^{1/3}$ and $t$. The following parameters have been used in eq 13 and 14: $T_1{}^* = 5000$ K, $P_1{}^* = 400$ J cm$^{-3}$, and $T_2{}^*$ 8191 (polystyrene); $X_{12} = 10$ J/cm$^3$, a typical value for dispersion forces. The dashed curves give the interactional and free volume contributions, and the horizontal line corresponds to the critical value of $\chi_{12}/V_1{}^*$ from eq 3, putting $V_1{}^* = 70$ cm$^3$ mol$^{-1}$ and letting $M_2 \to \infty$.

Using eq 13 coupled with eq 3, we have calculated critical temperatures in a number of cases with the same parameters as used by McMaster. Agreement with ref 6 is good. The details of the phase diagram, e.g., shape of spinodal or binodal, would no doubt be rather different since here we do not allow for any variation of $\chi_{12}$ with concentration. However, eq 13 should give adequate predictions of trends in temperatures of phase separation when $\tau$, $M$, or $X_{12}$ are varied. We do not expect an accurate prediction of a critical solution temperature or a $\chi_{12}$ parameter for some particular experimental situation.

If the $Q_{12}$ parameter is introduced, another term must be added to eq 10, namely $-Q_{12}/R$, or equivalently in eq 13, $X_{12}$ is replaced by an "effective" value of $X_{12} - TQ_{12}\tilde{V}_1$. Thus, although $X_{12}$ as obtained from heats of mixing may be negative, the "effective" $X_{12}$ for free energies may be positive if $Q_{12}$ is also negative. In the present work we put $Q_{12} = 0$ but will comment on the significance of this parameter.

## Discussion

**General.** Equation 13 for $\chi_{12}/M_1v_1{}^*$ shows that the interactional term tends to $\infty$ as $\tilde{V}_1{}^{1/3}$ decreases to 1 and $T$ tends to 0 K. On the other hand, the free volume term tends to infinity as $\tilde{V}_1{}^{1/3}$ tends to 4/3, i.e., $T$ tends to the vapor–liquid critical temperature of component 1. In Table I we have seen that for polymers $\tilde{V}_1{}^{1/3}$ is near 1, and hence we expect the interactional term to dominate. However, for a dilute solution of a polymer in a solvent, the reference component 1 is the solvent for which $\tilde{V}_1{}^{1/3}$ can easily approach 4/3 where the free volume term will dominate. Thus, we expect polymer–polymer and polymer–solvent systems to be fundamentally different. Various cases will now be discussed numerically. Since the $\chi$ parameter in the Flory–Huggins equation can be calculated from eq 13 (or 22 for nonnegligible P) the binodals and spinodals can be computed by standard methods. However, here we emphasize the temperature and pressure dependence of $\chi$ and the effect of the various parameters on phase separation at the critical point and, thereby, on the location of the cloud-point curve.

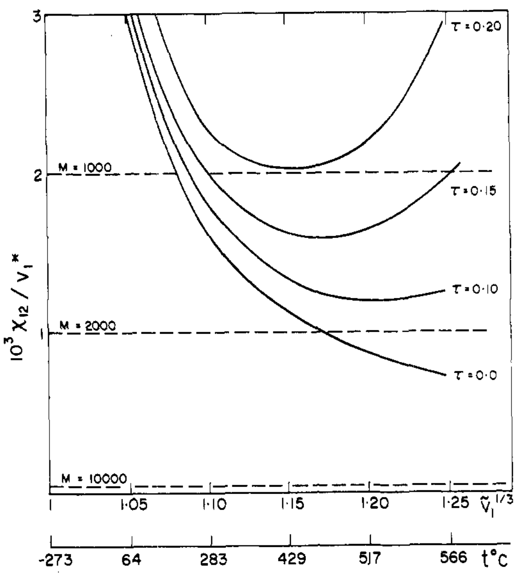

**Figure 2.** Polymer-polymer system with $X_{12} > 0$. The $\chi_{12}/M_1v_1^*$ parameter for a mixture of polymers interacting with dispersion forces with $X_{12} = 10$ J cm$^{-3}$ against $\tilde{V}_1^{1/3}$ and $t$, with different values of $\tau$. Polystyrene is the reference polymer, $T_1^*$ 8191 K, $P_1^* = 500$ J cm$^{-3}$, and the horizontal lines are critical values of $\chi_{12}/M_1v_1^*$ from eq 3 with $M_1 = M_2$ and $v_1^* = v_2^* = 1$ g cm$^{-3}$.

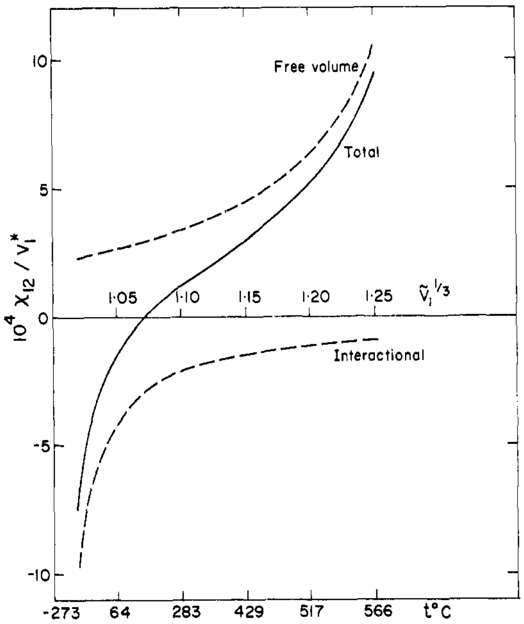

**Figure 3.** Polymer-polymer system with $X_{12} < 0$. The $\chi_{12}/M_1v_1^*$ parameter for a mixture of compatible polymers with $X_{12} = -1.3$ J cm$^{-3}$ against $\tilde{V}_1^{1/3}$ and $t$ showing the favorable interaction contribution. Polystyrene is the reference polymer, $T_1^* = 8191$ K, $P_1^* = 500$ J cm$^{-3}$, and $T_2^* = 7201$ K corresponding to poly(vinyl methyl ether). The critical value of $\chi_{12}/M_1v_1^*$ is 0 for high molecular weight polymers.

**The Temperature Dependence of $\chi$ for a Polymer-Solvent System.** Figure 1 shows $\chi_{12}/M_1v_1^*$ against $\tilde{V}_1^{1/3}$ and $T$ for a typical polymer-solvent system, as calculated from eq 13. The relevant values of the reduction parameters are given in the legend. Being the sum of the interactional and free volume contributions, the total $\chi_{12}/M_1v_1^*$ has the characteristic U-shaped temperature dependence discussed in ref 11.

The value of $\chi_{12,c}$ was calculated from eq 1 for a polymer of infinite molecular weight, $M_2 \rightarrow \infty$, and a solvent with $M_1v_1^* = 70$ cm$^3$ mol$^{-1}$. The system shows the UCST and LCST with an interval of complete miscibility in between. Although both the interactional and free volume terms are important in $\chi$, the UCST is essentially due to the increase of the unfavorable interactional term with decrease of $T$, while the LCST is caused by the increase of the free volume term with increase of $T$. If $X_{12}$ and/or $\tau$ were increased, the U-shaped $\chi$ curve would move higher and the UCST and LCST would coalesce, as found in various systems[7] where the polymer and solvent are never completely miscible. On the other hand, if the molecular weight of the polymer were to be decreased, $\chi_{12,c}$ would move up, spreading apart the UCST and LCST as studied in ref 7.

**The Temperature Dependence of $\chi$ for a Mixture of Polymers with $X_{12} > 0$.** Figure 2 shows $\chi_{12}/M_1v_1^*$ against $\tilde{V}_1^{1/3}$ and $T$ where both components 1 and 2 are now polymers, with $X_{12} = 10$ J cm$^{-3}$ = 100 atm, a typical value for dispersion force interactions. The chosen values of $\tau$ are smaller than those in Figure 1 in order to be more appropriate to a mixture of polymers or oligomers. The critical values of $\chi_{12}/M_1v_1^*$ have been drawn using eq 3 for various values of $\bar{M}$ and setting $v_1^* = v_2^* = 1$ cm$^3$/g. As expected, polymer-polymer behavior is dominated by the interactional term, i.e., curves where $\tau \neq 0$ are all close to that drawn for $\tau = 0$. For $\bar{M} = 10^4$ and higher, the system is unstable throughout the temperature range considered here. For $\bar{M} = 10^3$ and $\tau = 0$, the system becomes compatible with rising $T$ at a UCST. With increasing $\tau$ compatibility between the polymers is lessened. A LCST would exist at sufficiently high temperature. However, the $\chi(T)$ curves are extremely flat so that degradation would occur before the LCST could be reached. The main result of the theory stems from the zero critical value of $\chi$ when $M$ is very large. Since the free volume contribution to $\chi$ is always positive, compatibility of high polymers requires a *negative* interactional term, i.e., $X_{12} < 0$, and the presence of a specific interaction between the polymers.

**The Temperature Dependence of $\chi$ for a Compatible Polymer Pair with $X_{12} < 0$.** Figure 3 shows $\chi_{12}/M_1v_1^*$ against $\tilde{V}_1^{1/3}$ and $T$ for a typical pair of compatible polymers of high molecular weight where $\chi_{12,c}/M_1v_1^* \simeq 0$. Polymer compatibility thus corresponds to a negative value of $\chi_{12}$ and incompatibility to a positive value. Since $X_{12}$ is negative the interactional term is negative, i.e., favorable to mixing, and it balances the unfavorable free volume term. In eq 13, equating the contact energy and free volume terms, we have

$$\frac{-(X_{12}/P_1^*)}{\tau^2} = \frac{\tilde{V}_1^{1/3} - 1}{2(4/3 - \tilde{V}_1^{1/3})} \simeq \frac{1}{7} \tag{15}$$

so that for $\tau \sim 0.15$ and $P_1^* \sim 400$ J cm$^{-3}$, the very small value of $X_{12} \simeq -2$ J cm$^{-3}$ suffices to compatibilize the polymers. (It is probably more accurate to state that $X_{12} - TQ_{12}\tilde{V}_1$ is small and negative. $X_{12}$ itself could be strongly negative but counterbalanced by a negative $Q_{12}$ value.)

The S-shaped curve of Figure 3 should be typical for $\chi(T)$ in the case of a compatible polymer pair. At low temperatures the system is compatible. However, as the temperature is increased the magnitude of the favorable interactional term decreases rapidly until it can no longer outweigh the unfavorable free volume term to give a negative value of $\chi$ and a LCST occurs at $\chi = 0$ followed by incompatibility at higher $T$. In contrast to the LCST in polymer-solvent systems caused by an increasing free volume term, the LCST is caused here primarily by the interactional term becoming less negative. Using eq 15 and differentiating eq 13, we find the ratio of the temperature dependences of the two contributions to $\mathrm{d}\chi/\mathrm{d}T$ at the LCST to be given by

$$\frac{\mathrm{d}\chi/\mathrm{d}T(\text{interactional})}{\mathrm{d}\chi/\mathrm{d}R(\text{free volume})} = \frac{3(4/3 - \tilde{V}_1^{1/3})}{4(\tilde{V}_1^{1/3} - 1)} \simeq 3 \tag{16}$$

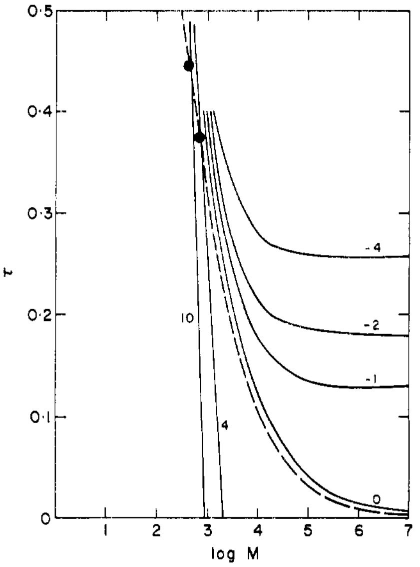

**Figure 4.** Critical values of $\tau$ corresponding to phase separation for polymer–polymer systems of molecular weight $\overline{M}$ and indicated values of $X_{12}$. The temperature is fixed at 135 °C, $\tilde{V}_1^{1/3} = 1.067$, and starred parameters are as described in the text. Regions below and to the left of the full curves correspond to compatible systems. The dashed curve from eq 17 divides systems showing UCST (to the left) from systems showing LCST (to the right). The dots at intersections of dashed curve with curves for $X_{12} = 4$ and 10 J cm$^{-3}$ thus correspond to coalescence of UCST and LCST.

Since $\tilde{V}^{1/3}$ is close to unity for polymers, the variation of the interactional term is larger than that of the free volume contribution. The role of free volume at the LCST is less than in the work of McMaster where emphasis is placed on the free volume term as the cause of the LCST. However, most of the examples in ref 6 put $X_{12} = 0$, hence the emphasis on the free volume term.

If indeed $Q_{12} < 0$, then the favorable $\chi$(interactional) will reflect the effective $X_{12}$, i.e., $X_{12} - TQ_{12}\tilde{V}_1$. With increase of $T$ the value of this parameter can change from negative to positive, giving a much more rapid temperature dependence than when $Q_{12} = 0$. This corresponds to a breakup of the favorable interactions due to the increased temperature. In such a case, the role of free volume would be even less than when $Q_{12} = 0$. An intriguing possibility would be the occurrence of a LCST followed at higher temperature by a UCST, such as occurs in aqueous solutions of amines and ethers.

**The Critical Conditions in Terms of $\tau$, $X_{12}$, and $M$.** It is now of interest to consider the values of $\tau$ and $X_{12}$ which will lead to compatibility or incompatibility of typical polymer mixtures of different values of $M$. Values of $P_1^*$, $T_1^*$, and $\tilde{V}_1^{1/3}$ for the reference polymer have been taken to be 500 J cm$^{-3}$, 8191 K, and 1.067, corresponding to polystyrene at 135 °C, values taken by McMaster[6] to correspond to a typical situation, and $v_1^* = v_2^* = 1$ cm$^3$ g$^{-1}$. Values of $\tau$ for different $\overline{M}$ at constant $X_{12}$ have been generated by equating eq 13 to the critical value of $\chi_{12}$, given by eq 3. They are shown in Figure 4. $\tau$ and $\overline{M}$ to the right and above any curve correspond to phase separation, values below and to the left to miscibility, while the curves themselves are critical lines corresponding to systems at critical points.

When $X_{12}$ is negative, compatibility exists as $\overline{M} \to \infty$ and again one sees that only a small negative value of $X_{12}$ suffices to compatibilize a high molecular weight system having $\tau \sim 0.15$. The points along the curves for $X_{12} = 0$ all correspond to LCST. For $X_{12} > 0$, compatibility is only possible for low molecular weights or low $\tau$ values. As $X_{12}$ is raised, the maximum molecular weight allowing compatibility is rapidly decreased. For $X_{12} > 0$, the curves correspond to UCST except at very high values of $\tau$ where they become LCST. On each curve of constant $X_{12}$ there is a value of $\tau$ where the UCST and LCST coincide, signifying a minimum in $\chi$ vs. $T$. Differentiating $\chi$, we find the values of $\tau$, $(X_{12}/P_1^*)$, and $\tilde{V}_1^{1/3}$ to obtain a LCST when $X_{12} > 0$ are related by

$$\frac{\tau^2}{(X_{12}/P_1^*)} \geq \frac{3}{2}\left(\frac{4/3 - \tilde{V}_1^{1/3}}{\tilde{V}_1^{1/3} - 1}\right)^2 \tag{17}$$

Putting $\tilde{V}_1 = 1.067$ and $P_1^* = 500$ J cm$^{-3}$, values used to generate the curves in Figure 4, eq 17 gives $\tau = 0.77$ for $X_{12} = 10$ or $\tau = 0.31$ for $X_{12} = 4$ J cm$^{-3}$. These values are too high for a polymer–polymer system, so that a LCST would not be expected. As another example, the highest value of $\tilde{V}_1^{1/3}$ which could be reached by a polymer mixture might be 1.15 corresponding to 430 °C for polystyrene. If $\tau = 0.15$ is the largest value expected for polymer–polymer systems, then eq 17 indicates that $X_{12}$ must be smaller than 5 J cm$^{-3}$ which is low for dispersion force interactions. This calculation suggests that polymer–polymer systems showing both the UCST and LCST should be difficult to find. On the other hand, polymer–solvent systems showing both of these CST are well known.[7]

## The Effect of Pressure on Phase Equilibria in Polymer–Polymer Systems

**$\chi$ as a Function of $P$.** An expression similar to eq 10 has been used[8] for $\chi$ as a function of pressure

$$\chi_{12} = \underbrace{\frac{-U_1}{RT}\left(\frac{X_{12}}{P_1^*}\right)}_{\text{interactional}} + \underbrace{\frac{C_{\text{p},1}}{2R}\left[\tau + \frac{\beta_1 P}{\alpha_1 T}\pi\right]^2}_{\text{free volume}} \tag{18}$$

where

$$-\pi = 1 - (P_1^*/P_2^*) \tag{19}$$

and $\alpha_1$ and $\beta_1$ are the thermal expansion coefficient and isothermal compressibility of the reference liquid 1 at pressure $P$. It is essential to use a theoretical model to evaluate these quantities as well as $-U_1$ and $C_{\text{p},1}$. In the Flory model,

$$\frac{\beta_1 P}{\alpha_1 T} = \frac{\tilde{P}_1\tilde{V}_1^2}{1 + \tilde{P}_1\tilde{V}_1^2} \tag{20}$$

$U_1$ is still given by eq 11 and $C_{\text{p},1}$ under pressure is given by

$$C_{\text{p},1} = \frac{P_1^* V_1^*}{T_1^*}\tilde{C}_{\text{p},1} \tag{21}$$

so that eq 18 becomes

$$\frac{\chi_{12}}{M_1 v_1^*} = \frac{c_1}{M_1 v_1^*}\left[\frac{1}{\tilde{V}_1\tilde{T}_1}\frac{X_{12}}{P_1^*} + \tfrac{1}{2}\tilde{C}_{\text{p},1}\left\{\tau + \frac{\tilde{P}_1\tilde{V}_1^2}{1 + \tilde{P}_1\tilde{V}_1^2}\pi\right\}^2\right] \tag{22}$$

with

$$\tilde{C}_{\text{p}}^{-1} = (1 - \tfrac{2}{3}\tilde{V}^{-1/3}) - \frac{2(1 - \tilde{V}^{-1/3})}{1 + \tilde{P}\tilde{V}^2} \tag{23}$$

The equation of state is now

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3} - 1} - \frac{1}{\tilde{T}\tilde{V}} \tag{24}$$

For any pressure and temperature, $\tilde{V}^{1/3}$ must be obtained from eq 24 hence eq 23 and 22 give $\chi_{12}/M_1 v_1^*$ as a function of $P$ (practically, it is easier to choose $\tilde{V}^{1/3}$ then obtain the pressure to which it corresponds through eq 22).

**The Pressure Dependence of the LCST for a Compatible Polymer Pair.** It is well-known[8] that the pressure dependence of the LCST is large for a polymer–solvent system,

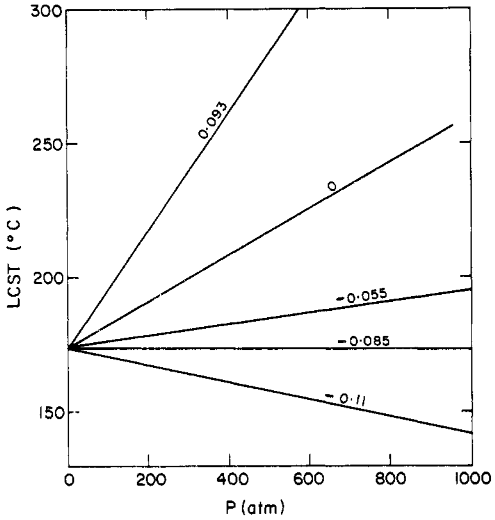

**Figure 5.** The pressure dependence of LCST for a compatible polymer-polymer system. The values of $P_1^*$, $T_1^*$, and $T_2^*$ are as in Figure 3, i.e., relevant to the polystyrene-poly(vinyl methyl ether) system, $\tau = -0.138$ and $X_{12} = -1.3$ J cm$^{-3}$, the LCST at 174 °C for $P = 0$. The curves are calculated for different values of $P_2^*$, values of $\pi$ being indicated. $\pi = 0.093$ corresponds to the PS-PVME system.

typically ~0.5 K atm$^{-1}$. On the other hand, the pressure dependence of a UCST is usually much smaller and not very different from that found for a mixture of small-molecule liquids, e.g., ~0.05 K atm$^{-1}$. The UCST in a mixture of polymers will have a similarly small pressure dependence, but it is of more interest to examine the dependence of LCST for a pair of compatible polymers. The pressure dependence is given[8a] by the relation

$$\left(\frac{\mathrm{d}T}{\mathrm{d}P}\right)_{\mathrm{c}} = -\frac{(\partial\chi/\partial P)_T}{(\partial\chi/\partial T)_P} \simeq \frac{T\Delta V_M}{\Delta H_M} \qquad (25)$$

We have calculated the numerator and denominator of eq 25 at zero pressure and then used eq 15 for $X_{12}$ in order to refer to the LCST in a compatible mixture, i.e., the favorable contact interaction and unfavorable free volume terms are balanced. We find that

$$\left(\frac{\mathrm{d}T}{\mathrm{d}P}\right)_{\mathrm{LCST}} \Big/ \frac{T_1^*}{P_1^*} = 18(\tilde{V}^{1/3} - 1)(4/3 - \tilde{V}^{1/3})^2\tilde{V}^{1/3} \times \left[ -\frac{\pi}{\tau} + \frac{(40 - 27\tilde{V}^{1/3})(\tilde{V}^{1/3} - 1)}{18(4/3 - \tilde{V}^{1/3})^2} \right] \qquad (26)$$

(Evaluating the right-hand side for polymer 1.) The best-known compatible pair is probably polystyrene-poly(vinyl methyl ether) studied by Nishi and Kwei.[19] Using the data in Table I, we have $-\pi/\tau = 0.68$ hence eq 26 gives $(\mathrm{d}T/\mathrm{d}P)_{\mathrm{LCST}} = 0.13$ K atm$^{-1}$. Similarly we find for the poly(vinyl chloride)-poly(capralactone) system[20] $(\mathrm{d}T/\mathrm{d}P)_{\mathrm{LCST}} = 0.2$ K atm$^{-1}$. Such large pressure dependences should be easily detectable. Figure 5 shows calculated LCST as a function of pressure for different sets of $\pi$ and $\tau$ parameters. The $T$ and $P$ values have been calculated using eq 22 for $\chi_{12}/M_1v_1^*$ and equating to 0 which is the critical value of $\chi_{12}$ for high molecular weight polymers. In the pressure range used, the LCST is a monotonic function of the pressure without maximum or minimum (the latter was found in one case in ref 6).

It is at first sight surprising that the pressure dependence of the LCST for a polymer-polymer system is predicted to be of the same magnitude as that for a polymer-solvent system, since pressure would be expected to have rather little effect on the free volumes of the polymers. However, although $(\partial\chi/\partial P)_T$ is indeed small for the polymer-polymer system, so is $(\partial\chi/\partial T)_P$, or in eq 25 both the $\Delta V_{\mathrm{M}}$ and $\Delta H_{\mathrm{M}}$ of compatible polymers are small.

In eq 26 the second term in the square bracket, dependent on $\tilde{V}^{1/3}$, has a typical value of 0.5. For positive values of $\pi/\tau$ greater than this, a negative value of $(\mathrm{d}T/\mathrm{d}P)_{\mathrm{LCST}}$ is predicted, i.e., the LCST would be lowered by pressure, as exemplified by one of the curves in Figure 5. The behavior corresponds to a positive value of $\Delta V_{\mathrm{M}}$ coupled with the negative value of $\Delta H_{\mathrm{M}}$ necessary for the occurrence of the LCST. A lowering of the LCST by pressure is extremely rare. It has recently been observed by Schneider[21] in certain aqueous systems, but so far never in a nonaqueous system. Its occurrence for a compatible polymer mixture requires the more flexible polymer of the pair, i.e., lower $T^*$, to have also the stronger cohesion, i.e., higher $P^*$, giving $\tau$ and $\pi$ of the same sign. This combination is no doubt less usual than high flexibility and low cohesion but not impossible.

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