Temperature Dependence of Polystyrene–Poly(vinyl methyl ether) Compatibility in Trichloroethene

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ABSTRACT: Cloud points have been obtained for mixtures of polystyrene (PS) and poly(vinyl methyl ether) (PVME) with trichloroethene using four PS fractions from 2 100 to 110 000 molecular weight. Although PS and PVME are compatible at ordinary temperatures, the ternaries show a large region of incomplete miscibility which decreases in size with increasing temperature and disappears. After a temperature interval of complete miscibility whose width depends on the polymer molecular weight, a region of immiscibility again appears, increasing in size with T. (For high PS molecular weight the low and high temperature regions of immiscibility coalesce.) These results are examples of the "$\Delta\chi$ effect" where polymer incompatibility in solution is due to the difference between the strengths of interactions of the two polymers with the solvent. Values of the χ parameter for the interaction of PS and PVME with trichloroethene have been obtained from 40–150 °C using the gas–liquid chromatography technique, and $\Delta\chi$ decreases with T and then increases at high T. With these values and also χ for the PS–PVME interaction, theoretical spinodals have been calculated using the Flory–Huggins theory. They are consistent with the experimental cloud points.

Two polymers (component 2 and 3) interacting through the usual dispersion forces will be incompatible in the absence of solvent. The free-energy parameter characterizing their interaction (χ_{23}) contains two positive, unfavorable contributions, and if the polymers are of high molecular weight a very small unfavorable interaction suffices to cause phase separation.[1] The two contributions in χ_{23} arise from differences between the two pure polymers in: (1) strengths of their dispersion force interactions and (2) chain flexibilities, hence liquid state free volumes. However, many compatible pairs are now known, as reviewed by Krause.[2] In these systems, the χ_{23} parameter still contains an unfavorable positive contribution from the free-volume difference, but interaction is no longer just of the dispersion force type. A specific attractive interaction due to hydrogen bonding or charge transfer can decrease contribution (1) so that the total χ_{23} lies below its critical value, or indeed χ_{23} may become negative, i.e. favorable to mixing. However, the specific interaction will be weakened by thermal motion on increasing T, and thus the polymers should become incompatible at high T. Furthermore, the free volume contribution also becomes more unfavorable with increase of T, constituting a second (but probably less important) cause of incompatibility.[3] In any case one might expect that compatible polymers will phase separate on heating, whereas with low molecular weight systems this occurs on cooling. The compatible pair used here, polystyrene (PS)–poly(vinyl methyl ether) (PVME), is typical and the high-temperature phase separation has been studied by Nishi and Kwei.[4]

Scott[5] and Tompa,[6] using the Flory–Huggins polymer solution thermodynamics, predict that the effect of adding a solvent (component 1) to the polymer pair is merely to dilute the 2–3 contacts. Thus an incompatible pair will produce a stable ternary system if sufficient solvent is added, while a compatible pair will give a stable ternary at all solvent concentrations. However, this prediction was made under the assumption that the two polymer–solvent interactions were of equal strengths. Relaxing this restriction, the Flory–Huggins theory now shows[7,8] that phase separation of the ternary system is caused not only by a positive χ_{23} value but also by any difference in strengths of the polymer–solvent interactions, i.e., by $|\chi_{12} - \chi_{13}| = |\Delta\chi|$. If χ_{23} is negative as for a compatible pair, but $|\Delta\chi|$ is sufficiently large, the phase diagram will contain a closed region[7,8] or loop within which phase separation occurs. This corresponds to a separation of the ternary into two phases where the concentrations in total polymer remain the same as the original system, but the concentrations of individual polymers are higher or lower (tie lines horizontal in Figures 3 or 4). If χ_{23} is made more negative, computer calculations of the spinodal show that the region will disappear so that all three components are miscible. However, if χ_{23} continues to become extremely negative, corresponding to the rare case of strong favorable interaction, the closed region again appears,[9] caused now by the polymer–polymer contacts being too strong to allow the dispersal of the pair into the solvent. The two phases are now different in concentrations of the total polymer, i.e., they are dilute and concentrated. However, in each phase the polymer composition remains the same as in the original ternary (tie lines vertical in Figures 3 or 4). This behavior is not seen in our experiments.

Thies and collaborators[10] have observed that solutions of the PS–PVME pair in benzene, toluene, and tetrachloroethene are clear and here $|\Delta\chi|$ has been found[11] to be small. However, phase separation was found[10] for PS–PVME in chloroform, trichloroethene, and dichloromethane, where $|\Delta\chi|$ is large.[11] A recent note[12] shows that the closed region of immiscibility does occur for the $CHCl_3$/(PS–PVME) system, and the spinodals computed from the $|\Delta\chi|$ values are in good qualitative agreement with the experimental phase diagrams. Furthermore, $|\Delta\chi|$ decreases[11] with increase of T, and in conformity with this, the closed loop disappears.[12] In the present work, a more detailed study will be made of the trichloroethene/(PS–PVME) system where the temperature dependence of the phase diagrams provides further evidence of the "$|\Delta\chi|$ effect".

Experimental Section

The PS samples of various molecular weights from Pressure Chemical Co., Pittsburgh, Pa., have $\overline{M}_w/\overline{M}_n$ ratios less than 1.1. The PVME sample (Gantrez 093) from GAF Corporation, New York, N.Y., gave viscosity average molecular weight values of 10 000 in 2-butanone but 14 000 in benzene. We use the latter value in predicting phase diagrams since it corresponds to the value used in ref 4. The trichloroethene was reagent grade. Cloud-point temperatures were obtained visually for ternary mixtures in sealed glass tubes. Values of χ_{12} and χ_{13} were determined using the gas–liquid chromatographic method[11] with trichloroethene at infinite dilution in the PVME and in PS of low molecular weight ($\overline{M}_n = 600$) chosen so as to have a glass transition temperature well below the range of experimental temperatures. The loading of the columns was ~8% of the Chromosorb W support. Values

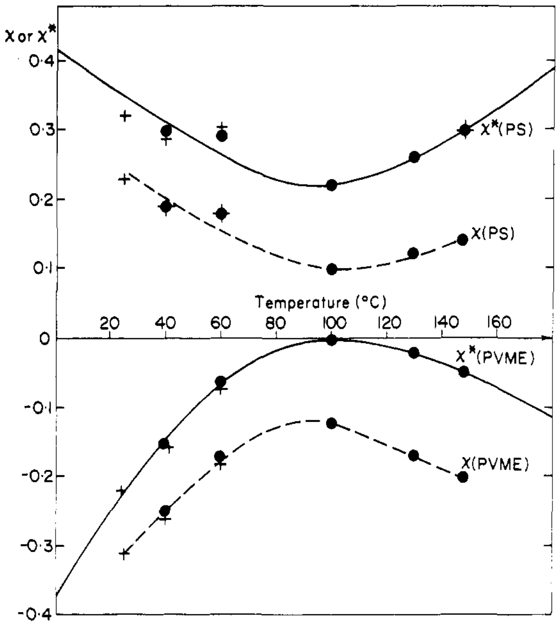

Figure 1. The temperature dependence of χ^* (full lines) and χ (dashed lines) for the interaction of trichloroethene with polystyrene (12) and with poly(vinyl methyl ether) (13), as determined by the GLC method. Crosses from C. S. Su, Ph.D., Thesis, McGill University, 1977.

of V_g^0 were extrapolated to zero flow rate of the carrier gas, this correction being important at high temperatures.

Results and Discussion

Polymer–Solvent Interaction Parameters and the $|\Delta\chi|$ Effect. Values of V_g^0, *the specific retention volume*, were found between 40 and 148 °C for trichloroethene (component 1) in the vapor phase, and with PS 600 (component 2) and PVME (component 3) as pure stationary phases. The values of V_g^0 are converted into χ parameters using the relation:[14]

$$\chi_{12} = \ln\left(\frac{273.2 V_g^0 v_{2,sp}}{P_1 V_g^0 V_1}\right) - \left(1 - \frac{V_1}{M_2 v_{2,sp}}\right) - \frac{P_1^0}{RT}(B_{11} - V_1) \qquad (1)$$

where P_1^0, B_{11}, V_1 are the trichloroethene vapor pressure, second virial coefficient, and liquid molar volume, and M_2 and $v_{2,sp}$ are the polymer molecular weight and specific volume. In the present work, we are particularly interested in the difference $\chi_{12} - \chi_{13}$. Thus subtracting from eq 2 its analogue for χ_{13}, we have

$$\chi_{12} - \chi_{13} = \ln\left(\frac{v_{2,sp}}{v_{3,sp}} \Big/ \frac{V_{g,2}^0}{V_{g,3}^0}\right) + \left(\frac{V_1}{M_2 v_{2,sp}} - \frac{V_1}{M_3 v_{3,sp}}\right) \qquad (2)$$

In this simple relation the properties of the vapor phase component have almost been eliminated.

Equation 1 is based on the original formulation of the Flory–Huggins theory which expresses the combinatorial entropy of the solution in terms of the volume fractions. More recently, the use of segment fractions instead of volume fractions has been favored, giving[13] an expression identical to eq 1 but with the "core" volumes V_1^* and $v_{2,sp}^*$ replacing V_1 and $v_{2,sp}$ yielding a value χ_{12}^* instead of χ_{12}. This is usually ~0.1 different from χ_{12} and also its temperature dependence is slightly different since V_1 and $v_{2,sp}$ will have different variations with T, while V_1^* and $v_{2,sp}^*$ are constant. However, predictions in the present work depend on $\chi_{12} - \chi_{13}$ and eq 2 indicates that this quantity is virtually independent of whether molar or "core" volumes are used.

In Figure 1 we show the χ and χ^* data for the interaction of trichloroethene with PS and PVME as a function of T, the accuracy of these values being ±0.03. It will be noted that values of $\Delta\chi$ are the same as those of $\Delta\chi^*$, and we feel that systematic errors will be smaller in $\Delta\chi$ than in the parameters for the individual polymers. For PS, the χ_{12} and χ_{12}^* parameters are positive. The temperature dependence of χ_{12}^* is directly related[13] to the heat of dilution of the polymer, the parameter characterizing this being given by

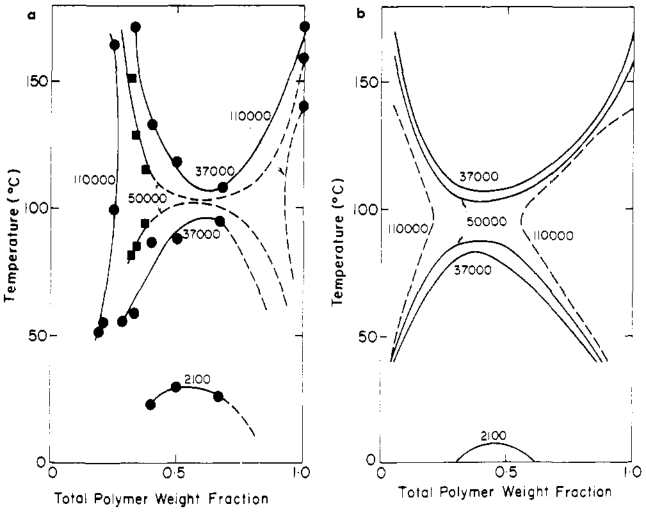

Figure 2. (a) Cloud-point temperatures for mixtures of equal weights of PVME and PS of indicated molecular weights with trichloroethene, as a function of the weight fraction of total polymer in the mixture. The curves correspond to vertical cuts through the domes in Figure 5. (b) Simulation of Figure 2a using theoretical spinodals calculated following ref 7 with χ_{12}^* and χ_{13}^* data from Figure 1 and χ_{23} from eq 4 and numbers of segments as in text.

$$\chi_{12,H}^* = -T\partial\chi_{12}^*/\partial T \qquad (3)$$

The temperature dependence of χ_{12} is less directly related to the thermodynamics (see eq 17 of ref 13). According to eq 3, the decrease of χ_{12}^* in the low-temperature range indicates the interaction enthalpy to be positive. However, χ_{12}^* increases again at high T, where $\chi_{12,H}^*$ has become negative. This behavior is consistent with the increasing free volume contribution to χ_{12}^* as the high-temperature phase separation is approached. On the other hand, for PVME the χ_{13} and χ_{13}^* parameters are negative at low T, becoming less negative with increase of T, indicating that the trichloroethene–PVME interaction is exothermic. This unusual behavior is due to the specific interaction (hydrogen bonding) between the chlorinated hydrocarbon (proton donor) and the ether (proton acceptor). It is consistent with the negative excess heats, entropies, and free energies found in such systems.[14] At high T, χ_{13}^* is close to zero but apparently becomes slightly more negative with increasing T, which would correspond to a change in sign of the heat and also of the entropy of the interaction. The negative slope of χ_{13}^* at high T is, however, close to being within experimental error.

For the ternary phase diagrams, the significance of Figure 1 lies in the observation that $|\Delta\chi|$ is large at low temperature, and hence one expects incompatibility of the PS and PVME in trichloroethene. However, $|\Delta\chi|$ decreases with increasing T and should lead to compatibility at higher temperature. At $T > 100$ °C, we expect incompatibility to set in once again due to the increase of $|\Delta\chi|$ with T which is apparent in Figure 1.

Polymer–Polymer Interaction and the Effect of χ_{23}. The phase behavior of the PS–PVME system has been investigated by Nishi and Kwei[4] for a constant molecular weight of PVME and a range of PS molecular weights. Our mea-

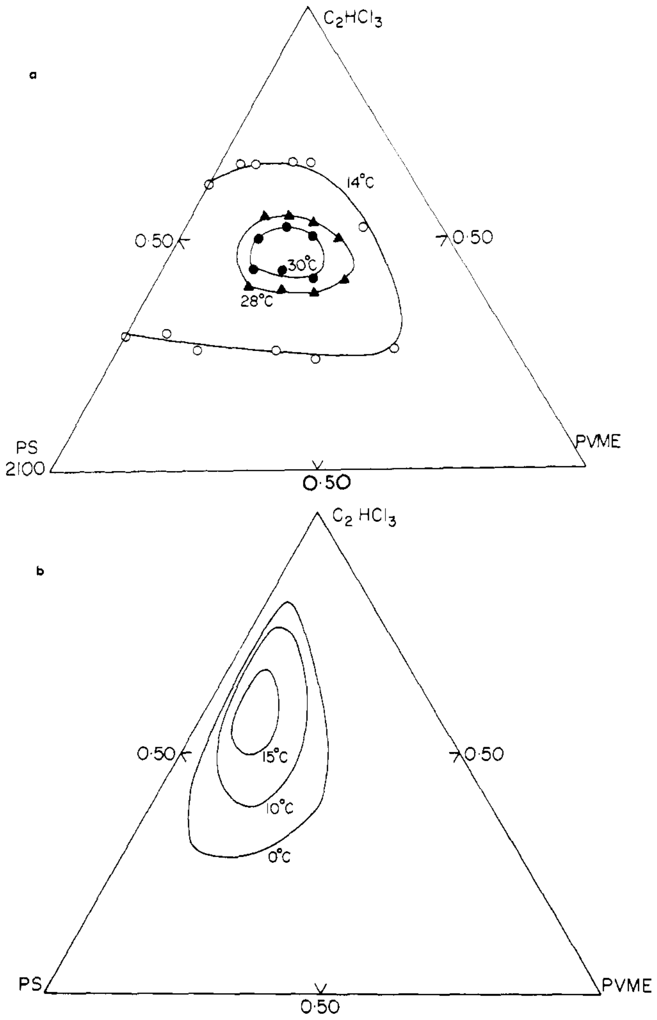

Figure 3. (a) Ternary phase diagrams for trichloroethene/(PS 2100–PVME) at indicated temperatures. The closed regions of immiscibility which decrease in size with increasing T correspond to horizontal cuts through the lower dome of Figure 5. (b) Simulation of Figure 3a showing theoretical spinodals calculated with χ_{12}^* and χ_{13}^* data from Figure 1 and χ_{23} from eq 4.

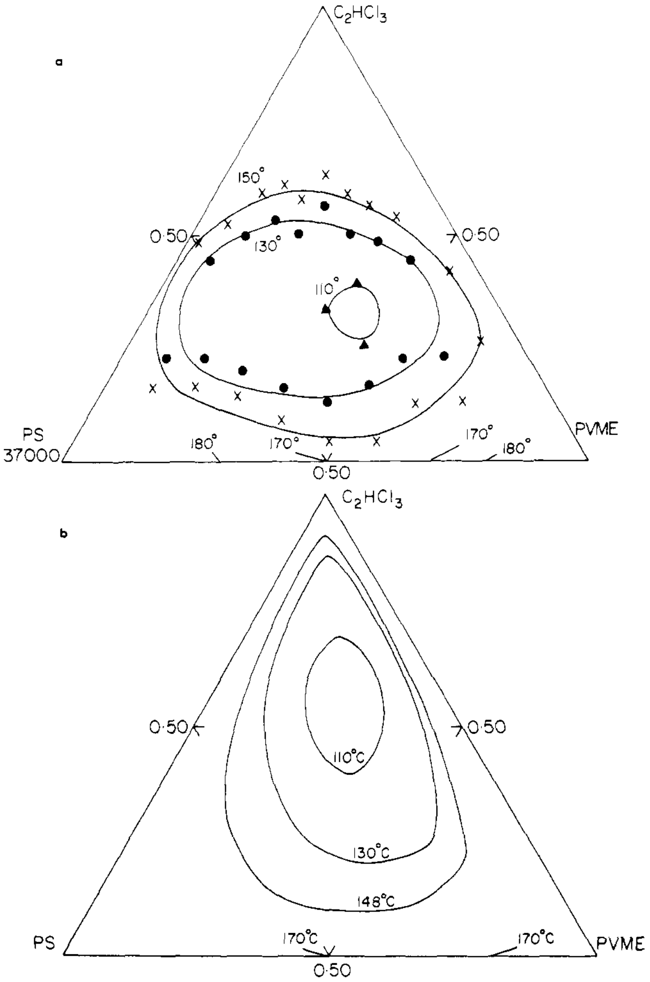

Figure 4. (a) Ternary phase diagrams for trichloroethene/(PS 37000–PVME) at indicated temperatures. The closed regions of immiscibility which increase in size with T finally cut the PS–PVME axis to give immiscibility in the polymer mixture. They correspond to horizontal cuts through the upper inverted dome of Figure 5. (b) Simulation of Figure 4a showing theoretical spinodals calculated with χ_{12}^* and χ_{13}^* data from Figure 1 and χ_{23} from eq 4.

surements of cloud-point temperatures in various PS–PVME mixtures are consistent with those of ref 4. All these systems phase separate on raising the temperature (LCST) and hence the interaction parameter χ_{23} for PS–PVME interaction will also increase with T. Figure 1 of ref 11 shows the linear dependence of χ_{23}' on T from an analysis of the results of ref 4. We will use the same χ_{23}' dependence, slightly modified to better express our own results, and also with χ_{23}' normalized to interacting volumes of the two polymer chains taken equal to the volume of the trichloroethene molecule. One has

$$\chi_{23}' = 8.85 \times 10^{-5}(t - 70) \qquad (4)$$

with t in °C. The data are for temperatures between 95 and 200 °C. However, extrapolation to lower temperatures appears justified, and the relation shows that below 70 °C χ_{23}' is negative, promoting polymer compatibility at the lower temperatures. The PS–PVME attraction presumably arises from a weak electron transfer interaction between the aromatic and ether components.[15] However, above 70 °C χ_{23}' becomes increasingly positive. In the 2–3 mixture without solvent, phase separation will take place at the critical value of χ_{23}' given in ref 1. In the ternary system χ_{23}' will also promote phase separation at high T.

Experimental Cloud Points. Figure 2a shows cloud-point temperatures for four ternaries containing the PS samples of 2.1, 37, 51, and 110 × 10^3 molecular weights together with the single PVME sample and trichloroethene. In each system, equal weights of PS and PVME are taken, but the weight fraction of total polymer is varied.

In the absence of trichloroethene, phase separation occurs only on raising the temperature. The experimental cloud points for our PS–PVME mixtures were respectively 171, 159, and 140 °C (Figure 2b) for the 37, 51, and 110 × 10^3 molecular weight PS samples. The PS 2100–PVME system remained clear up to 200 °C and a calculation of the critical temperature using eq 4 and ref 1 shows that phase separation would only be expected above 550 °C. Starting with the ternary trichloroethene (PS 37000–PVME), turbidity occurs at temperatures below 95 °C and again above 110 °C, the high and low regions of limited miscibility being separated by a small 15 °C interval where the components are completely miscible. If the PS molecular weight is lowered, the stability of the system is enhanced due to an increase of the combinatorial entropy. Thus, the low-temperature region does not now occur until below 32 °C, while the high-temperature region was never observed and must lie above 180 °C. Increasing the PS molecular weight from 37 000 to 51 000 brings together the low- and high-temperature regions of immiscibility as seen in Figure 2a. It proved difficult to see whether the two regions had coalesced or whether a small temperature interval of

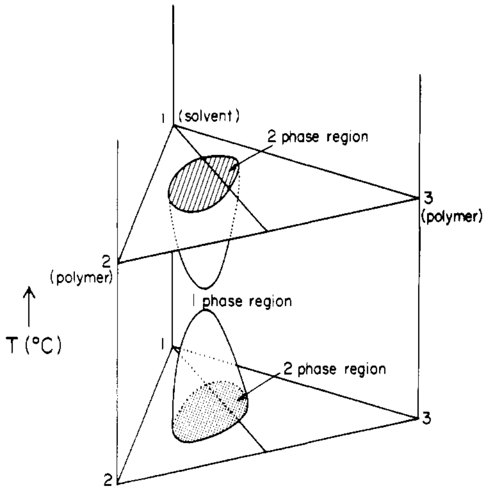

Figure 5. The ternary phase behavior which corresponds to χ^* data from Figure 1 showing the two domes of immiscibility and one-phase region between.

complete miscibility was left, and the dashed lines in Figure 2a are estimates based on the theoretical spinodals shown in Figure 2b. In any case, on increasing the PS molecular weight to 110 000 the high- and low-temperature regions of immiscibility have completely coalesced as shown in Figure 2a.

Figures 3a and 4a give more detailed cloud-point diagrams where the PS:PVME composition is no longer limited to 50:50 as in Figure 2a. In Figure 3a for trichloroethene/(PS 2100–PVME), a large region of incomplete miscibility occupies much of the triangle at 14 °C. Although the polymers are completely miscible, the binary system trichloroethene/PS 2100 shows immiscibility. This has disappeared at 28 °C, but a closed region remains in the ternary system. This decreases rapidly in size with increase of temperature and has completely disappeared at 32 °C. Thus, in the three-dimensional (*T*, composition) space the closed region becomes a dome with its tip at 32 °C. This behavior of the ternary system is very similar to that reported[12] for chloroform/(PS 2100–PVME) where the tip of the immiscibility dome is at 55 °C. Figure 4a gives the cloud points in the high-temperature region for trichloroethene/(PS 37000–PVME). Here the closed region of immiscibility appears in the middle of the triangle at 110 and expands as the temperature rises to 130 and 150 °C. Thus, here the dome is inverted with its tip at low temperature. The (*T*, polymer weight fraction) curves in Figure 2a correspond to vertical cuts through the domes while the closed regions in Figures 3a and 4a are horizontal cuts across the domes. The two domes and the cuts are illustrated in Figure 5.

Theoretical Spinodals. Spinodals have been predicted for the systems using the Flory–Huggins theory and following ref 7. The results are shown in Figures 2b–4b. The trichloroethene was put equivalent to one "segment" and the numbers of "segments" in the polymers were equal to the ratios of the polymer and trichloroethene molar volumes. Values of χ_{12}^* and χ_{13}^* were taken from Figure 1, and it was verified that spinodals calculated using χ_{12} and χ_{13} were almost identical which follows from the equality of $\Delta\chi^*$ and $\Delta\chi$. Equation 4 gave the values of χ_{23} which were extrapolated down to 0 °C, i.e., below the range of temperatures on which eq 4 was based. Spinodals were computed for all of the systems on triangular diagrams as in Figures 3b and 4b and then these were used to plot the (*T*, polymer weight fraction) cuts in Figure 2b. An attempt was made to find the high-temperature phase separation for trichloroethene (PS 2100–PVME) but the ternary was predicted completely miscible up to at least 200 °C in agreement with experiment. Further extrapolation to higher temperatures of the χ_{12}^* and χ_{13}^* data of Figure 1 was judged to be too inaccurate to be meaningful.

A comparison of Figures 2a and 2b shows that in all cases the experimental cloud-point curves are consistent with the theoretical spinodals, confirming the role of $\Delta\chi$. In the low-temperature range, phase separation is entirely due to $\Delta\chi$, χ_{23} being negative. At high temperature, the increase of $\Delta\chi$ with *T* noted in Figure 1 again leads to phase separation. Qualitatively similar spinodals are obtained at high *T* if $\Delta\chi$ remains large but does not actually increase with *T*, the high-temperature phase separation being brought about by the increase of χ_{23} with *T*. However, if $\Delta\chi$ is set to zero keeping only χ_{23}, the ternary phase separates at a higher temperature than the PS–PVME mixture, in complete disagreement with experiment. Thus, at high as well as low *T*, the influence of $\Delta\chi$ is apparent.

The theoretical spinodals of Figures 3b and 4b are also in qualitative agreement with the experimental cloud points of Figures 3a and 4a. However, the incomplete miscibility of the PS 2100–trichloroethene system at 14 °C is not predicted. This presumably means that the value of the χ_{12} parameter by the GLC method at infinite dilution of trichloroethene in PS is lower than the values toward the middle of the concentration range. However, the GLC values give at least a good qualitative representation of the phase diagrams. In particular, both theory and experiment indicate that the region of immiscibility shifts from the PS to the PVME side of the triangular diagram in passing from PS 2100 to PS 37000. Since the molecular weight of the PVME is 14000, that is consistent with the usual observation that the solution is least stable on the side of the diagram toward the lower molecular weight polymer.

Although the present work, with ref 12, appears to be the first experimental indications of the "$\Delta\chi$ effect", we believe it must be of wide occurrence in ternaries containing two polymers and a solvent. This was indeed the prediction made by using the theory of Flory and Huggins in ref 7 and 8 and demonstrates the continuing usefulness of the theory for the understanding of complex phenomena in polymer systems.

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References and Notes

(1) The 2-3 interaction parameter is extensive in the interacting volumes of the 2 and 3 polymer molecules and must be normalized to a reference volume or reference number of segments. In the Flory definition of χ_{23}, the 2-3 interaction is normalized to the r_2 segments of polymer 2 interacting with r_2 segments of polymer 3, and χ_{23} is thus proportional to the molecular weight of polymer 2. The Tompa χ_{23} is normalized to the contact between a pair of equal-sized 2 and 3 "segments" usually taken to be equal in volume to the repeat unit of one of the polymer chains. However, the choice of a "segment" is arbitrary. In ternary systems, it is often preferable to normalize to the volume of the solvent molecule giving the χ_{23}' parameter. According to the Flory-Huggins theory the critical values of these parameters are:

$$\frac{\chi_{23}(\text{Flory})}{V_2} = \frac{\chi_{23}(\text{Tompa})}{v} = \frac{\chi_{23}'}{V_1} = \frac{1}{2}\left[\frac{1}{V_2^{1/2}} + \frac{1}{V_3^{1/2}}\right]^2$$

Here V_1, V_2, and V_3 are the molar volumes of the solvent and the two polymers and v is the molar volume of a "segment".

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Configurational Thermodynamics of the Liquid and Glassy Polymeric States

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ABSTRACT: The basis, assumptions, and essential results of a molecular theory and comparisons with experiment are reviewed. An effective principle of corresponding states obtains and correlations between the scaling parameters, exceptions, and implications are discussed. An important quantity is the hole or unoccupied volume fraction h. In the equilibrium liquid its volume and temperature dependence results from the minimization of the configurational Hemlholtz free energy. The relation between liquid–glass transition lines for variable and constant formation histories is obtained in the form of a generalized Ehrenfest equation in terms of h. PVT studies clearly indicate the continuing significance of structural contributions to the thermodynamic functions far below T_g, as expressed by variations of the h function. The entropy surface of a given glass, however, is not uniquely determined by this function. It is proposed to accomodate this feature in the frame of the present molecular theory through c, the number of effectively external degrees of freedom. While c remains practically constant in the liquid range, it should decrease with decreasing temperature in the glass, in contrast to h, which decreases more slowly. Finally, future directions for the liquid and the glass under quasiequilibrium conditions are suggested.

The many-body problem represented by the theoretical description of a disordered system, such as the liquid state at equilibrium, has remained a classical problem since van der Waals' times. Almost all efforts have been concentrated on "simple" liquids, i.e., those with spherically symmetrical force fields. Two types of analytical approaches can be distinguished. One starts out from rigorous statistical mechanical relationships and then by necessity continues by introducing well-defined approximations. In the second the point of departure is an intuitively more or less appealing model of the liquid state which then can be evaluated comparatively easily.

It is a theory of the second kind which is the primary concern here, because it has been extended to chain molecular fluids and when properly modified is quantitatively successful. We refer to the theory of Lennard-Jones and Devonshire (LJD). Its basis, results, and extensions are reviewed in several textbooks of statistical mechanics and it suffices here to recall its basic feature. The fluctuating field exerted by the surrounding constituents on a given particle is replaced by an average field which is defined by placing the former on a lattice and permitting the central molecule to move in the cell formed by its neighbors under a prescribed pair potential. In the simplest formulation correlations between particles entrapped in adjacent cells are neglected.

A pioneering extension of this model to chain molecular liquids was presented some time ago by Prigogine and his colleagues,[2] who dealt not only with the one-component systems of interest here but also developed a basic approach to mixtures. In spite of the well-known deficiencies of the cell theory, a solid-like theory, when applied to rare gas and similar liquids, it has been more successful for oligomer fluids[3] and amorphous polymers.[4,5] Moreover it became the starting point for semiempirical extensions.[6] The introduction of additional disorder by vacancy sites[7] improves the situation considerably in respect to the configurational thermodynamic functions. The presence of a hole or free volume fraction as a function minimizing the configurational free energy leads quite naturally to the consideration of liquid–glass boundaries, the glassy state as a partial equilibrium system, and the connection between the liquid and its glasses, generated in a specified manner.

We take this occasion first to recapitulate and to comment on the assumptions of the theory and to point to conclusions derived from applications to amorphous polymers and polymer melts, including some recent data. Second we consider implications for the glassy state.

(I) The Liquid State

(A) Assumptions. **(1)** The linear chain is subdivided into segments, each moving in the field of its intermolecular neighbors. The dissymmetry due to the intramolecular neighbors is disregarded. The basic intersegmental pair potential is taken to be of the 6–12 form and the resulting cell potential is simplified at ordinary temperatures to a square well. At low temperatures, in practice the cryogenic range for polymer glasses, an expansion of the LJD cell potential, yields a quasiharmonic expression, with the force constant an explicit function of volume.

(2) In addition to the geometric parameter, the number s of segments per chain, a dynamic parameter arises in the following manner: In the evaluation of the configurational partition function, only those modes of motion are to be included which are determined or modified by intermolecular interactions, in other words, external degrees of freedom. Their identification is clear-cut in the simple structures which have been the usual testing ground for theories of the liquid state. There, the number $3c$ of pertinent degrees of freedom equals 3 or 6 for a spherically symmetrical and a rigid (no internal rotations) asymmetric structure, respectively. Another extreme immediately identified is the ideally flexible chain, where the energy barriers for internal bond rotation are low in comparison with intermolecular effects. If furthermore no flexible (in this sense) side chains are present, $3c = s - 3 + 6$