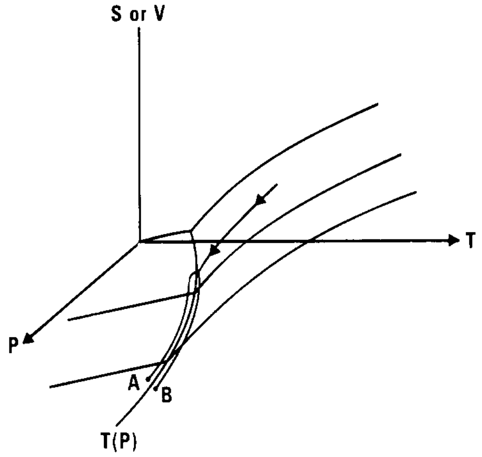

Figure 1. According to the assumption of Davies and Jores, two paths infinitesimally apart on either side of the transition line result in z_i values at A and B that are finitely different even though the points are infinitesimally separated. This problem can be avoided by assuming that the z_i are constant along the $T(P)$ line.

glasses was proved in ref 3, but the proof was qualified by the condition that a $T(P)$ line exists (see paragraph after eq 2.25 of ref 3). Goldstein, although agreeing with the logic of the argument, maintains that $r \geq 1$ because the volume change ΔV may be finite along the glass transition line even though the entropy change may be zero. Gupta and Moynihan[9] argue that only knowledge of the behavior of the system at a point is sufficient to prove that $r \geq 1$.

In order to proceed further and clarify the matter we must examine the nature of the freezing-in assumption of Davies and Jones[10] more critically. It is evident that whatever is assumed must be compatible with the time-dependent equations (eq 1). In fact, the DJ assumption of a freezing-in is no more than a guess of a possible solution of the kinetic equations. We wish now to show that certain sets of frozen parameters z_i are *not* compatible with these equations. Let $T(P)$ be a transition line. According to the DJ assumption, on one side (high-temperature side) of the $T(P)$ line the z_i adjust themselves to minimize free energy. On the other side they are frozen. Referring to the figure we see that two paths infinitesimally close result in finitely different z_i ($z_A - z_B$ are not small). This means that the driving forces are finite and since the L_{ik} are continuous through the transition line the equations give finite $\dot{z}_i$ contrary to assumption. However, if the z_i were constant along the transition line the DJ assumption would not violate the equations. But, for this case $r = 1$.[2,8,9] Thus, either the DJ assumptions are incompatible with eq 1 or $r = 1$.

Two other observations of the DJ assumption are in order. (1) The DJ specification is incomplete. If one has freezing as one goes into the glass, one must have unfreezing as one comes out of the glass. In general, a separate unfreezing transition line, $T(P,T_0P_0)$, may be postulated for each point of entry T_0, P_0 into the glass. This concept is intimately connected to the assumption by Goldstein[8] of a nonzero ΔV during unfreezing. (2) Let us assume that a particular motion along a given path $T_1(P)$ results in a given set $z_{i,1}(t)$. Now let us pick an intersecting second path $T_2(P)$. By choosing $T_2(t)$ and $P_2(t)$ properly one can, in general, force one of the z_i (say z_k) to have the same time dependence, but all other z_i are different

$$z_{k,1}(t) = z_{k,2}(t)$$
$$z_{i,1}(t) \neq z_{i,2}(t) \qquad i \neq k \tag{2}$$

Thus, the set $z_i(t)$ for one history is not, in general, reproducible for another history. This means that the very concept of freezing-in has severe limitations.

Finally, we observe that the question of the evaluation of the time-dependent Prigogine-Defay ratio $r(t)$ is a meaningful question. The answer has apparently not yet been found, but an argument can be given that $r < 1$ at least sometimes. Choose a $T(t),P(t)$ so that for $t < t_0$ the system is changing so slowly that equilibrium obtains and for $t > t_0$ the system changes so fast that heat does not have a chance to escape (i.e., an adiabatic process). For this case we have, using easily derived relations between adiabatic and nonadiabatic coefficients,[11]

$$r = \frac{(C_P - C_S)(\beta_T - \beta_S)}{TV(\alpha_P - \alpha_S)^2} = (1 - C_v/C_P)^2 < 1 \tag{3}$$

Thus, it seems that $r(t)$ values both greater and less than one are possible. Equation 3 does *not* prove that $r < 1$ is obtainable from eq 1 because the derivation of eq 1 never assumed adiabatic conditions.

The above comments should make it plain that the view presented here of the temporal behavior of the parameters of glass theory differs fron that of Goldstein. Even though the configurational entropy S_c of a glass equals zero in the glassy state, one can still have motion within the glass. This is known both experimentally and theoretically.[3] One could say that there is no entropy of activation below the glass temperature, only energy of activation. Above the glass temperature there is both energy and entropy of activation. Concerning the behavior of f and n_0 a fair statement of facts would seem to be that far below the glass transition they are constants, but from zero to (say) 50 °C below the glass temperature they can be made to vary by changing forces and time. The experimentally observed properties of a glass will not be those of equilibrium *nor* will they be those of constant f and n_0. They can be determined theoretically only by solving the time-dependent equations for which the entropy theory supplies the necessary foundation (all theories of time-dependent behavior require prior knowledge of equilibrium statistical mechanics as a necessary point of departure).

Finally, the question arises as to whether or not $r > 1$ for real glasses. It seems that if one uses extrapolations of α_g and β_g (especially β_g) from far below T_g then $r > 1$ *can* be correct. However, an examination of experimental volume vs. pressure curves often fails to reveal any break in the compressibility and this fact makes it difficult to accept $\Delta\beta$ values with any degree of confidence.

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On the Molecular Weight Independence of Cloud Point Curves

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Recently a theory for the semidilute range of polymer solutions was proposed. Accordingly,[1] in a good solvent the be-

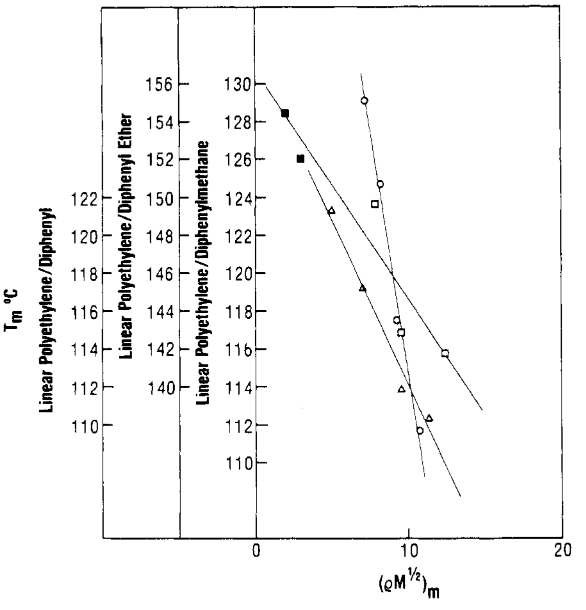

Figure 1. $(\rho M^{1/2})_m$ plotted against the respective T_m for three LPE–solvent systems: (■) LPE, M_w = 153 000 and 140 000 in diphenyl ether, ref 3; (△) LPE, M_w = 50 900, 56 800, 136 800, and 442 100 in diphenyl, ref 11; (○) LPE, M_w = 21 300, 34 900, 76 300, and 136 800 in diphenyl methane, ref 11; (□) LPE, M_w = 50 900, 56 800, and 136 800 in diphenyl ether, ref 11.

havior of macromolecules may be described by means of some concentration-dependent scaling parameters. In an extention of this theory, a temperature–concentration diagram for polymer solutions in poor solvents was put forth,[2] claiming a molecular weight independence of the precipitation curves (or cloud point curves, CPC) of the polymer upon the reduction of the temperature T below the theta temperature. Cotton et al.[2] maintain that when the precipitation curves are plotted with the coordinates $10^{-3}\,(T - \Theta)M^{1/2}$ against $\rho M^{1/2}$ one obtains a molecular weight independent curve, i.e., curves obtained for different homologues of the same polymer would superpose one on top of the other. Here ρ is the polymer volume fraction, easily obtained from c the concentration in g/cm^3 and the density of the bulk polymer.

From the superposability of the cloud point curves of a given polymer one gathers that at the maxima of these curves the product

$$(\rho M^{1/2})_m = \text{constant} \qquad (1)$$

The temperature to which the maximum in each curve reaches is denoted by T_m.

In this note literature data are used to show that: (a) at T_m, $(\rho M^{1/2})_m$ is not a constant for a given polymer/solvent system; (b) for the same polymer in different solvents the products $(\rho M^{1/2})_m$ are not the same; (c) different polymers yield different $(\rho M^{1/2})_m$ products.

Discussion

It has been repeatedly shown[3–6] that in the CPC the concentration corresponding to T_m, c_m may be the same as the critical concentration for phase separation, c_c, only when the polymer is monodisperse:

$$c_m = c_c \text{ when } M_w/M_n = M_z/M_w = 1 \qquad (2)$$

and that c_c is very sensitive to the molecular weight distribution (MWD).[3] Here M_n, M_w, and M_z stand for number average, weight average, and z average molecular weight. At the very same time c_m was found to be very insensitive to rather large variations in the MWD.[3] Therefore, the choice of c_m and $(\rho M^{1/2})_m$ for the purpose of comparing different samples of the same polymer is a prudent one.

For monodisperse polymer T_m is equal to the critical temperature T_c. Therefore[7]

$$1/T_m = (1/\Theta)(1 + (1/\psi)(1/x^{1/2} + 1/2x)) \qquad (3)$$

where x is the ratio of molar volumes of polymer to solvent and ψ is a parameter characterizing the entropy of dilution of polymer with solvent. Since χ_1, the interaction parameter, is related to x at $T_c = T_m$ by[7]

$$\chi_{1c} = 0.5 + 1/x^{1/2} \qquad (4)$$

it becomes apparent that $(\Theta - T_m)$ and χ_{1c} are dependent on x and that solutions of a polymer of a given M and MWD in different solvents, whose molar volumes differ, may yield different $(\Theta - T_m)$ and χ_{1c} values. On the other hand, when the molar volumes of two solvents are close to one another, χ_{1c} and $(\Theta - T_m)$ would be about the same. In this case the difference between the two solvents may be manifested in a change in the c_m value, when the CPC is plotted against concentration, or in the $(\rho M^{1/2})_m$ value, when the CPC is plotted against $\rho M^{1/2}$. Also, with an increase in the c_m value, or the corresponding ρ value, the shape of the peak of the CPC becomes much broader. The variations in the c_m and resultant $(\rho M^{1/2})_m$ values and in the CPC peak shape were amply demonstrated by Shultz and Flory[8] for polystyrene (PS) in cyclohexane and cyclohexanol, by Janckel and Keller[9] for PS in 16 different solvents, by Stacy and Arnett[10] for linear polyethylene (LPE) in four solvents, and by Nakajima et al.[11,12] for LPE in over 30 solvents. Note that in these instances the same polymer fractions in different solvents are compared. It is obvious from this that $(\rho M^{1/2})_m$ for a particular polymer fraction in one solvent is, in general, not the same as in another solvent.

In Figure 1, $(\rho M^{1/2})_m$ for three LPE/solvent systems are plotted against T_m. Each point represents the peak position of the CPC of a particular LPE fraction; the higher T_m is the higher is the molecular weight of the fraction. For the calculation of $(\rho M^{1/2})_m$ weight average molecular weights are used in all cases. One notes that in the case of LPE the values of $(\rho M^{1/2})_m$ decrease with an increase in T_m for each LPE/solvent system. That is, $(\rho M^{1/2})_m$ decreases with an increase in M. It is also important to notice that the slopes of the lines connecting the points of each system are not the same and that the lines do not fall one on the others. The data above are typical, as are the PS data to be discussed below. Under no circumstance, however, do they exhaust the data available in the literature.

When the $(\rho M^{1/2})_m$ values of PS in various solvents are plotted against T_m, in Figure 2, the magnitude of $(\rho M^{1/2})_m$ is seen to increase with the increase in T_m and M. The separate lines with their individual slopes are reminiscent of the LPE/solvent behavior.

In Figure 3, $(\rho M^{1/2})_m$ for the system PS–cyclohexane are plotted against T_m. The data of several authors[6,15–21] covering the molecular weight range of $51\,000 \leqslant M_w \leqslant 43\,500\,000$ are represented. Except for the four points of Schultz and Flory[15] which show significant scatter (probably due to variability in the MWD of the fractionated samples), the data show a distinct tendency of $(\rho M^{1/2})_m$ to increase with temperature. That is, the higher M is and the smaller $(\Theta - T_m)$ the larger is $(\rho M^{1/2})_m$. Surprisingly, Cotton et al.[2] use the data of Shultz and Flory[15] that show a wide scatter. The three lines in the figure may reflect the fact that the c_m and ρ values were obtained by different techniques, each technique yielding a different c_m for a given molecular weight. This point was demonstrated by Borchard and Rehage[22] several years ago. Nonetheless, it is important to re-emphasize that for the

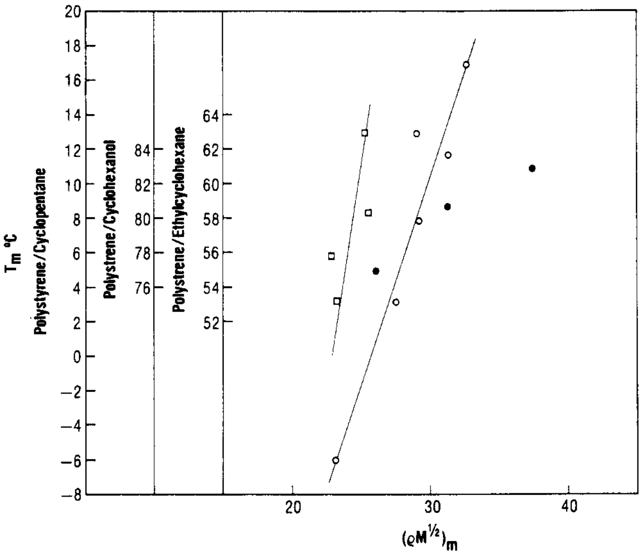

Figure 2. $(\rho M^{1/2})_m$ plotted against the respective T_m for three PS–solvent systems: (●) PS, M_v = 84 000, 236 000 and 881 000 in cyclohexanol, ref 8; (□) PS, M_w = 80 000, 123 900, 152 900, 238 700, and 569 000 in ethylcyclohexane, ref 13; (○) PS, M_w = 37 000, 97 200, 209 000, 400 000, 670 000, and 2 700 000 in cyclopentane, ref 14.

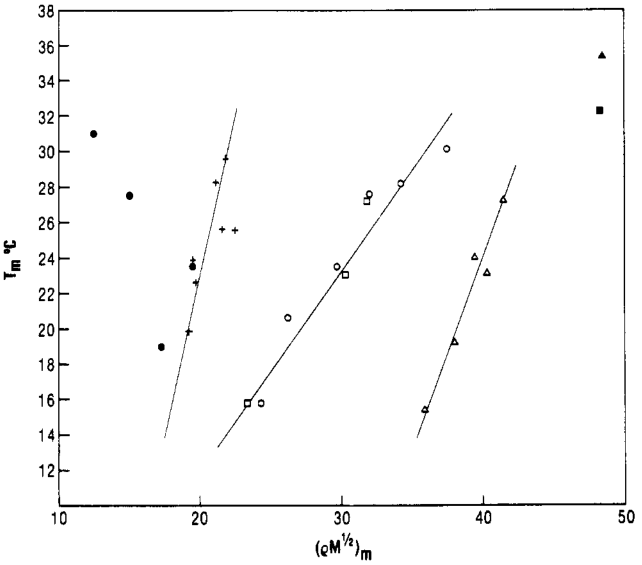

Figure 3. $(\rho M^{1/2})_m$ plotted against the respective T_m for the PS–cyclohexane system: (△) M_w = 51 000, 111 000, 166 000, 200 000, and 527 000, ref 6; (●) M_v = 43 600, 89 000, 250 000, and 1 270 000, ref 15; (○) M_w = 51 000, 93 000, 166 000, 394 000, 527 000, and 1 500 000, ref 16; (+) M_w = 80 000, 123 900, 152 900, 238 700, 253 000, 569 000, and 1 190 000, ref 17; (□) M_w = 51 000, 163 000, and 520 000, ref 18; (■) M_w = 3 200 000, ref 19; (▲) M_w = 43.5 × 10⁶, ref 20 and 21.

system Ps–cyclohexane, $(\rho M^{1/2})_m$ increases with M and with the approach to theta temperature, irrespective of the technique employed to obtain T_m, c_m, and the resultant $(\rho M^{1/2})_m$.

A comparison of the three figures reveals that while $(\rho M^{1/2})_m$ for LPE are of the order of 10 or less, the values for PS are 20 and above. Similar differences exist, for example, in the cases of *cis*-polybutadiene[23] whose $(\rho M^{1/2})_m$ are of the order of 10, while those of polyisobutylene in diisobutyl ketone[15] reach a value larger than 35.

From the above it is apparent that: (a) the product $(\rho M^{1/2})_m$ is not a constant for a polymer/solvent system; (b) $(\rho M^{1/2})_m$ is not the same for a given polymer in different solvents; and (c) $(\rho M^{1/2})_m$ is different for different polymers.

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On the Chain Conformation of Poly(tetrafluoroethylene) in the Crystalline Modification above 30 °C

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The possibility that the chain conformation of poly(tetrafluoroethylene) (PTFE), in the crystalline pseudo-hexagonal modification which is stable above 30 °C, may correspond to disordered successions of helical stretches having opposite sense of spiralization has been put forward in the past by De Santis et al.,[1] Brown,[2] Clark,[3] Bates and Stockmayer,[4] and Corradini.[5]

The possibility that neighboring chains may lack a strict periodic correlation in the atomic positions, except that chain axes maintain their parallelism in a pseudo-hexagonal array (with interaxial nearest distances of 5.66 Å instead of 5.59 Å, as in the low-temperature modification), has been discussed and proved feasible by the energetic calculations of Giglio and D'Ilario in a recent paper.[6] In this note, we wish to report a related contribution arising from recent theoretical and experimental work on the subject.

Under atmospheric pressure, poly(tetrafluoroethylene) shows two first-order transitions, at 19 and 30 °C, respectively.[7]

Below 19 °C, the chain conformation may be described as a one-atom helix, characterized by a unit twist $t = 360° (6/13) = 166.15°$ and a unit height $h = 1.292$ Å.[7] Thus, the conformation corresponds locally to a nearly planar zigzag, with internal rotation angles σ all equal to 163.5°[8] or all equal to −163.5°, according to the sense of spiralization (Figure 1a).