plained by changes in urea molecular weight since this is constant. The copolymer with the highest urea T_g has the lowest urethane-segment molecular weight and the lowest urethane content in the urethane segment.

Modifications of the chemical structure of the urea segments influences the χ parameter between the urea and urethane segments. Polymers IB, IC, and IIC have the same urethane segments but chemically different urea segments. The deviation of the urea relaxation region in the block copolymer from the urea homopolymer relaxation region can be rationalized in terms of differences in χ parameters. The χ parameters were not measured, but from these data it would be surmised that the urea based on 1,6-hexamethylenediamine has the lowest χ parameter and the urea based on bis(3-aminopropyl)methylamine has the highest χ parameter.

Conclusions

It can be concluded that decreasing the urethane content of the urethane segments and increasing the molecular weight of the urethane and/or urea segments increases the aggregation of urea-*b*-urethane copolymers into pure urethane and urea domains. The T_g of the pure urethane domains is a function of the urethane content of the urethane segments and can be calculated from one of the equations used to calculate the T_g of random copolymers or miscible polymers. The T_g of the pure urethane domains is not a function of molecular weight. The distribution of molecular weights in the polyether diols and in the urethane segments may result in solubilization of the short urethane segments or urethane segments containing the low molecular weight diols in the urea domains.

The chemical structure of the urethane and urea segments determines the χ parameter between the segments. Modification of the chemical structure of either the urea or urethane segments will result in changes in the χ parameter and therefore the degree of solubilization of the segments.

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Effects of Pressure on the Equilibrium Properties of Glass-Forming Polymers

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ABSTRACT: The entropy theory (Gibbs–DiMarzio theory) of the glass transition is extended to incorporate the effects of pressure. The second order transition temperature T_2 increases with increasing pressure but approaches a finite asymptote at very high pressure (>10 kbars). This conclusion is unlike that of an isofree volume theory, according to which the transition temperature should increase without bound. The variation of T_2 with pressure is shown to satisfy the Ehrenfest relations $\mathrm{d}T_2/\mathrm{d}P = TV\Delta\alpha/\Delta C_\mathrm{p} = \Delta\beta/\Delta\alpha$, even though the theory appears, at first sight, to be a double order parameter theory of the transition. The point is that the apparent order parameters are not independent. A useful classification of order parameters is presented. The theory also predicts that the volume decreases along the transition line as pressure increases, in contradistinction to an isofree volume theory. This volume decrease is in accord with known experimental data and can also be used to explain the densification of glasses. Finally, it is suggested how the relevant kinetic parameters associated with this theory can be determined experimentally.

I. Introduction

In previous papers[2] Gibbs and DiMarzio characterized the equilibrium properties of amorphous polymers by using a statistical mechanical theory (hereafter referred to as GD theory). In the approximation represented by use of the counting procedures of Flory or Huggins on the Meyer lattice, the polymer liquid was shown to traverse an Ehrenfest[3] second-order phase transition at a temperature T_2. The decrease of the configurational entropy to very small values as the putative transition temperature T_2 is approached from higher temperatures was identified as the underlying cause of the increasing sluggishness of transport properties that is manifest in the intervention of the glass transition at a temperature T_g (where $T_g > T_2$).

Whether this decrease in configurational entropy on (infinitely slow) cooling would be found in an exact (equilibrium) theory to terminate abruptly (Figure 1a) at a true second-order transition (i.e., with a discontinuity in slope) at the temperature T_2, as in the approximate GD theory, or whether it would be found to terminate somewhat more gradually

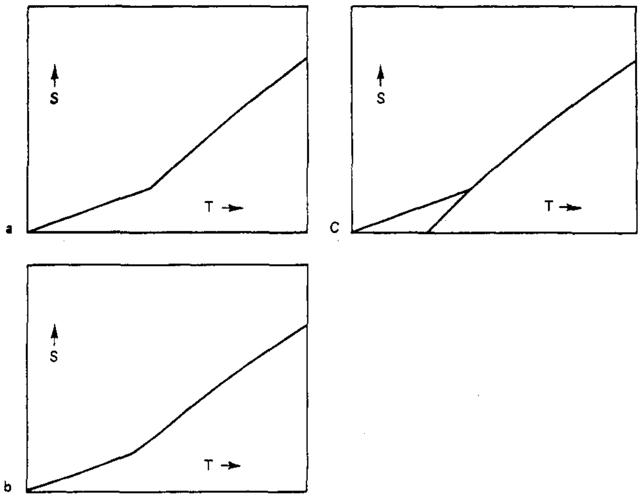

Figure 1. Plot of a first-order property, entropy, vs. temperature. (a) Illustrates a sharp second-order transition. (b) Illustrates a diffuse second-order temperature. (c) An extrapolation from high temperature to low temperature results in an entropy catastrophe (Kauzmann paradox).

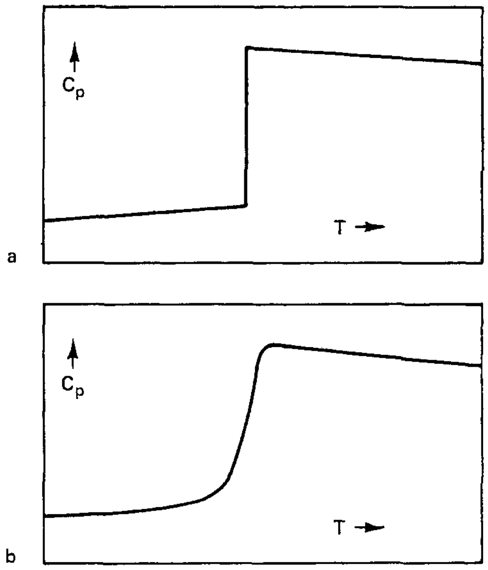

Figure 2. Plot of a second-order property, specific heat, vs. temperature. (a) A sharp second-order transition. (b) A diffuse second-order transition. Most experimental curves for glasses resemble (b) more than (a).

(Figure 1b) is a question that cannot be answered at present. As stated in a 1960 review[4] by one of us, it is appropriate to "adopt a cautious view and assume only that the second-order transition temperature T_2 predicted by the quasi-lattice calculation is a convenient reference point on the bend of a curve of at present undetermined sharpness". That this bend cannot be spread out over an arbitrarily large temperature range is clear from the fact that bendless extrapolations of experimental data through and below the glass temperature lead surprisingly quickly to the peculiar results of values less than the corresponding values for the corresponding crystalline phases (Figure 1c).[5] Thus the temperature range over which the bend can occur is limited, and the reference temperature T_2 should be reasonably well-defined.

In the terminology of Mayer and Streeter[6] the "transition" could be designated as "diffuse second-order" (Figures 1b and 2b) if not actually true second-order (Figures 1a and 2a), just as the helix–coil "transition" (displayed by polypeptides and polynucleotides in solution) is an example of a "diffuse first-order" transition (Figure 3b). When it is convenient to define a single transition, or reference, temperature in the case of the helix–coil transition, one often chooses the inflection point in a plot of some first-order thermodynamic property vs. temperature. In the case of a diffuse Ehrenfest second-order transition one could analogously choose the inflection point in a curve of some second-order thermodynamic property (e.g., the heat capacity), or one could also choose the inflection point in the plot of some first-order property (e.g., the entropy).

Inasmuch as there exists no theoretical or experimental evidence as to whether the transition is diffuse or true second order whereas there is available for use the approximate GD theory which gives a vanishing of the configurational entropy at the temperature T_2, it is more convenient to take as the transition or reference temperature T_2 the temperature where the configurational entropy would vanish in the absence of an inflection and more gradual reduction to zero of the configurational entropy (see Figure 1b). The reason for this is that any theory, such as that of Adam and Gibbs,[7] that attempts to relate the temperature dependence of kinetic properties of supercooled liquids (and thus the glass transition) to the configurational entropy must be used in conjunction with either the GD theory for the latter or experimental data and extrapolations of the same, there being nothing else available, and both of these yield a description of the configurational entropy at any temperature T in terms of the parameter T_2 defined as a point of vanishing entropy. It is important to recognize, however, that even if the transition in nature should be diffuse, one is not introducing an error in the temperature range accessible to equilibrium measurement (that is, $T \geq T_g$) by using an approximate expression for the configurational entropy that does not give a diffuse transition. Misbehavior of such an expression below the lowest T_g that can be measured will not damage its utility in connection with the Adam–Gibbs equation (for example), as long as this approximate expression fits the entropy data adequately in the range in which it is to be used, that is $T \geq T_g$.

The key question then is not whether there exists a true, sharp second-order transition but rather whether the kinetic sluggishness manifest in the glass transition is properly attributable to the dearth of configurational entropy at low temperature. One way of obtaining evidence on this question is to investigate the possibility of correlation between the temperature T_g, as determined in experiments of fixed time scale, and the temperature T_2, defined either as suggested above or as an inflection point (in the entropy–temperature curve) yielded by some yet-to-be obtained theory.

The assumption of a correlation between the glass-transition temperature T_g and the reference temperature T_2 yielded by the GD theory has resulted in remarkably good agreement with a wide class of experimental data. The dependences of T_g on such parameters as molecular weight,[2a] copolymer composition,[8] plasticizer concentration[9] and cross-linking[10] have been given a molecular interpretation. The agreement with experiment does not, however, require that the theoretical T_2 and the experimental T_g be equal; an approximately constant difference (e.gg., $T_g - T_2 = 50$ °C) for any given type of substance and any given time scale of T_g measurement would, for example, be sufficient.

Heretofore the effects of pressure on T_2 have not been considered. In this paper the effects of pressure on the equilibrium properties of glass-forming polymers are evaluated by generalizing GD theory.

In section II the theory including pressure effects is presented. In section III the thermodynamics of the transition is discussed. The consequences of the model are examined in some detail in section IV.

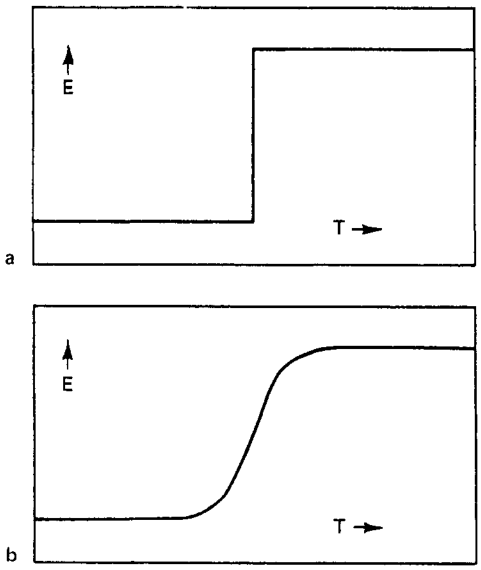

Figure 3. First-order properties vs. temperature. (a) A sharp first-order transition. (b) A diffuse first-order transition.

II. Theory

(A) The Model. GD theory is a statistical thermodynamic theory of an amorphous system of polymer molecules. It utilizes a lattice model in which n_x polymer molecules each occupy x lattice sites. The total number of lattice sites is $N_0 = xn + n_0$, the number of unoccupied sites being n_0. Each site is associated with a unit cell of volume C.

The total volume V is then given by

$$V = CN_0 \tag{2.1}$$

The volume of the system can vary with temperature and pressure as a result both of configurational changes and also of changes in amplitudes of vibration. In the lattice model the former are treated as giving rise to variations in the number of holes (n_0) and the latter as implying variations in the cell size C. In this paper we consider the case in which the site size C is assumed to be independent of temperature and pressure.

The total energy of the system is a sum of inter- and intramolecular contributions,

$$E = \Phi + n_x \sum_i f_i E_i \tag{2.2}$$

where f_i is the fraction of molecules in internal state i with intramolecular energy E_i.

The intermolecular energy Φ is given by[1,2]

$$\Phi = z_a n_0 S_x/2 \equiv E_h n_0 S_x$$

with (2.3)

$$S_x = \frac{[(z-2)x+2]n_x}{[(z-2)x+2]n_x + zn_0}$$

where $-\alpha$ is the energy of a segment–segment bond, z is the coordination number of the lattice, and $E_h = z\alpha/2$ is the hole energy. Segment–hole contacts are assigned a zero energy. Φ represents the total energy required to form n_0 holes.

The second term in (2.2), the single (polymer) molecule energy, can, in principle, be determined exactly for any given polymer. However, it is often sufficient to employ the rotational isomer approximation. For this approximation, various conformations of a polymer molecule give rise to different intramolecular energies because the potential energy of, say, the kth bond in the chain is dependent (for $k \geq 2$) upon the orientation of bond $k+1$ with respect to bond $k-1$. Each bond is assumed to occur in any of several discrete rotational potential energy wells. In this approximation the intramolecular energy E_i of a molecule in molecular state i is given by

$$E_i = \sum_m a_m{}^i \epsilon_m \tag{2.4}$$

where m enumerates each of the possible rotational potential wells, $a_m{}^i$ is the number of bonds of the molecule in the mth well when the molecule is in molecular state i, and ϵ_m is the energy associated with the mth well (potential energy of the well bottom plus vibrational free energy). In the simplest case we assume that there is only one low-energy well of energy ϵ_1 and that there are $z-2$ high-energy wells of energy ϵ_2. Let f be the fraction of bonds in all the molecules that are in wells of energy ϵ_2. Then the total energy can be expressed as[1,2]

$$E = \Phi + (x-3)n_x[f\epsilon_2 + (1-f)\epsilon_1] \tag{2.5}$$

In the formal treatment that follows, the general form, eq 2.2, for the intramolecular energy will be retained. However, specific calculations will be based on the approximation in (2.5). It is important to realize that experimental disagreement with GD theory for particular systems need not invalidate the theory unless it can be demonstrated that the error is not in the approximate treatment of the single polymer states by (2.5).

(B) Evaluation of the Partition Function. (1) Above the Transition Temperature T_2. As has been noted previously[4] the introduction of the effects of pressure into the GD theory should be most easily achieved by use of a constant temperature–pressure ensemble and its associated "isothermal–isobaric" partition function.[11] This is

$$\gamma(T,P) = \sum_V \exp(-\beta PV)Z(T,V) \tag{2.6}$$

where

$$Z = Tr_v \exp(\beta H) \tag{2.7}$$

As usual $\beta = 1/kT$, H is the Hamiltonian of the system, and the symbol Tr_v denotes a sum ("trace") over all states of the system at volume V. The Gibbs free energy is related to γ by

$$G(T,P) = -kT \ln \gamma \tag{2.8}$$

and all the required thermodynamic quantities can be obtained from G by standard methods.

For the lattice model described above, the states of the system can be characterized by specification of n_0 and the f_i; that is, the sum over states can be replaced by a sum over the allowed values of n_0 and the f_i:

$$\gamma = \sum_{\{f_i\},n_0} W(\{f_i\},n_0) \exp[-\beta(PCN_0 + E(\{f_i\},n_0))] \tag{2.9}$$

where $E(\{f_i\},n_0)$ is given by eq (2.2) and $W(\{f_i\},n_0)$ is the number of configurations of the system that are allowed when there are n_0 holes and f_in_x molecules in internal state i. W is given by[2b]

$$W = \frac{N_0!z^{xn_x}\{([(z-2)x+2]n_x + zn_0)/2\}!(z-1)^{n_x}}{(n_0)![N_0z/2]!2^{xn_x}\prod_i (f_in_x)!} \tag{2.10}$$

The summation over the f_i can be easily performed by recognizing that the f_i dependent part of eq 2.10 is proportional to the coefficient of the generic term of a multinomial series.[2b] However, without introducing detectable error in the logarithm of γ (which is the important quantity thermodynamically) we can replace the sum with its maximum term, since the maximum term is overwhelmingly larger than any other term. The maximum term is obtained by differentiation with respect to the independent f_i

$$kT\frac{\partial \ln W(\{f_i\},n_0)}{\partial f_i} - \frac{\partial E(\{f_i\},n_o)}{\partial f_i} = 0 \qquad i \neq 1 \quad (2.11)$$

Solving eq 2.11 yields the equilibrium value of f_i, which is denoted as $f_{i,\max}$ since it also represents the value of f that corresponds to the maximum term (minimum free energy) in the partition function:

$$f_{i,\max} = \exp(-\beta E_i)/q \qquad (2.12)$$

where

$$q = \sum_i e^{-\beta E_i}$$

For the rotational isomer approximation 2.5 this becomes

$$f_{\max} = \frac{(z-2)\exp(-\Delta\epsilon/kT)}{1 + (z-2)\exp(-\Delta\epsilon/kT)} \qquad (2.13)$$

where $\Delta\epsilon = \epsilon_2 - \epsilon_1$ is the difference in the potential energy minima. In previous papers[2,8-10] $\Delta\epsilon$ is called the "flex energy" and f is the fraction of "flexed bonds".

Similarly, the sum over n_0 can be replaced by its maximum term:

$$kT\frac{\partial \ln W(\{f_i\},n_0)}{\partial n_0} - \frac{\partial E(\{f_i\},n_0)}{\partial n_0} - PC = 0 \qquad (2.14)$$

Equation 2.14 yields an implicit equation for $(n_0)_{\max}$:

$$\ln (V_0^{(z/2-1}/S_0^{z/2}) - \beta E_h S_x^{\,2} - \beta PC = 0 \qquad (2.15)$$

where $S_0 = 1 - S_x$ and V_0 is the volume fraction of holes:

$$V_0 = \frac{n_0}{n_0 + xn_x} = 1 - V_x \qquad (2.16)$$

Since the notation becomes cumbersome we have omitted the subscript (max) in eq 2.14 and 2.16. It should also be noted that eq 2.12 and 2.13 are identical to those obtained previously.[2,4] This is a consequence of the factorization of the partition function into one factor containing only the f_i dependence and another containing only the n_0 (and, therefore, pressure) dependence (f_i and n_0 are not coupled). Equation 2.15, which arises from the latter, differs from the corresponding equation of prior work by the addition of the PC/kT term.[12]

In summary, the Gibbs free energy, G_l, that is appropriate to the system above T_2, i.e., the "liquid" regime, is

$$G_l = E(\{f_i\},n_0) + PV(n_0) - kT \ln W(\{f_i\},n_0) \qquad (2.17)$$

where the f_i are given by eq 2.12 and n_0 is given by eq. 2.15.

(2) Below the Transition Temperature T_2. The significant result of GD theory is that for any given pressure *W approaches unity* at some finite temperature T_2. By "unity" is meant a number which may be of the order of the number of molecules n_x (or even of the number of monomer segments xn_x) in the system (but not of the order of e^{xn_x})! This implies that the system *configurational entropy* per mole,

$$S = k \ln W \qquad (2.18)$$

becomes zero at T_2 and will remain zero at temperatures below T_2.

It is important to recall at this point that the partition function involves a sum over all possible states (values of f and n_0). Only those states for which $W \geq 1$ are allowed, although use of either the Flory or the Huggins approximation (as in (2.10)) and subsequent use of Stirling's approximation spuriously introduce "states" for which $W < 1$. Application of the maximum term method to the system at a temperature below T_2 yields a value of W which is *less than unity* unless these spurious "states" are removed.

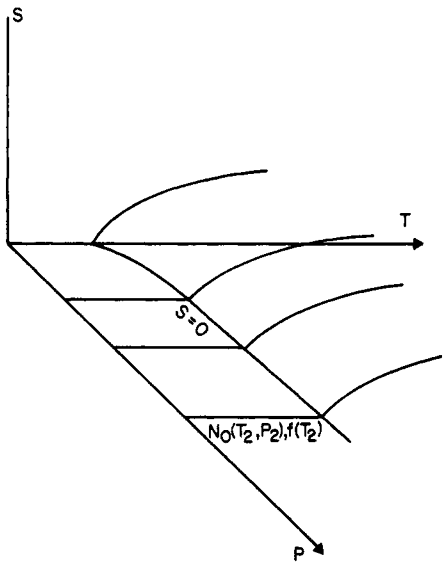

Figure 4. Along constant pressure lines below the line along which the configurational entropy equals zero (which defines a second-order transition), the amount of flexing f and number of holes n_0 are independent of temperature. However f and n_0 are pressure dependent.

To evaluate the partition function for $T < T_2$ we can still look for the maximum term among those for which $W \geq 1$. Below T_2 each term in the partition function is of the form

$$W(\{f_i\},n_0)\exp[-\beta(E(\{f_i\},n_0) + PV(n_0))]$$

but only those values of f_i and n_0 are allowed for which $W \geq 1$. What we will prove is that the maximum term, and thus the partition function, is given by

$$\gamma = \exp[-\beta(E_2 + PV_2)] \qquad (2.19)$$

where V_2 and E_2 are the volume and total energy that the system has at $T_2(P)$. The proof is relatively simple. At T_2 we have

$$(1)\ \exp[-\beta_2(E_2 + PV_2)] \gg W(f,n_0)\exp[-\beta_2(E(\{f_i\},n_0) + PV(n_0)] \qquad (2.20)$$

This inequality is true for values of n_0 and f_i which yield values of $W > 1$ or $W < 1$, because the maximum term occurs exactly for $W = 1$. We now raise each side of the inequality to the T_2/T power. This operation does not alter the inequality, and we obtain

$$\exp[-\beta(E_2 + PV_2)] \gg W^{T_2/T}\exp[-\beta(E(\{f_i\},n_0) + PV(n_0))]$$

Now for those sets (n_0,f_i) for which $W \geq 1$ and $T_2/T \geq 1$ we have

$$W^{T_2/T}\exp[-\beta(E(\{f_i\},n_0) + PV(n_0))] \geq W\exp[-\beta(E(\{f_i\},n_0) + PV(n_0))]$$

and thus

$$\exp[-\beta(E_2 + PV_2)] \gg W\exp[-\beta(E(\{f_i\},n_0) + PV(n_0))] \qquad (2.21)$$

which is the desired result.

The significance of this result is that for temperatures below $T_2(P)$ on any isobar P the values of f_i and n_0 are *independent of temperature* and are equal to the values found at T_2, i.e.,

$$\left.\begin{aligned} f_i(T) &= f_i(T_2) \\ n_0(T) &= n_o(T_2) \end{aligned}\right. \quad T < T_2(P) \qquad (2.22)$$

In the temperature–pressure plane the $T_2(P)$ line is determined by the condition $W = 1$. This line is illustrated in Figure

4. It is important to note that if the pressure is changed the values of f_i and n_0, and thus the free energy, will change because $T_2(P)$ changes. Stated another way, states below the $T_2(P)$ line, states which we will refer to as "glassy" states, are a *function of pressure only*. States above the $T_2(P)$ line, which we will call "liquid" states, are functions of both temperature and pressure.

In summary, the Gibbs free energy G_g that is appropriate to the system below T_2, the thermodynamically "glassy" regime, is

$$G_g = E_2 + PV_2 \tag{2.23}$$

where, as before, E_2 and V_2 are the energy and volume at $T_2(P)$.

III. Thermodynamics of the Transition

(A) Entropy. The configurational entropy of the "liquid" $(T > T_2)$ is[13]

$$S_l = -\left.\frac{\partial G_l}{\partial T}\right)_P = k \ln W$$

$$\frac{S_l}{k} = xn_x\left[-\frac{V_0}{V_x}\ln S_0 + \left(\frac{z-2}{2V_x}\right)\ln\left(\frac{V_0}{S_0}\right) - \frac{\ln S_x}{x} + \frac{\ln([(z/2-1)x+1]\,[z-1]/2)}{x} + \frac{S_{\mathrm{int}}}{kx}\right]$$

where

$$\frac{S_{\mathrm{int}}}{k} = -\sum_i f_i \ln f_i \tag{3.1}$$

The transition temperature $T_2(P)$ or the transition pressure $P_2(T)$ is determined by setting $S_l = 0$; n_0 and f_i are defined by eq 2.12 and 2.15.

The configurational entropy of the "glass" $(T < T_2)$ is

$$S_g = -\left.\frac{\partial G_g}{\partial T}\right)_P = 0 \tag{3.2}$$

The entropy is continuous across the transition:

$$S_l(T_2) = S_g(T_2) = 0 \tag{3.3}$$

The volume and energy are also continuous, but the derivatives of S, V, and E (second derivatives on G) are discontinuous at T_2. Therefore, the system undergoes a second-order phase transition in the Ehrenfest sense.[3] The discontinuous nature of the second-order properties will become evident in the next section.

(B) Second-Order Properties and dT_2/dP. The thermal expansion coefficients above and below T_2 are given by

$$\alpha_l \equiv \left.\frac{\partial \ln V}{\partial T}\right)_P = \frac{\partial n_0/\partial T)_P}{n_0 + xn_x} = -\left.\frac{\partial \ln V_x}{\partial T}\right)_P$$

$$\alpha_l = \left(\frac{V_0}{T}\right)\frac{(E_{\mathrm{h}}S_x{}^2 + PC)/kT}{zS_x/2 - 2E_{\mathrm{h}}S_0S_x/kT - ((z/2)-1)V_x} \tag{3.4}$$

and

$$\alpha_g \equiv \left.\frac{\partial \ln V_g}{\partial T}\right)_P = 0 \tag{3.5}$$

The configurational heat capacity of the liquid is

$$C_{\mathrm{p,l}} = T\left.\frac{\partial S_l}{\partial T}\right)_P = \left.\frac{\partial[E_l + PV_l]}{\partial T}\right)_P = xn_x\left\{\frac{\alpha_l}{V_x}[E_{\mathrm{h}}S_x{}^2 + PC] + \frac{C_{int}}{x}\right\} \tag{3.6}$$

where

$$C_{\mathrm{int}} = T\,(\partial S_{\mathrm{int}}/\partial T)$$

while for the glass, we have

$$C_{\mathrm{p,g}} = 0 \tag{3.7}$$

The variation of the transition temperature T_2 with pressure can now be easily evaluated:

$$\left.\frac{\partial T}{\partial P}\right)_S = -\left[\left.\frac{\partial S_l}{\partial P}\right)_T \Big/ \left.\frac{\partial S_l}{\partial T}\right)_P\right] = \frac{TV\alpha_l}{C_{\mathrm{p,l}}} \tag{3.8}$$

but

$$\frac{\mathrm{d}T_2}{\mathrm{d}P} \equiv \left.\frac{\partial T}{\partial P}\right)_{S=0}. \tag{3.9}$$

Thus

$$\frac{\mathrm{d}T_2}{\mathrm{d}P} = \frac{T_2V_2\alpha_l(T_2)}{C_{\mathrm{p,l}}(T_2)} \tag{3.10a}$$

where α_l and $C_{\mathrm{p,l}}$ are given by eq 3.4 and 3.6.

We note also that

$$\Delta\alpha = \alpha_l(T_2)$$

$$\Delta C_{\mathrm{p}} = C_{\mathrm{p,l}}(T_2) \tag{3.11}$$

at the transition, so that eq 3.10a can also be written as

$$\mathrm{d}T_2/\mathrm{d}P = T_2V_2\Delta\alpha/\Delta C_{\mathrm{p}} \tag{3.10b}$$

The compressibility of the liquid is given by

$$\beta_l = -\left.\frac{\partial \ln V_l}{\partial \mathrm{P}}\right)_{\mathrm{T}} = \left.\frac{\partial \ln V_x}{\partial P}\right)_T$$

$$= \left(\frac{V_0}{P}\right)\frac{PC/kT}{zS_x/2 - 2E_{\mathrm{h}}S_0S_x{}^2/kT - ((z/2)-1)V_x} \tag{3.12}$$

In the glassy state the volume is only a function of pressure (see section II.B.2), because we have ignored variations in the lattice site size C and the entropy is constant (zero). The compressibility of the glass can be obtained as follows: along the transition line the volume is continuous so that

$$\mathrm{d}V_g = \mathrm{d}V_l$$

or

$$\left.\frac{\partial \ln V_g}{\partial T}\right)_P \mathrm{d}T_2 + \left.\frac{\partial \ln V_g}{\partial P}\right)_{T=T_2}\mathrm{d}P = \left.\frac{\partial \ln V_l}{\partial T}\right)_P \mathrm{d}T_2 + \left.\frac{\partial \ln V_l}{\partial P}\right)_{T=T_2}\mathrm{d}P \tag{3.13a}$$

Using the definitions of α and β and recalling that $\alpha_g = 0$, eq. 3.13a becomes

$$\beta_g(T_2) = \beta_l(T_2) - \alpha_l(T_2)\frac{\mathrm{d}T_2}{\mathrm{d}P} \tag{3.13b}$$

or

$$\mathrm{d}T_2/\mathrm{d}P = \Delta\beta/\Delta\alpha \tag{3.13c}$$

which should be compared with eq 3.10b.

Since the glass is independent of temperature, we have

$$\beta_g(T,P) = \beta_g(T_2,P) \tag{3.14a}$$

and from eq 3.10a and 3.13b we also have

$$\beta_g = \beta_l(T_2) - \frac{T_2V_2\alpha_l{}^2(T_2)}{C_{\mathrm{p,l}}(T_2)} \tag{3.14b}$$

$$= \beta_l(T_2)\frac{C_{\mathrm{v,l}}(T_2)}{C_{\mathrm{p,l}}(T_2)} > 0 \tag{3.14c}$$

where C_{v} is the constant volume heat capacity.

IV. Discussion

(A) The Variation of T_2 with Pressure. In Figure 5 we have plotted transition temperature ($kT_2/\Delta\epsilon$) vs. pressure ($PC/\Delta\epsilon$) for various values of the ratio $\Delta\epsilon/E_{\mathrm{h}}$. It is seen from

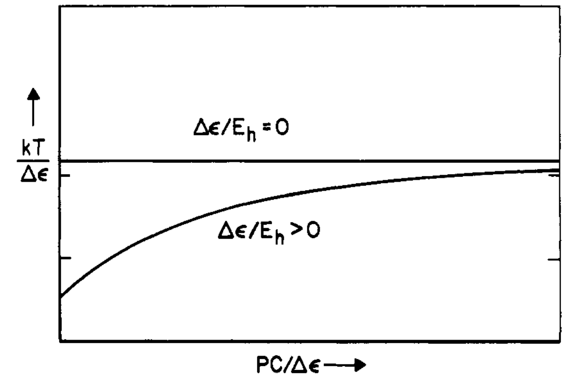

Figure 5. The normalized second-order transition temperature as a function of normalized pressure for various values of the ratio of stiffness energy to hole energy (schematic).

this figure that the transition temperature approaches a finite asymptote as the pressure becomes infinitely large, i.e.,

$$\mathrm{d}T_2/\mathrm{d}P \rightarrow 0 \text{ as } P \rightarrow \infty$$

Thus even in the absence of holes ($E_h \rightarrow \infty$ or $P \rightarrow \infty$) a transition is predicted at a finite temperature. At sufficiently high temperatures the polymer molecules become sufficiently flexible (f increases with temperature) that W exceeds unity even in the absence of holes.

This prediction is unlike the prediction of a free-volume theory that would require the free volume fraction to be constant along the transition line. This free-volume view would predict that the transition temperature would become infinitely large as the pressure becomes infinitely large.

Experimentally, the glass transition temperature (determined from dielectric measurements) for poly(vinyl chloride)[14,15] and poly(methyl acrylate)[14] does appear to be approaching an asymptote at high pressures. Dilatometrically determined glass temperatures for poly(vinyl acetate)[16] also suggest that T_g is leveling off at high pressures. However, these results are somewhat inconclusive, inasmuch as the range of pressures investigated was limited to less than 2.5 kbars; the theory suggests that the leveling-off effect should be easily observable in the 10-kbar range.

(B) The Ehrenfest Relations and Order Parameters. For a second-order phase transition Ehrenfest showed that the variation of the transition temperature T_2 with pressure is given by[3]

$$\frac{\mathrm{d}T_2}{\mathrm{d}P} = \frac{\Delta\beta}{\Delta\alpha} = \frac{T_2 V \Delta\alpha}{\Delta C_p} \tag{4.1}$$

which is the same result as that we obtained in section III.B for the model system under consideration. However, the thermodynamic arguments leading to eq 4.1 do not depend upon any particular model but are based on the following two general conditions: (1) in the T–P plane a $T_2(P)$ line exists which separates the two phases, and (2) all first derivatives of the free energy (S, V, and E) are continuous across the line, but the second derivatives (α,β,C_p) are discontinuous. The model described herein satisfies these conditions, and thus eq 4.1 is a natural and necessary consequence for this model.

Prigogine and Defay[17] have also derived eq 4.1 by a quasithermodynamic argument which uses the concept of an internal order parameter Z. The order parameter is assumed to have some constant value Z_c along the transition line. Davies and Jones[18] have extended these ideas to allow for several order parameters. They concluded that if two or more order parameters were necessary to characterize the transition, then the following inequality must hold along the transition line:

$$\Delta\beta/\Delta\alpha \geq TV\Delta\alpha/\Delta C_p \tag{4.2}$$

Recently, one of the present authors[19] showed that even in the case of a multiple order parameter description the *equality always holds* and $\mathrm{d}T_2/\mathrm{d}P$ is still given by eq 4.1, provided only that a $T_2(P)$ line exists.

Since a certain amount of confusion still exists in the literature concerning the inequality (4.2), it is worthwhile to reexamine the idea of order parameters. Within the framework of the order parameter description of a system one requires that in the high-temperature equilibrium phase the order parameters Z_i adjust themselves to minimize the Gibbs free energy; this condition can usually be satisfied if

$$\partial G/\partial Z_i = 0 \qquad i = 1, 2, \ldots \tag{4.3}$$

The set of eq 4.3 determines the order parameters as functions of temperature and pressure in the liquid phase, and we denote these Z_i as Z_{li}:

$$Z_{li} = z_{li}(T,P) \tag{4.4}$$

The low-temperature phase is separated from the high-temperature phase by a transition line $T_g(P)$. There are both kinetic and thermodynamic interpretations of how the transition occurs. These interpretations lead to two distinct classifications of order parameters:

class I, kinetic (history dependent)

class II, thermodynamic (history independent)

The history of the low-temperature phase (the glass phase) can be described in terms of the formation pressure P_2 and the time scale of the experiment τ_e. The dependence of the glass-order parameters Z_{gi} on P_2 and τ_e results in a further division of

$$\text{class I: (a) } Z_{gi}(T,P;P_2,\tau_e) = c_i(\tau_e),\ i = 1$$

$$\text{(b) } Z_{gi(T,P;P_2,\tau_e)} = h_i(P_2,\tau_e),\ i = 1, 2, \ldots$$

The usual notion of glassy state order parameters is that they have values that depend only on the rate of formation of the glass (class Ia), but in general one should allow glass order parameters to depend on the formation pressure (class Ib).

In the usual notion (class Ia) as applied to the case of a single order parameter ($i = 1$ only), the equation of constraint defining the $T_g(P)$ line in the T,P plane is simply $Z_{gl} = C_1(\tau_e)$ *at equilibrium* (at nonequilibrium this equation is satisfied below the $T_g(P)$ line for this history dependent class).

Below we will show that class Ia can only include the case $i = 1$; i.e., two or more *independent* order parameters are not possible in class Ia.

In cases in which there are two or more order parameters the $T_g(P)$ line is still characterized by a single equation of constraint, but this equation will in general involve a function of several or all of the order parameters.

Thermodynamic order parameters (class II) can be invoked whenever the transition occurs and the time scale of the experiment τ_e is much greater than the characteristic relaxation time for the system to come to equilibrium (an infinite τ_e would guarantee this condition). Under these conditions the order parameters would be history independent and be state functions:

$$\text{class II, } Z_{gi}(T,P;P_2,\tau_e\text{-}\infty) = f_i(T,P),\ i = 1, 2, \ldots$$

A single component, single phase system has only two degrees of freedom (phase rule); therefore, specification of T and

P completely determines the state of the system at any point on or above the $T_2(P)$ line in the case of class I and anywhere in the case of class II. Now if we impose an equation of constraint on the system, a degree of freedom will be lost (either T or P). *One equation of constraint will define a line $T(P)$ in the T–P plane, while two equations of constraint would define a point in the T–P plane.* Three or more equations of constraint constitute an overdetermined system of equations and do not have physical meaning. Examples of constraint equations are the setting of one of the Z_i equal to a constant or the setting of some function of the Z_i equal to a constant. Any such condition would define a $T(P)$ line. It is senseless to assert that two or more *independent* order parameters have some fixed or constant values along a "transition" line whether this line be history dependent or not (provided equilibrium obtains down to this line). Thus, class Ia can only include systems that are describable by *one order parameter.* If two or more independent kinetic order parameters are required to describe the transition, then they must belong to class Ib.

The "order parameters", f, n_0, of the simplest version (that based on eq 2.5) of the GD theory belong to class II. Above the $T_2(P)$ line (the liquid region) eq 2.11 and 2.14 are the minimizing conditions expressed by eq 4.3. The equation of constraint describing the transition line ($T_2(P)$ in this case) is (see eq 3.1 and also the Appendix)

$$S_1(f,n_0) = 0 \tag{4.5}$$

This equation of constraint is very complicated, but it nevertheless establishes a well-defined $T_2(P)$ line. Moreover, n_0 and f vary below the $T_2(P)$ line (the glassy region) in a manner that minimizes the free energy but is subject to the condition that the configurational entropy remain constant (zero). Even when a more correct treatment of intramolecular energy is allowed for and many f_i's are considered, the system behaves like one with a single order parameter in that the Ehrenfest relations always hold.

The usual notion of order parameters is that they are "frozen in" below the $T_g(P)$ line. As the above argument indicates, this cannot be true for more than one order parameter in class Ia. In the case where one order parameter is frozen in, discontinuities appear in those quantities that can be expressed at equilibrium as second derivatives of the free energy (e.g., thermal expansion coefficient); in this case the transition is either a true second-order transition (class II) or one that looks like a second-order transition (class I) though not itself a purely thermodynamic phenomenon. However, discontinuities may also appear in the second derivatives if the Z_i vary with T and P differently below the $T_2(P)$ line than above. In the present theory this is a result of the thermodynamic surfaces (S and V) having different functional forms above and below the transition; the equation of constraint 4.5 which determines the $T_2(P)$ line also holds below the line.

Order parameters are useful if they describe a cause and effect relationship for the transition. The simplest concept, and the one that arose first historically, is that there is a single order parameter (of class Ia) that has a constant value along and below the transition line. When the order parameter reaches some critical value (cause) the transition (effect) occurs. However, in class Ib the order parameters vary along the transition line, and the cause of the transition is described by the *one* unique relationship among the Z_i which is in general unknown. This seriously limits the usefulness order parameters of class Ib, unless the one equation of constraint can be determined. Even for this class the Ehrenfest relations hold. In class II order parameters have been useful in characterization of the transition lines for a number of different types of transitions (order–disorder in alloys, onset of ferromagnetism, etc.). In the present theory the equation serving this purpose is eq 4.5.

The above classification of order parameters depends on the idea that above the transition line the relaxation time to reach equilibrium is much smaller than the experimental time scale τ_e while below the transition line the relaxation times are much longer than τ_e. Experiments characterized by a finite τ_e will, in general, lead to Class Ib order parameters even if the transition has a thermodynamic basis characterized by class II order parameters. In the next section we consider an approach to determining the time dependence of the order parameters f and n_0 of the simple theory.

(C) Kinetics, Viscosity, and Glass Densification. The understanding of the kinetics of the glass transition cannot be accomplished without an understanding of the equilibrium properties of the glass-forming liquid. In fact, the only theories of nonequilibrium phenomena that have been developed are those that represent small deviations from equilibrium. The theory for the equilibrium properties of an amorphous polymer described in this paper now permits an approach to the more difficult problem presented by the kinetics of the system.

It has been suggested[19] that the equations of motion for order parameters should have the form of the Onsager equations.[20,21] If n_0 and f are the order parameters and $\dot{n}_0$ and $\dot{f}$ are their time derivatives, then

$$\dot{n}_0 = L_{11}\frac{\partial G}{\partial n_0} + L_{12}\frac{\partial G}{\partial f}$$

and (4.6)

$$\dot{f} = L_{21}\frac{\partial G}{\partial n_0} + L_{22}\frac{\partial G}{\partial f}$$

where L_{11} is the correlation function[22] of $\dot{n}_0$ with itself, L_{12} that of $\dot{n}_0$ with $\dot{f}$, and L_{22} that of $\dot{f}$ with itself. The fact that G contains f and n_0 as a sum of separated terms suggests that f and n_0 are uncorrelated and therefore

$$L_{12} = L_{21} = 0 \tag{4.7}$$

This results in a decoupling of the $\dot{n}_0$ equation from the $\dot{f}$ equation since the driving forces $\partial G/\partial n_0$ and $\partial G/\partial F$ are dependent only on n_0 and f, respectively.

The kinetics of the system is embodied in the time behavior of n_0 and f as expressed in eq 4.6. The problem is to determine the autocorrelation functions L_{11} and L_{22} as a function of temperature and pressure. This seems experimentally feasible; for example, volume relaxation measurements should be a direct measure of n_0 [see eq 2.1]. The experiments would involve displacing the system from its equilibrium position by imposing a small temperature or pressure jump and then following the volume relaxation. Denoting the equilibrium value of n_0 by $n_0{}^*$ and expanding $\partial G/\partial n_0$ in a Taylor series around $n_0{}^*$, we obtain from eq 4.3, 4.6, and 4.7

$$\dot{n}_0 = L_{11}\left.\frac{\partial^2 G}{\partial n_0{}^2}\right)_{n_0=n_0{}^*}(n_0 - n_0{}^*) \tag{4.8a}$$

or

$$(n_0 - n_0{}^*) = (n_0 - n_0{}^*)_{t=0}e^{-t/\tau} \tag{4.8b}$$

where

$$1/\tau = -L_{11}\left.\frac{\partial^2 G}{\partial n_0}\right)_{n_0=n_0{}^*} \tag{4.9}$$

and it is understood that the appropriate value of $L_{11(T,P)}$ is that near the T and P where the system was originally at equilibrium. Equation 4.8 indicates that small displacements from equilibrium result in exponential decay of n_0 (and thus volume) with a characteristic relaxation time τ which is directly related to the autocorrelation function L_{11} by eq 4.9.[23] Thus, in principle, volume relaxation measurements should provide a means of determining L_{11}.

A similar procedure is available for L_{22} if f can be determined experimentally. Recent infrared[24] and Raman[25] measurements have detected trans-gauche populations; experiments of that kind might provide the necessary probe for following the time dependence of f.

Another important question is: How does the above kinetic description relate to a transport property like viscosity? At present there are no theories of viscosity or diffusion that answer this question. However, Adam–Gibbs theory[7] is a theory of viscosity that relates the viscosity η to the excess configurational entropy of liquid. Their equation is

$$\ln \eta = \ln \eta_0 + C/TS_c \tag{4.10}$$

where C and η_0 are constants and S_c is the GD configurational entropy. One of the present authors[26] has suggested that it is the excess volume above T_2, $(V - V_2)$, that governs the viscosity and an equation similar to (4.10) is obtained except that $(V - V_2)$ replaces TS_c. Neither theory addresses the problem of relating time fluctuations in n_0 and f with viscosity.

Below T_2 we can expect that the relaxation times should become extremely large. This fact along with the observation that n_0 decreases with increasing pressure along the $T_2(P)$ line [see proof below] suggests that a glass can be permanently densified by first applying a high-pressure P' on the liquid and then cooling to a temperature not only below $T_2(P')$ but also to below $T_2(P'')$ (where P'' is the final pressure of practical interest, e.g., atmospheric pressure) at which temperature the pressure is then relieved. If n_0 has a very long relaxation time, the glass would retain its smaller volume (higher density) even at the reduced pressures. This phenomenon has in fact been observed in poly(vinyl acetate)[16] and polystyrene.[27]

It should also be mentioned that experimentally the volume of a glass at T_g decreases with increasing pressure. This has been observed in poly(vinyl acetate),[16,28] polypropylene,[29] polystyrene,[27,30] and poly(*o*-methylstyrene).[30] This experimental fact is in accord with the present theory, according to which $V_l(T_2)$ decreases with increasing pressure. Goldstein has shown it is not in agreement with an isofree volume theory of the glass transition.[31]

The proof that the volume decreases along the $T_2(P)$ line is relatively simple. We wish to show that

$$\mathrm{d} \ln V_l(T_2)/\mathrm{d}P < 0 \tag{4.11}$$

To prove the above inequality we first recognize that

$$\frac{\mathrm{d} \ln V_l(T_2)}{\mathrm{d}P} \equiv \left.\frac{\partial \ln V_l}{\partial P}\right)_{S=0} \tag{4.12}$$

and thus, from the chain rule for derivatives and eq 3.9, we obtain

$$\frac{\mathrm{d} \ln V_l(T_2)}{\mathrm{d}P} = \alpha_l(T_2) \frac{\mathrm{d}T_2}{\mathrm{d}P} - \beta_l(T_2) \tag{4.13a}$$

Substituting eq 3.13b into 4.13a, we obtain

$$\mathrm{d} \ln V_l(T_2)/\mathrm{d}P = -\beta_g < 0 \tag{4.13b}$$

which completes the proof.

(D) On the Validity of the Model. In defense of the lattice model, we should mention that it has been successfully applied in the theories of fluid phase equilibria[32-35] and liquid crystals.[36-38] In the case of the isotropic–nematic liquid crystal phase transition the transition has been attributed to the inability of the molecules (treated as rigid rods) to pack in an isotropic (random) array except at large free volumes.[36-40] The nematic liquid crystal phase consists of a parallel arrangement of the rigid molecules. Thus, the same packing difficulty that causes the formation of the glass causes the formation of nematic liquid crystals. The difference is that in the liquid crystal the parallel arrangement is allowed, whereas in glasses it is not, the lower energy shapes of the molecules comprising glasses not being able to pack in a semiregular array either for thermodynamic or for kinetic reasons.

One obvious deficiency of the lattice model employed here is that the vibrational modes of the molecules have been ignored. This is why the heat capacity (eq 3.7), the thermal expansion coefficient (eq 3.5), and the entropy (eq 3.2) are equal to zero below T_2. In reality vibrational contributions will contribute to α, β, and C_p both below and above T_2. A proper treatment of the vibrational modes would lead to a temperature and pressure dependent cell size C. Lattice models that, in principle, allow for a variable cell size are available.[41,42]

V. Conclusions

The results of this paper have been discussed above. Here we restate briefly the main conclusions:

(1) The second-order phase transition temperature initially increases with pressure and eventually approaches a finite asymptote at high pressures. A rough estimate is that pressures in excess of 10 kbars will be necessary for unambiguous observation of the asymptotic behavior.

(2) Although the simple theory might naively be classified as a double order parameter theory (f and n_0), the Ehrenfest relations are satisfied; i.e.,

$$\frac{\mathrm{d}T_2}{\mathrm{d}P} = \frac{T_2 V \Delta\alpha}{\Delta C_p} = \frac{\Delta\beta}{\Delta\alpha}$$

(3) It is senseless to assert that two or more order parameters have constant values along the transition line.

(4) The experimental fact that glasses can be permanently densified[14,25] and that the volume of the glass along the $T_g(P)$ line decreases with increasing pressure[16,27-30] is in accord with the present theory.

(5) It may be experimentally feasible to determine the relevant kinetic parameters associated with this theory by a procedure outlined here.

Appendix. Rotational Isomer Approximation

It is easily verified that for the rotational isomer approximation, eq 2.5, we have for eq 3.1 and 3.6 the following contributions

$$\frac{S_{\mathrm{int}}}{kx} = \left(\frac{x-3}{x}\right) (f \ln [(z-2)(1-f)/f] - \ln (1-f)) \tag{A1}$$

$$\frac{C_{\mathrm{int}}}{x} = k \left(\frac{x-3}{x}\right) f(1-f) (\left(\frac{\Delta\epsilon}{kT}\right)^2 \tag{A2}$$

References and Notes

(1) (a) National Bureau of Standards; (b) Work supported in part by NSF-MRL-C-177, 178 and USPHS GM10906-14; (c) Brown University; (d) Supported by the Army Materials and Mechanics Research Center, Watertown, Mass., Contract No. DAAG46-75-0052; (e) Univerity of Massachusetts.

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perature. As pointed out in ref 4, the assumption that the dearth of configurational entropy in the region of the glass temperature is the essential basis of the glass transition accounts for the fact that the glass temperature is always found below the melting point in the case of crystallizable substances.
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Fractionation of Electroneutral Polymer by Gel Electrophoresis in the Presence of Ionic Detergent

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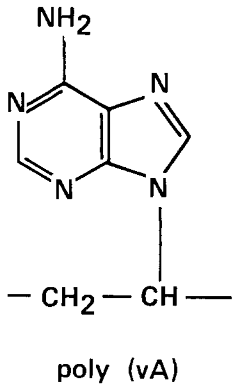
ABSTRACT: An electroneutral polymer, poly(9-vinyladenine), in aqueous solutions binds an ionic detergent and thus acquires electromobility; the polymer can then be fractionated by electrophoresis in polyacrylamide gels and size proportional fractionation is achieved through the sieving action of the gel. Binding of sodium dodecyl sulfate was measured by equilibrium dialysis, and values of 0.45 g of detergent/g of polymer were obtained at 3–4 mM detergent concentration and 0.05–0.1 ionic strength.

The estimation of molecular weight of macromolecules is of importance both in polymer chemistry and biochemistry. In recent years a method involving a modified system of gel electrophoresis[1,2] has gained wide acceptance in the field of protein research. In this method a protein is chemically reduced to a single polypeptide chain, or chains, and these are equilibrated with a solution of the anionic detergent, sodium dodecylsulfate (SDS). Polypeptides bind the detergent and this process is believed to confer on them a size proportional electric charge and also a more homogenous conformation.[3–5] Electrophoresis is then performed using gels of cross-linked polyacrylamide and polypeptides are separated according to their molecular weight through the sieving action of the gel.[1,2] In the field of synthetic polymers, electrophoresis has been used rarely (ref 6 lists 48 references). There is considerable evidence that, similarly to proteins, the synthetic polymers bind strongly the detergents in a similar manner to proteins. Anionic detergent was found to solubilize water insoluble polymers (e.g., poly(vinyl acetate)) and the solubilized polymers behave like polyanions with highly expanded chains.[7] SDS furthermore dissociates[8] some complexes formed by poly(9-vinyladenine) [poly(vA)]. This led us to study the applicability of the SDS gel electrophoresis method to a synthetic polymer. Using poly(vA) we found that the fractionation of the polymer is easily achieved.



poly (vA)

Results and Discussion

The anionic detergent, SDS, above a certain concentration exists in solution as an equilibrium mixture of monomeric and micellar forms.[3] The binding of SDS to poly(vA) was investigated by equilibrium dialysis and values around 0.45 g SDS/1.0 g poly(vA) were obtained (Table I). The conditions