the order parameters freeze in, and they do not minimize the Gibbs free energy of glass; the transition is no longer an equilibrium one and can be regarded as a freezing-in transition. This view is also corroborated by the Prigogine–Defay r_g ratios as given in Table VI. In all cases $r_g > 1$, especially for polymers with a lower T_g. This agrees well with findings described by other authors[30,37] and supports the view that glass transition is a freezing-in process controlled by more than one independent order parameter.

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Molecular Interpretation of the Glass Transition Temperature of Polymer–Diluent Systems

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ABSTRACT: An explicit expression based on both classical and statistical thermodynamics has been derived for predicting the glass transition temperature of polymer–diluent mixtures. The result is expressed in terms of the molecular weight, size, and concentration of the diluent, the number of lattice sites, the monomer molecular weight, and the transition isobaric specific heat increment. The prediction of the theory is in good agreement with published experimental data and, therefore, can be used for molecular engineering.

The depression of the glass transition temperature (T_g) by plasticizers and its composition dependence in compatible polymer blends have been known for some time.[1,2] There has, however, been strong interest recently[3-7] in deriving predictive expressions for T_g in terms of fundamental compositional parameters. Empirical equations based on data fitting, relations from the free volume hypothesis and from the point of view of classical thermodynamics, have been reported.[3-11] However, there has been no effort to interpretate T_g by using statistical mechanics since the work of DiMarzio and Gibbs.[12] Their work does not predict T_g explicitly, and the present work complements and extends their development by deriving an explicit expression for T_g of polymer–diluent systems.

In the study of an order–disorder transition, the Bragg–Williams approximation[13] has been known for its simplicity and success in displaying essential features of the phenomenon. In this paper, the method is adopted in the determination of the configurational partition function. The glass transition temperature is related to nondimensional parameters which are a function of the molecular weight and concentration of diluent, number of lattice sites, monomer molecular weight, and transition isobaric heat capacity increment of the polymer. The theoretical equation is then compared with published experimental data.

Derivation

The glassy state represents a situation of frozen-in disorder which is in a state of quasiequilibrium, and the glass transition has been explained by using both equilibrium thermodynamics and kinetic theories. Theoretical treatments of the glass transition have been either purely equilibrium[14,15] or purely kinetic[16] in nature. In this paper, our approach to the problem is an equilibrium one. First, we consider the discontinuity conditions which occur at the glass transition temperature. A relation expressing the glass transition temperature (T_g) of a polymer–diluent mixture in terms of the glass transition temperature (T_{g0}) of a pure polymer, the excess heat capacity, and configurational entropy is derived from classical thermodynamics. Then, statistical thermodynamics is used to determine the configurational partition function.

According to the viewpoint of Gibbs–DiMarzio,[14] the glass formation is considered as a result of the system's loss of configurational entropy

$$S_c = S^{\text{liquid}} - S^{\text{glass}} \tag{1}$$

For pure polymers, $S_c(0,T)$ and the heat capacity at constant pressure, C_p, are related by

$$S_c(0,T) = \int_{T_{g0}}^{T} \Delta C_p(T')\,\mathrm{d}\ln T' \tag{2}$$

where ΔC_p is the difference in heat capacity between the supercooled liquid and glass. In addition to the temperature (T), the configurational entropy of a polymer–diluent system is also a function of the number of diluent molecules (N). $S_c(N,T)$ is calculated from

$$S_c(N,T) = \int_{T_g}^{T} \Delta C_p(N,T')\,\mathrm{d}\ln T' \tag{3}$$

When the energy contributed from the vibration about the lattice sites is neglected, the Gibbs–DiMarzio theory[14] sets the entropy $S^{\text{glass}}(0,T) = 0$ at the thermodynamic transition temperature T_2. The equilibrium transition temperature T_2 is the lower bound of the obtainable glass transition temperature. Recently, Gorden, Rouse, Gibbs, and Risen[4] suggested that the composition dependence of diluents on T_g and T_2 is the same. Thus, we may assume that $S^{\text{glass}}(N,T) = S^{\text{glass}}(0,T) = 0$. Applying these conditions together with the approximation of transition increments of isobaric heat capacity as temperature independent and independent of composition, eq 2 and 3 lead to

$$\ln\left(\frac{Tg}{T_{g0}}\right) = -\frac{1}{\Delta C_p}[S^{\text{liquid}}(N,T) - S^{\text{liquid}}(0,T)] \tag{4}$$

In general, the entropy is related to the configurational partition function (Q) by the following equation

$$S = k\ln Q + kT\left(\frac{\partial \ln Q}{\partial T}\right)_p \tag{5}$$

where k is Boltzman's constant. Substituting eq 5 into eq 4, we obtain

$$\ln\left(\frac{T_g}{T_{g0}}\right) = -\frac{k}{\Delta C_p}\left[\ln\left(\frac{Q_N^{\text{liquid}}}{Q_0^{\text{liquid}}}\right) + T\frac{\partial}{\partial T}\ln\left(\frac{Q_N^{\text{liquid}}}{Q_0^{\text{liquid}}}\right)\right] \tag{6}$$

The ratio of partition functions may be evaluated by any one of the theories of mixtures such as the Bragg–Williams theory, the Flory–Huggins theory,[17] and many refined polymer liquid theories[19-23] reviewed recently by Sanchez.[1] The Flory–Huggins theory is a direct generalization of the Bragg–Williams approximation in the lattice model of small molecules.[18] The theories of Flory–Huggins and their many modifications are mainly concerned with the possible configurations of polymer molecules on lattice sites. In the problem of plasticizing high polymer by small molecules, the first order interest is to determine the possible configurations of diluent molecules on polymer lattice sites rather than the arrangements of polymer molecules because the glass temperature of a pure polymer is known. Therefore, the Bragg–Williams approach is more suitable for the evaluation of the ratio of partition functions. Since the purpose of the paper is to find the ratio T_g/T_{g0}, the main contribution to the partition function is from the mixing of solvent molecules among lattice sites.

Consider N diluent molecules randomly distributed in a lattice of $N + L$ sites where L is the number of vacant lattice sites. Let us assume that each diluent molecule occupies a single lattice site. We write[18]

$$Q_0^{\text{liquid}} = 1 \tag{7}$$

and

$$Q_N^{\text{liquid}} = \frac{(N+L)!}{N!L!}\exp\left(\frac{NL}{N+L}\frac{z\epsilon}{2kT}\right) \tag{8}$$

where z is the lattice coordinate number, $\epsilon = \epsilon_{NN} + \epsilon_{LL} - 2\epsilon_{NL}$, and ϵ_{NN}, ϵ_{LL}, and ϵ_{NL} are energies of each NN, LL, and NL pair. Substituting eq 7 and 8 into eq 6, we get the final result

$$\ln\left(\frac{T_g}{T_{g0}}\right) = \beta\{(1-\theta)\ln(1-\theta) + \theta\ln(\theta)\} \tag{9}$$

where $\beta = k(N + L)/\Delta C_p$ and $\theta = N/(N + L)$. Both β and θ are nondimensional parameters. In polymer–diluent systems, the number of diluent molecules (N) and the number of lattice sites ($N + L$) are defined by

$$N = m_d N_A/M_d \text{ and } N + L = zm_p N_A/M_p \tag{10}$$

where N_A is Avogadro's number, m is the mass, and M is the molecular weight. The subscripts d and p identify the diluent and polymer, respectively. M_p is the molecular weight of monomer. Thus,

$$\theta = \frac{N}{N+L} = \frac{M_p}{zM_d}\frac{\omega}{1-\omega} = \frac{V_p}{zV_d}\frac{\phi}{1-\phi} \tag{11}$$

where ω is the mass (or weight) fraction of the diluent. The corresponding volume fraction is ϕ, and V is the molar volume. Relations among the mass, volume, and molar fractions of the diluent are listed in the Appendix.

In the derivation of eq 9, it is important to note that the assumption of a temperature independent ΔC_p and the application of the Bragg–Williams approximation implicity require θ to be small. Therefore, we may take the approximation $\Delta C_p = m_p \Delta C_{pp}$ and get

$$\beta = zR/M_p\Delta C_{pp} \tag{12}$$

where ΔC_{pp} is the excess transition isobaric specific heat of the polymer.

Experimental Verification

We have derived the dependence of the glass transition temperature of polymer–diluent mixtures as a function of nondimensional parameters β and θ. For a given polymer, β is usually fixed. Adding a low molecular weight diluent to a polymer affects the values of θ. The effects of concentration, molar volume, and flexibility of plasticizer on T_g have been considered.[12] In this paper, the concentration and molecular weight (or molar volume) of diluent are combined with the number of sites and monomer molecular weight of the polymer and treated as a single parameter θ.

Consider various diluents in polystyrene which has the following properties:[8] M_p = 104.15 g/mol; V_p = 101.0 cm^3/mol; z = 2; $M_p\Delta C_{pp}$ = 6.45 cal/(mol K); and T_{g0} = 358.5 K. The depression of the glass transition temperature of polystyrene by diluents of different molecular

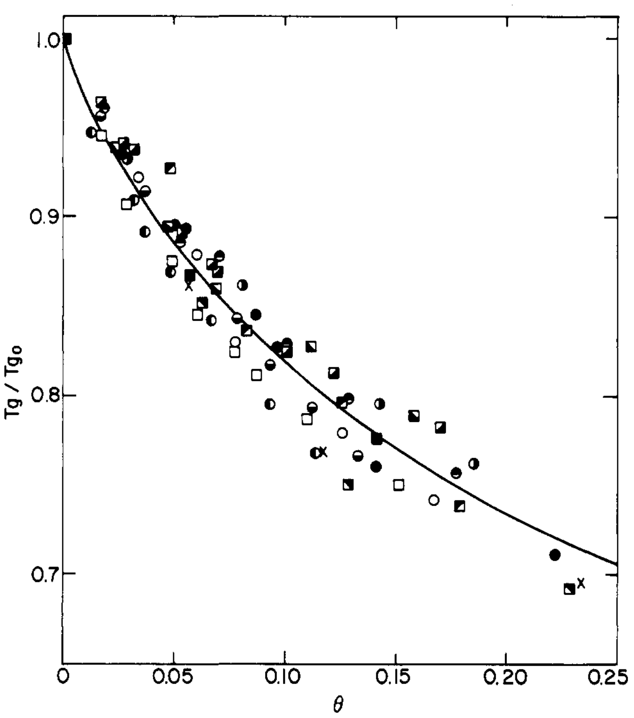

Figure 1. Glass transition temperature depression of polystyrene by diluents of different molecular weight, size, and concentration.

Table I
Various Diluents in Polystyrene

diluent	M_d, g/mol	V_d, cm³/mol	symbol in Figure 1
methyl acetate	74.08	79.30	○
CS_2	76.14	60.28	◒
C_6H_6	78.12	88.87	◒
CH_2Cl_2	84.93	64.20	◑
ethyl acetate	88.11	98.34	◐
$C_6H_5CH_3$	92.14	106.03	●
n-butyl acetate	116.16	131.70	□
$CHCl_3$	119.38	80.94	◪
$C_6H_5NO_2$	123.11	102.28	◩
methyl salicylate	152.15	128.95	◪
CCl_4	153.82	96.49	◪
phenyl salicylate	214.22	171.38	×
β-naphthyl salicylate	264.22	214.00	■

weight, molar volume, and concentration is shown in Figure 1 in terms of the nondimensional parameters T_g/T_{g0} vs. θ. The solid curve represents theoretical calculations. The symbols for the experimental points are described in Table I. The predicted behavior is in good agreement with the observed behavior. The normalized T_g is a monotonic decreasing function of θ. Therefore, the plasticizing efficiency decreases as the molecular weight, size, and volume of diluent increase. Increasing the diluent concentration also reduces T_g.

In the derivation of eq 9, θ was implicitly assumed to be small which does not limit the usefulness of the theory. The theory applies well to composites containing a low content of small-molecule solvent to a high concentration of large plasticizers (see Figure 1). The simplicity of the treatment, broad range of application, and good comparison with experiment suggest the usefulness of the theory such as in molecular engineering.

Appendix

The relationships between the molar fraction ($x = x_d$), volume fraction ($\phi = \phi_d$), and weight fraction (or mass fraction $\omega = \omega_d$) of diluent are:

$$x_d = \frac{\omega_d/M_d}{\omega_p/M_p + \omega_d/M_d} = \frac{\phi_d/V_d}{\phi_p/V_p + \phi_d/V_d} \tag{A1}$$

$$\phi_d = \frac{x_d V_d}{x_p V_p + x_d V_d} \tag{A2}$$

$$\omega_d = \frac{x_d M_d}{x_p M_p + x_d M_d} \tag{A3}$$

There is only one independent variable.

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