Conformational effects on glass transition temperature and relaxation phenomena of polymers

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The glass transition temperature, T_g, of a polymer has been defined as the temperature at which the segmental motions of molecular chains in the quasiequilibrium glassy state overcome the intermolecular attractions. As the thermodynamic criterion of T_g, both of the conditions $\Delta F = 0$ and $-f_r = f_r^v$ should be accepted, where f_r and f_r^v are the conformational free energy and the intermolecular cohesive free energy per structural unit, respectively, and ΔF the free energy difference per molar chain between the frozen solid part and the flow part, still unfrozen at a given temperature in the vicinity of T_g. The equation for T_g has been derived by use of the criterion for T_g in the present work. The conformational effect on relaxation phenomena (the WLF equation) in polymers has been thermodynamically examined by use of the partition function taking into account both the conformational character of the polymer and the free volume for the polymer liquid. The constant C_2' in the WLF equation, the ratio of ϕ_g/α_f (with α_f and ϕ_g being the difference in the volume expansion coefficients and the volume fraction ϕ at T_g, respectively), derived from the partition function, are in good agreement with the experimental values.

INTRODUCTION

Glass transition and relaxation phenomena in polymers have been extensively investigated by means of thermal analysis, dilatometry, dynamic measurements, etc. Some fundamental problems are left unsolved, although theoretical attempts[1–4] have been made to explain these phenomena. The conformational effect on the glass transition temperature and relaxation phenomena should be more inclusively discussed by use of the partition function taking into account the conformational character of the polymer chain. Use of the partition function based on lattice theory[5] is insufficient to discuss the effects caused by the chain conformation.

It has been suggested[6] that the chain conformation in the bulk including the melt is generally the random coil type and the chain dimension is almost consistent with the unperturbed one. The presence of ordered regions in the bulk is in dispute for some polymers[7,8], considered to be stiff. From this viewpoint it is desirable to establish the partition function in the bulk taking the inherent conformational character of the polymer chain into account.

In this work the conformational effect on the glass transition temperature, observed by means of thermal analysis etc., and relaxation phenomena (the WLF equation[9]) has been examined by use of a modified partition function taking into account both the conformational character of the polymer and the free volume of the polymer liquid.

THEORETICAL AND DISCUSSION

Partition function and derivative thermodynamic quantities

The configurational partition function Ω normalized per unit volume and taking into account both the conformational character and the free volume of the polymer liquid is expressed by:

$$\Omega = \frac{Z^N(T)}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3Nx/2}\left(\frac{q}{v_f}\right)^{Nx}\exp\left(\frac{NxU_0}{RT}\right) \qquad (1)$$

where N is the number of polymers, $Z(T)$ the conformational partition function for a chain at T, m the mass of the structural unit, R the gas constant, k Boltzmann's constant, h Plank's constant, U_0 the intermolecular cohesive energy per molar structural unit, x the degree of polymerization, and $q(<1)$ the packing factor of the core. The quantity v_f is the free volume per structural unit and is defined by:

$$v_f = \int_{\text{unit}} \exp[-\{\Psi(\rho) - \Psi(0)\}z/2RT]\,\mathrm{d}\rho = qv\exp(U_0/RT)$$

with $U_0 = \Psi(0)z/2$ and the apparent volume of the structural unit given by:

$$v = \frac{1}{q}\int_{\text{unit}} \exp[\{-\Psi(\rho)\}z/2RT]\,\mathrm{d}\rho$$

where z is the coordination number and $\Psi(\rho)$ the potential energy at a vector ρ from the centre of the core.

By use of equation (1) under the assumption of constant q, the free energy difference ΔF (= $F_{\text{solid}} - F_{\text{flow}}$) per molar chain between the frozen solid part and the flow part, still

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Table 1 Numerical values of $N_A h_u^c$, $N_A s_u^c$, h_u^c/s_u^c, U_0 and C_2' at T_g for various polymers

Polymer	T_g[17] (K)	U_0[18] (cal/mol)	C_2'	$N_A h_u^c$ (cal/mol)	$N_A s_u^c$ (cal/mol K)	h_u^c/s_u^c (K)
Polyethylene	148	680	55.1	110.3	1.30	84.8
Poly(ethylene terephthalate)	342	3900	55.6	275.8	7.32	37.7
Nylon-6	323	8500	23.1	486.7	11.3	43.1
Nylon-6,6	323	17 000	11.5	970.0	22.6	42.9
Nylon-6,10	313	17 000	10.4	1704.2	29.2	58.2
Isotactic Polypropylene	255	1360*	76.5	328.9	1.68	195.8
	263	1360*	80.6	344.7	1.74	198.1
Isotactic Polystyrene	373	4300	57.1	537.6	2.08	259.0
		4300	51.0	1123.0	2.03	552.7

* Molar cohesive energy of the $-CH(CH_3)-$ group

unfrozen at a given temperature in the vicinity of T_g, is now readily obtained with the aid of thermodynamic relations, yielding:

$$\frac{1}{x}\Delta F = -N_A(h_u^c - Ts_u^c) - U_0 - TR\ln v_f + TS_d \qquad (2)$$

with

$$S_d = \frac{3}{2}R\ln\left(\frac{2\pi mkT}{h^2}\right) - \frac{R}{Nx}\ln N!$$

where N_A is Avogadro's number. The quantities h_u^c and s_u^c are the conformational enthalpy and the entropy per structural unit, respectively, and are expressed by:

$$N_A h_u^c = \left(RT^2\frac{\mathrm{d}\ln Z(T)}{\mathrm{d}T}\right)\Big/x$$

and

$$N_A s_u^c = \left(R\ln Z(T) + RT\frac{\mathrm{d}\ln Z(T)}{\mathrm{d}T}\right)\Big/x$$

Assuming that the cohesive state of polymer chains is in quasiequilibrium frozen at T_g, the condition of $\Delta F = 0$ should be accepted as the criterion of T_g. At T_g the molar quantities $N_A h_u^c$ and $N_A s_u^c$ are given by:

$$N_A h_u^c = RT_g^2\left(\frac{\alpha_f}{\phi_g}\right) - U_0 - T_g\Delta S_g \qquad (3)$$

and

$$N_A s_u^c = RT_g\left(\frac{\alpha_f}{\phi_g}\right) + R\ln\frac{\phi_g v_0}{1-\phi_g} - S_d - \Delta S_g \qquad (4)$$

with

$$\frac{\alpha_f}{\phi_g} \approx \frac{\alpha_f}{\phi_g} + \frac{\alpha_f}{1-\phi_g} = \left(\frac{\mathrm{d}\ln v_f}{\mathrm{d}T}\right)_v \qquad \text{(ref 10)}$$

where ΔS_g is the entropy difference per mole structural unit between the frozen solid part and the flow part in quasiequilibrium at T_g, α_f the difference between the volume expansion coefficient below T_g and that above T_g; ϕ_g the free volume fraction ϕ at T_g and v_0 the core volume of the structural unit.

Glass transition temperature

Assuming equivalence of the viscosity relationship between a single chain in the bulk and the surrounding chains at the glass transition temperature T_g, then T_g should be taken as the temperature at which the segmental motions of molecular chains are frozen to the glassy state or overcome the intermolecular attractions. Thus, as supported by the numerical values of $N_A f_r$ at T_g which are negative for all polymers listed in *Table 1*, the condition of $-f_r = f_r^v$ in addition to $\Delta F[= xN_A(f_r + f_r^v)] = 0$ in equation (2) should be accepted as the thermodynamic criterion of T_g.

Then T_g is given as:

$$T_g = \frac{-f_r}{s_u^c} + \frac{h_u^c}{s_u^c}$$

or

$$\frac{N_A f_r^v - U_0}{R\ln v_f - S_d} \qquad (5)$$

where the quantities f_r and f_r^v are the conformational free energy and the intermolecular cohesive free energy per structural unit, respectively.

Very recently Flory has formulated $Z(T)$ by[11,12]:

$$Z(T) = J^*\left(\prod_{i=2}^{n-1} U_i\right)J \qquad (6)$$

$J^* = [100]$ and $J = \mathrm{col}(111)$, where the matrix U_i is related to the potential energy for the internal rotation about the ith bond and n represents the number of bonds of the polymer chain. The calculation of $Z(T)$ has been performed for polypropylene (PP) and polystyrene (PS) by use of a model with five and two rotational isomeric states proposed by Flory[13,14]. For other polymers a model with three rotational isomeric states has been used[11]. The numerical vlaues of $N_A h_u^c$ and $N_A s_u^c$ calculated by use of $Z(T)$ with the rotational isomeric states are listed in *Table 1*. For PE and PP, in which the dependences of x on the thermodynamic quantities ($N_A h_u^c$, $N_A s_u^c$ and $N_A f_r$) have been found, the values at $x = \infty$ for PE and $x = 200$ for PP are used.

Lee and Sewell have proposed the experimental relation

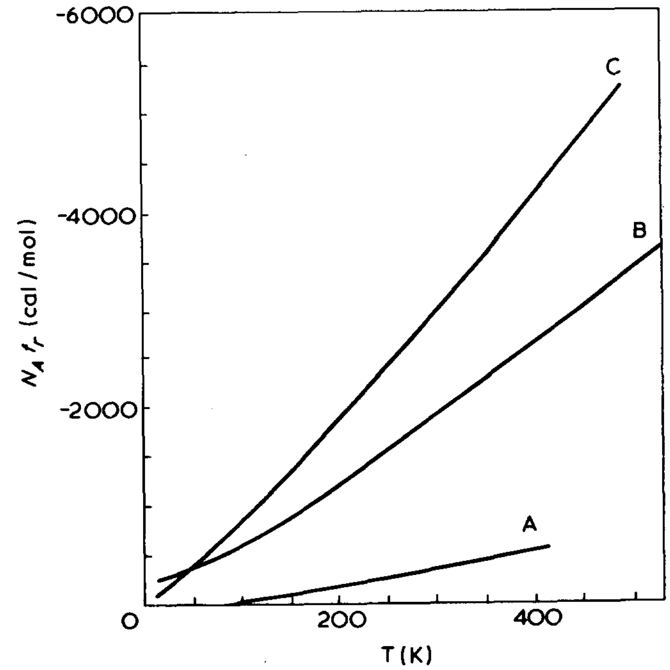

Figure 1 Conformational free energy vs. temperature: A, PE; B,PET; C, nylon-6

between T_g and the cohesive energy density ($CED = L/V$) by the following equation[15]:

$$T_g = K\left(\frac{L}{V}\right) + C \qquad (7)$$

with $K = 2$ K cm^3/cal and $C = 70 \pm 20$ K and where L and V are the molar latent heat of vaporization of a liquid and its molar volume, respectively.

Except for isotactic PP(i-PP) and isotactic PS(i-PS) with helical conformations in the crystalline state, the values of h_u^c/s_u^c at T_g in *Table 1* are almost the same in the range of $C = 70 \pm 20$K, though they depend slightly on the type of polymer. The value of $(h_u^c/s_u^c)_{f_r=0}$ extrapolated to $f_r = 0$ in the curves relating the conformational free energy and the temperature ($T_g < T < T_m$) for polyethylene (PE), poly(ethylene terephthalate) (PET), and nylon-6 are larger by several degrees than those at T_g, as is shown in *Figure 1*. The values of h_u^c/s_u^c at T_g for i-PP and i-PS are much larger than the value of $C = 70 \pm 20$K. The relation by Lee and Sewell is of no avail for PP and PS.

Constant C_2' in the WLF equation

The ratio ϕ_g/α_f in equations (3) and (4) corresponds to the constant C_2' in the following WLF equation[9,16]:

$$\log a_T(T_g,T) = -C_1'(T - T_g)/(C_2' + T - T_g) \qquad (8)$$

where $a_T(T_g,T)$ is the shift factor, and constants C_1' and C_2' are given by 17.44 and 51.6K, respectively. The numerical values of the constant C_2' in the present work are calculated by:

$$C_2' = \frac{\phi_g}{\alpha_f} = \frac{RT_g^2}{N_A h_u^c + U_0 + T_g \Delta S_g} \qquad (9)$$

The values of h_u^c/s_u^c at T_g are also listed in *Table 1* in order to compare $(h_u^c/s_u^c)_{T=T_g}$ with C_2' evaluated by the assumption that $\Delta S_g \approx 0$ in equation (9). The two values of C_2' for i-PS are evaluated by using the $N_A h_u^c$ values brought out by the adoption of two different potential energies for a conformation about a skeletal bond. The C_2' value for the crystalline polymers also lies in the vicinity of 51.6K in agreement with the amorphous polymers. In particular, the experimental value $C_2' = 56.6$K for i-PS[3] is in good agreement with the C_2' value of 51.0 ~ 57.1K by equation (9). Although equation (8) is valid for the amorphous polymer, it seems that equation (8) is applicable even to the crystalline polymer which is in the amorphous state.

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