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A Molecular Model for Cooperative Local Motions in Amorphous Polymers

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ABSTRACT: A simple molecular model has been proposed for rotational motions of simple molecules in liquids and for local segmental motions in condensed polymer systems. In order to describe the behavior of cooperative segmental motions, we consider a model in which gears are rotating synchronously. The gear model predicts that the number of cooperatively moving segments increases with decreasing temperature and diverges at a critical temperature, T_0. Thus the relaxation time also diverges at T_0 as given empirically by the Vogel equation. This model as well explains the nonexponential correlation function given by the Kohlrausch–Williams–Watts equation and the diluent effect on the relaxation time.

Introduction

The primary relaxation process in amorphous polymers has been investigated by many authors by means of dielectric, mechanical, and other methods.[1] Although phenomenological features of the primary process have been well established, its molecular mechanism has not been explained theoretically.

A most familiar theory for mobility of polymer segments is the free-volume theory first proposed empirically by Doolittle.[2] This theory has been used successfully in an explanation of varieties of dynamic properties of amorphous polymers such as the temperature dependence of viscosity and relaxation time or shift factor.[3,4] However, the free-volume theory is phenomenological and does not provide us with a detailed molecular picture for the segmental motions.

Molecular theories based on a crankshaft model have been developed by Monnerie and his co-workers[5,6] and several other authors.[7-10] An approach based on an Ising model has also been studied theoretically by Budimir and Skinner.[11] In these models diffusion of a local conformation of a polymer chain has been described to express the correlation function of orientation of the segments. However, the effects of intermolecular interactions, which

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must be significant in condensed systems, have not been explicitly taken into account. Accordingly, these theories are in principle applicable only to dilute polymer solutions.

A more general theory termed "coupling model" has been proposed by Ngai and his co-workers[12-14] who assume that a test molecule and the surrounding species have time-dependent interactions. Thus, the relaxation time for the motion of the test molecule depends on time. They propose that the rate of change of a dynamical quantity $d\psi/dt$ is proportional to $-f(t)\psi$, where $f(t)$ is a function of time t. Starting from this equation, they successfully explained various relaxation behavior.[13,14]

As discussed below, several facts indicate that the primary process in a condensed polymer system is originated from cooperative motions of the segments. Since polymer segments are nonspherical, they rotate synchronously like gears together with the neighboring segments.[15,16] Due to their thermal vibration, such a synchronous motion is occasionally broken. The probability of such a cooperative motion is expected to depend strongly on temperature, the shape of the molecule, and the intermolecular forces. In this article, we develop a gear model to explain the rotational motion of simple molecules and segments of amorphous polymers in bulk and concentrated solution.

General Feature of Segmental Motion

Before discussing the model, we summarize the four major features of the primary relaxation process prevailing mainly in the dielectric data. Any models concerned with the segmental motions are demanded to explain all these three features.

1. **Temperature Dependence of the Relaxation Time.** The temperature dependence of the relaxation time, τ, for the segmental motion obeys the empirical equation proposed by Vogel[17] and others[18]

$$\log \tau = A + B/(T - T_0) \qquad (1)$$

where A, B, and T_0 are parameters and log is the common logarithm. The apparent activation energy, E_a, of the process thus decreases with increasing temperature T

$$E_a = 2.303RBT^2/(T - T_0)^2 \qquad (2)$$

where R is the gas constant. This equation indicates that E_a becomes infinity at T_0.

2. **Correlation Function.** The correlation functions for various relaxation processes associated with the segmental motions are cast into the Kohlrausch-Williams-Watts (KWW) equation[19,20]

$$\phi = \exp[-(t/\tau_K)^{1-n}] \qquad (3)$$

where τ_K is a parameter with the dimension of time t and n is another parameter. A typical value of n is 0.45.[20] The Fourier-Laplace transform of eq 3 provides a response function in the frequency domain. In the case of the dielectric relaxation, the complex dielectric constant, ϵ^*, is empirically given by the Havriliak-Negami equation[21]

$$\epsilon^* - \epsilon_\infty = \Delta\epsilon/[1 - (i\omega\tau_H)^{1-\alpha}]^\beta \qquad (4)$$

where ϵ_∞ is the unrelaxed dielectric constant, $\Delta\epsilon$ is the relaxation strength, i is the imaginary number, ω is the angular frequency, τ_H is the nominal relaxation time, and α and β are constants having values between zero and unity. Equations 3 and 4 are numerically similar but mathematically not equivalent.[22]

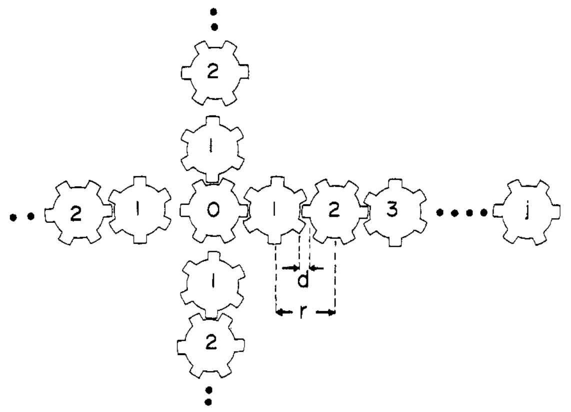

Figure 1. Schematic representation of the gear model. This figure shows the case of $z = 4$: Among the four first neighbors, two of them are in the decoupled state with respect to the 0th gear.

3. **Relaxation Behavior in Mixed Systems.** If two polymers are miscible, the dielectric or mechanical loss curve of their blend exhibits a single loss peak in a frequency range between the relaxation frequencies of the pure components.[23] This property is often used as a criterion of miscibility.[24] The existence of a single loss peak indicates that the segments of the both components move cooperatively. Polymer/diluent systems also exhibit a single loss peak at an intermediate frequency between the relaxation frequencies of the polymer and the diluent when the polymer concentration is higher than about 40%.[25-28]

4. **Relaxation Behavior of Simple Molecules.** The three features mentioned above are also observable in simple molecules such as toluene, dibutylphthalate, and *o*-terphenyl.[29-32] However, it is known that the Vogel and KWW behaviors do not always occur together. Laughlin and Uhlmann[31] reported that the viscosity of *o*-terphenyl deviates from the Vogel equation at low temperature near the glass transition temperature. On the other hand, the dielectric loss of *o*-terphenyl conforms well to the KWW equation.[29] Although there exist unusual cases, supercooled liquids of simple molecules mostly exhibit the behavior similar to amorphous polymers. Thus the connectivity of segments forming a chain molecule is not essential in explaining the segmental motion in condensed polymer systems. We neglect in our gear model the effect of connectivity of segments as a crude approximation.

Gear Model

As a simple model of cooperatively moving segments, we consider a model that a reference gear with index 0 rotates synchronously with surrounding gears as shown in Figure 1. The index j represents a jth neighbor of the reference gear 0. Here it is noted that, to apply this model, the actual segments should not necessarily have the spherical shape as shown in Figure 1.

We assume that the potential $U(r)$ between the two adjacent gears is given by

$$U(r) = f(r - r_0)^2/2 \qquad (5)$$

where f is the force constant, r is the distance between the centers of the two adjacent gears, and r_0 is the distance when they are in gear. The depth of the teeth of the gear is d. If the molecule is activated beyond the distance $r_0 + d$, two gears are out of gear and move independently. The probability p that two gears are in gear is given by

$$p = 1 - \exp(-U_0/k_BT) \quad (6)$$

$$p \simeq U_0/k_BT - (U_0/k_BT)^2/2 \quad (7)$$

where U_0 equals $U(r_0+d)$. The high temperature approximation, eq 7, is considered to be a good approximation when temperature is higher than the glass transition temperature, T_g. If the number of the nearest neighbor gears is z, the number N of the gears that move cooperatively together with the reference gear may be given by

$$N \simeq 1 + pz + pz[p(z-1)] + pz[p(z-1)]^2 + ... \quad (8)$$

where we neglected the probability of "circular coupling" that the jth gear is in gear with any of the gears with an index less than $j - 2$. At temperatures below a certain critical temperature, T_c, $p(z-1)$ becomes greater than unity and hence N diverges. Above T_c, N becomes

$$N = (1 + p)/[1 - p(z-1)] \quad (9)$$

It may be reasonable to assume that z is on the order of 10. Thus, p is on the order of 1/10, and p^2 or higher order terms of p can be neglected. Under this approximation eq 9 is rewritten as

$$N \simeq 1/(1 - pz + p^2z) \quad (10)$$

The gear model predicts that at a temperature near T_c many molecules move cooperatively, but at a high temperature they move almost independently.

Comparison with Vogel Equation

In this section the average relaxation time, τ, is calculated on the basis of the gear model and is compared with eq 1. We assume that the activation energy for rearrangement of gears is proportional to N. Then the temperature dependence of τ for rotation of the reference gear may be written as

$$\tau = (1/W) \exp[\epsilon N/k_BT] \quad (11)$$

where W is the frequency of rotational vibration of the gear and ϵ is the minimum activation energy. We assume that W and ϵ are independent of T. From eqs 7, 10, and 11, we obtain

$$\log \tau = \log (1/W) + (\epsilon/2.303k_B)/[T - (zU_0/k_B)(1 - 3U_0/2k_BT)] \quad (12)$$

where the terms of U_0/k_BT with the order higher than the third power have been neglected. We see that eq 12 has a similar form to the Vogel equation (eq 1) at a high temperature. In order to compare eq 12 with eq 1, we may approximate eq 12 as follows. From eq 7 and 9, we find that U_0/k_BT_c is approximately $1/z$. Therefore, when temperature T is approximately $1.5T_c$, eq 12 is rewritten as

$$\log \tau \simeq \log (1/W) + (\epsilon/2.303k_B)/[T - (z - 1)U_0/k_B] \quad (13)$$

Figure 2 shows the comparison of eqs 12 and 13 for z = 5, 10, and 15. Both equations are compared in the temperature of $zU_0/k_BT < 0.75$ because empirically it is known that the glass transition temperature, T_g, is equal to $1.3T_0$.[33] In the range of $T < T_g$, the high-temperature approximation used above is probably invalid.

As is seen in Figure 2, both equations agree well. Thus the empirical Vogel parameters are given by

$$A = \log (1/W) \quad (14)$$

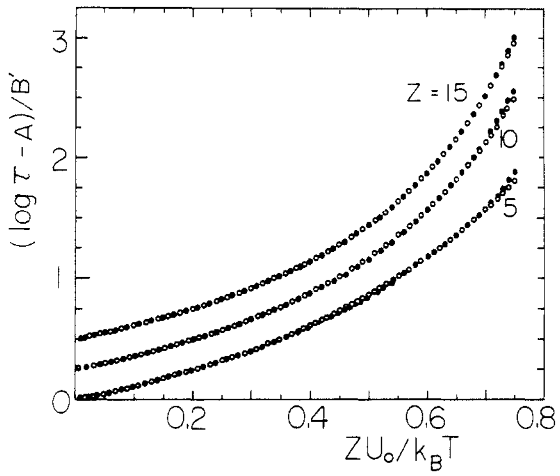

Figure 2. Comparison of the Vogel equation (eq 13) and the temperature dependence of relaxation time, τ, given by the gear model (eq 12). Open circles indicate eq 12 and closed circle eq 13. A and B' represent log $(1/W)$ and $\epsilon/(2.303zU_0)$, respectively. Plots for z = 10 and z = 15 are shifted upward by 0.25 and 0.5, respectively.

$$B = \epsilon/(2.303k_B) \quad (15)$$

$$T_0 = (z - 1)U_0/k_B \quad (16)$$

We see in Figure 2 that eq 12 for z = 5 deviates slightly from eq 13 in the low-temperature range of $0.7 < zU_0/k_BT < 0.75$. As discussed in the previous section, it is known that in some cases the experimental data do not conform to the Vogel equation over a wide temperature range. This might be explained in terms of the gear model as the effect of z that depends on the chemical structure of molecules.

The critical temperature, T_c, at which the relaxation time becomes infinite is given from eq 6 with $p(z-1)$ = 1:

$$T_c = (U_0/k_B) \ln [(z - 1)/(z - 2)] \quad (17)$$

We have derived the Vogel equation on the basis of the high-temperature approximation. Near T_0, the temperature dependence of τ is different from the Vogel equation. Since most of experiments are made at a temperature much higher than T_0, experimental T_0 should be compared with eq 16 rather than eq 17. However, the true critical temperature is given by eq 17.

The Vogel equation was explained by Williams, Landel, and Ferry[3] in terms of the free-volume concept proposed by Doolittle.[2] The present gear model is quite consistent with the free-volume theory: When the two gears are out of gear, free volume is created and hence the larger is the free-volume content and the shorter is the relaxation time.

The Vogel equation was also derived by Adam and Gibbs[33] on the basis of the concept of cooperatively rearranging subsystems. The Adam–Gibbs theory (AG theory) assumes that the average transition probability, $W(T)$, of rearrangement is given by

$$W(T) = A \exp(-z^*\Delta\mu/k_BT) \quad (18)$$

where z^* is the minimum size of the subsystem and $\Delta\mu$ is the potential barrier for the cooperative rearrangement per molecule. The temperature dependence of $W(T)$ is given by the temperature dependence of z^*, which is proportional to configurational entropy s_c of the subsystem

$$z^* = N_A s_c / S_c \tag{19}$$

where S_c is the molar configurational entropy and N_A is Avogadro's number. At a critical temperature T_2, s_c becomes equal to S_c and hence z^* becomes equal to the macroscopic size. When the configurational heat capacity, ΔC_p, is proportional to temperature, the AG theory successfully predicts the Vogel equation.[32] The AG theory is very similar to the present gear model in two respects: First, eq 18 is similar to eq 11, and, second, both theories assume that the number of molecules associated with the cooperative rearrangement diverges at the critical temperature.

However, the correspondence between the AG and the gear models is not clear. We note that the AG model assumes that the supercooled liquids have the perfectly ordered configuration with $S_c = 0$ at T_2 at which τ diverges. On the other hand, the gear model assumes that some gears are still decoupled at T_c. Thus the gear model predicts that S_c does not vanish at T_c.

Kohlrausch–Williams–Watts Equation

We apply the gear model to explain the correlation function for dielectric polarization expressed empirically by the KWW equation.[19,20] Dielectric relaxation of the gearlike molecules having dipole moment μ is considered. The complex dielectric constant, ϵ^*, is generally given by the Fourier transform of the time derivative of the correlation function ϕ[34]

$$\epsilon^*(\omega) = \epsilon_\infty + \Delta\epsilon \int_0^\infty (-\mathrm{d}\phi/\mathrm{d}t) \exp(-i\omega t)\, \mathrm{d}t \tag{20}$$

$$\phi(t) = \langle \mu_o(0)\cdot\mathbf{M}(t)\rangle / \langle \mu_o(0)\cdot\mathbf{M}(0)\rangle \tag{21}$$

where $\langle\ \rangle$ denotes the ensemble average, $\mu_o(0)$ the dipole moment of the reference dipole at time 0, and $\mathbf{M}(t)$ the vectorial sum of the dipole moments in the system at time t. As shown in Figure 1, the reference gear is surrounded by z first neighbors, $z(z-1)$ second neighbors, and so on. In order to calculate $\langle \mu_o(0)\cdot\mathbf{M}(t)\rangle$, we have to take into account the spatial and time correlations of the gears.

First we consider the spatial correlation. At a certain time $t = 0$, the reference gear and the surrounding gears are correlated as described in the previous section. The number of the jth neighbor gears, N_j, having the correlation with the 0th gear is equal to $pz[p(z-1)]^{j-1}$. Approximating $pz \simeq p(z-1)$, we rewrite N_j as

$$N_j = \exp(-j/\xi) \tag{22}$$

where ξ is the correlation length measured with a scale of the diameter r of the gear. We find that ξ is equal to $1/\ln\,[p(z-1)]$ and is equal to $1/\ln\,(T/T_0)$. From eqs 21 and 22, $\phi(t)$ is written as

$$\phi(t) = \frac{\langle \mu_o(0)\cdot\mu_o(t)\rangle + \sum \exp(-j/\xi)\langle \mu_o(0)\cdot\mu_j(t)\rangle}{\langle \mu_o(0)\cdot\mu_o(0)\rangle + \sum \exp(-j/\xi)\langle \mu_o(0)\cdot\mu_j(0)\rangle} \tag{23}$$

where the suffices o and j indicate the reference and jth dipoles, respectively, and the summation is performed from $j = 1$ to infinity. This equation has a form of the weighted sum of the correlation functions and is sensitive to the weighting factor. Although the gear model predicts the factor given by eq 22, it is considered that $\phi(t)$ may be given generally by a form of eq 23, which has a form that with an increase in j the factor decreases exponentially. Thus, ξ is the key parameter determining the j dependence of $\phi(t)$.

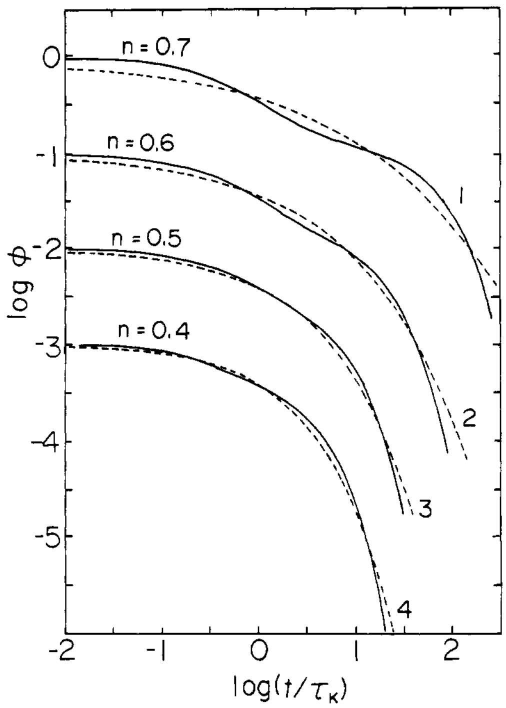

Figure 3. Comparison of the Kohlrausch–Williams–Watts equation (eq 3; dashed line) and the ϕ calculated with eq 24 (solid line). For the KWW equation, τ_K is taken to 1. The curves 1–4 correspond to n = 0.7, 0.6, 0.5, and 0.4, respectively. The values of τ_o, τ_c, and ξ for these curves are given in Table I. The curves 2–4 are shifted to downward by 1, 2, and 3 decades, respectively.

Second we consider the time correlation $\langle \mu_o(0)\cdot\mu_j(t)\rangle$ between the 0th and jth gears. A one-dimensional array of gears is considered (see Figure 1). We see that the 0th and jth gears are correlated while all gears from the 0th to jth are in gear, but when any pair of the gears between them becomes out of gear, the 0th and jth gears are totally uncorrelated. The probability $\psi(t)$ that the two adjacent gears being in gear at $t = 0$ are still in gear at time t may be given by a form

$$\psi(t) = \exp(-t/\tau_c) \tag{24}$$

$$\tau_c = (1/W) \exp(U_o/k_B T) \tag{25}$$

where τ_c is the correlation time. Then the correlation of the 0th and jth gears is proportional to $\psi(t)^j$ and may be given by

$$\langle \mu_o(0)\cdot\mu_j(t)\rangle = \langle \mu_o(0)\cdot\mu_o(t)\rangle \exp(-jt/\tau_c) \tag{26}$$

For the autocorrelation function $\langle \mu_o(0)\cdot\mu_o(t)\rangle$, the correlation functions proposed by Monnerie et al.[5,6] or by Hall and Helfand[7] should be used to account for the intramolecular correlation of polymer chains. However, for the sake of simplicity, we assume that $\langle \mu_o(0)\cdot\mu_o(t)\rangle$ decays single exponentially with a correlation time τ_o. It is noted that τ_o is the correlation time for the rotational diffusion and is approximately equal to τ given by eq 11. On the other hand, τ_c is the correlation time for coupling of two gears, and therefore τ_o is different from τ_c. From eqs 23 and 26, $\phi(t)$ is finally given by

$$\phi(t) = \frac{[1 - \exp(-1/\xi)] \exp(-t/\tau_o)}{1 - \exp(-1/\xi - t/\tau_c)} \tag{27}$$

This equation is quite different from the KWW equation but is a result of the present model.

Figure 3 shows the comparison of eq 27 and the KWW equation. For the values of n from 0.4 to 0.7, the best

Table I
Comparison of the Parameters of the KWW Equation and Those of eq 22

τ_K	n	τ_0	τ_c	ξ
1	0.4	3.5	0.8	2
1	0.5	6.0	1.2	3
1	0.6	17	2.5	6
1	0.7	60	3	7

fit of eq 27 has been obtained with the values of τ_0, τ_c, and ξ listed in Table I. We note that, though the $\phi(t)$ curve has a structure, it is close to the KWW equation. The agreement of both equations becomes better for lower values of n.

Diluent Effects

In polymer/diluent systems, we assume that polymer segments and solvent molecules are modeled by gears with different sizes and force constants. The relaxation time of the segment is calculated on the basis of the three coupling probabilities p_{11}, p_{12}, and p_{22} where the suffices 1 and 2 represent the polymer segment and the solvent molecule, respectively.

For the sake of simplicity, we assume that the sizes of the segment and the solvent are the same. Their coordination numbers, z, are also the same. Among the z first neighbors of a certain test segment, n_{11} segments and n_{12} solvent molecules are coupled with the test segment

$$n_{11} = Czp_{11} \tag{28}$$

$$n_{12} = (1 - C)zp_{12} \tag{29}$$

where C is the mole fraction of the segments in the system. Similarly the numbers n_{21} of the polymer segments and n_{22} of the solvent molecules coupled with a test solvent molecule is given by

$$n_{21} = Czp_{12} \tag{30}$$

$$n_{22} = (1 - C)zp_{22} \tag{31}$$

Then the total number of the segments, N_1, and that of the solvent N_2 moving cooperatively with the test segment are given by a form

$$\begin{pmatrix} N_1 \\ N_2 \end{pmatrix} = \mathbf{A}^{j-1} \begin{pmatrix} n_{11} \\ n_{12} \end{pmatrix} \tag{32}$$

$$\mathbf{A} = \begin{pmatrix} n_{11} & n_{12} \\ n_{21} & n_{22} \end{pmatrix} \tag{33}$$

where $\mathbf{A}^0$ is defined as the unit matrix. This equation is calculated straightforwardly by diagonalizing $\mathbf{A}$ into Λ with a matrix $\mathbf{X}$ satisfying $\Lambda = \mathbf{X}^{-1}\mathbf{A}\mathbf{X}$.

Unfortunately, the result of this calculation is rather tedious. Thus, we use the very crude approximation that the teeth of the solvent gears are much shallower than those of polymer segments and hence $p_{11} \gg p_{12} \gg p_{22}$. We neglect p_{22} and the terms of p_{11} and p_{12} of higher than second order. Then the total number N of the cooperatively moving gears is approximately given by a form:

$$N \simeq 1/[1 - (p_{11} - p_{12})zC] \tag{34}$$

Similar to eqs 7, 10, and 15, we express $T_0(C)$ of solutions with concentration C

$$T_0(C) = T_0{}^{\circ}C(1 - p_{12}/p_{11}) \tag{35}$$

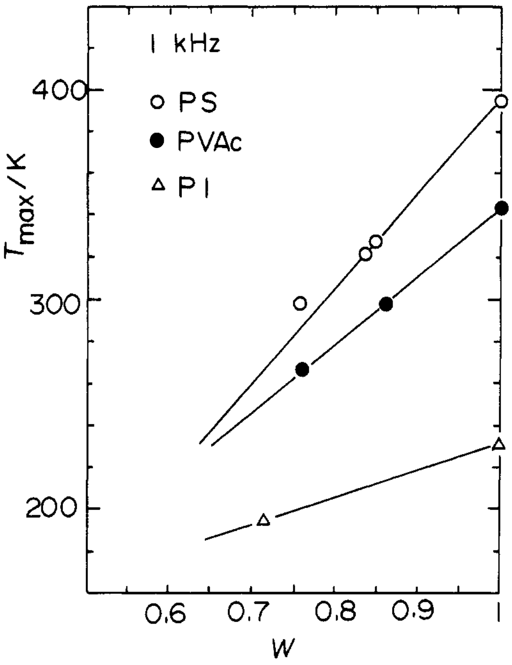

Figure 4. Concentration, w, dependence of the loss maximum temperatures $T_{\max}$ for toluene solutions of polystyrene,[25] poly(vinyl acetate),[26] and polyisoprene.[28] For polystyrene and poly(vinyl acetate) p_{12}'s are assumed to be zero, but for polyisoprene p_{12}/p_{11} is assumed to be 0.52.

where $T_0{}^{\circ}$ denotes the critical temperature in the bulk state and is equal to zTp_{11}. Here we assumed that $z \simeq z - 1$. The relaxation time τ is given by a form similar to eq 13:

$$\log \tau = A + B/[T - CT_0{}^{\circ}(1 - p_{12}/p_{11})] \tag{36}$$

The loss maximum temperature, $T_{\max}$, at a certain fixed frequency f is given by a form:

$$T_{\max} = C(1 - p_{12}/p_{11})T_0{}^{\circ} - B/(A + \log 2\pi f) \tag{37}$$

Figure 4 shows the comparison of eq 37 and the experimental $T_{\max}$ for toluene solutions of polystyrene,[25] poly(vinyl acetate),[26] and polyisoprene.[28] Here we expect that when T_0 of the solvent is much lower than that of the polymer, p_{12}/p_{11} is negligibly small. This is the case for polystyrene and poly(vinyl acetate). As shown in Figure 4, the concentration dependence of $T_{\max}$ of these two polymers can be explained by the gear model. However, for the polyisoprene/toluene system, p_{12} is not negligible since T_0 of polyisoprene is 175 K[28] and that of toluene is 100 K. The latter is estimated from the empirical law proposed by Adam and Gibbs[33] that $T_g/T_0 \simeq 1.3$ where the glass transition temperature T_g of toluene is 131 K.[25] We assumed that p_{12}/p_{11} in this system is an adjustable parameter and is taken to be 0.52.

Concluding Remark

The gear model has been applied to express the temperature dependence of the relaxation time, the correlation function for the dielectric relaxation, and the concentration dependence of the relaxation time for the primary processes of amorphous polymers. It has been found that the model successfully explains these behaviors. However, the present model assumes highly idealized segments in contrast to real ones having very irregular shape. We consider that the units of various crankshaftlike motions correspond to the gears in the present model. Thus, it is needed to estimate the average depth of the teeth and the force constant of the gear from real crankshafts. By extending the present model, we may predict the behavior of the segmental motion in terms of the molecular shape and intermolecular interaction of the segments.

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Scattering by Deformed Swollen Gels: Butterfly Isointensity Patterns

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ABSTRACT: We discuss the case of gels prepared by statistical cross-linking of semidilute solutions. When swollen, such gels should show large-scale inhomogeneities related to the random distribution of tie points. We argue that, under uniaxial stretching, the concentration fluctuations spectra should exhibit an unusual anisotropy, which should be revealed by scattering experiments. We expect the scattering intensity in the direction parallel to the stretching to be stronger than in the perpendicular one.

I. Introduction

Properties of gels are strongly influenced by large-scale heterogeneities in the network structure.[1,2] In the swollen state these imperfections manifest themselves in a nonuniformity of polymer concentration. In practice the heterogeneities may arise for very different reasons. We have analyzed recently how in the case of cross-linking of a polymer solution, the random distribution of tie points may lead to important fluctuations in the local cross-linking density even when the reaction has been stopped far beyond the gel point.[3] These fluctuations, almost undetectable in the reaction bath, are revealed by swelling of the network. As a result the swollen gels should exhibit fractal heterogeneities in polymer concentration. Recent scattering experiments seem to confirm this picture.[4] The purpose of this article is to show the importance of the concentration heterogeneities to the properties of the uniaxially deformed gels. In particular we argue that even a very small uniaxial stretching should lead to an unusual scattering spectrum characterized by an increase of intensity in the direction parallel to the stretching and to isointensity curves of very unusual shape, known as "butterfly patterns".[5] Very recently, Onuki,[11]

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