tative picture should be pursued further by the development of a rigorous mathematical formulation. The outstanding unsolved problem is the derivation of an expression for M, the orientation parameter, in terms of the nature of the chain segment, the temperature, the geometrical constraints, and the applied forces. This derivation must recognize the nonequilibrium cooperative character of the glassy state, and so is a substantial undertaking.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation Polymers Program. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of the research. We thank Dr. C. S. P. Sung for bringing ref 2 to our attention and Dr. John Bendler for bringing ref 16 to our attention. We also thank Dr. Louis Zapas, Dr. A. F. Yee, and Dr. Ted Steger for valuable discussions.

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Kinetics of Free Volume and Physical Aging in Polymer Glasses

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Received January 18, 1984

ABSTRACT: A recently developed molecular kinetic theory, based on the idea that the glass relaxation is a result of the collapse of a series of free volumes having different levels of energies of hole formation, is applied to the phenomenon of physical aging in polymer glasses near the glass transition. Detailed comparisons between the prediction of the theory and a well-known experiment on the volume recovery of poly(vinyl acetate) are made. Defining the relaxation spectrum by a single Williams–Watts parameter β enables us to derive a new expression linking the relaxation of a macrosystem to that of localized state on the basis of scaling concept. This apparent relaxation serves as the basis of kinetic calculations. The favorable comparison between theory and experiment supports the pertinent introduction of β and substantiates our basic physical picture of linking the equilibrium and nonequilibrium behaviors of free volumes to the distribution of hole energies, its mean value, and the reference conditions. The reference free volume fraction is interpreted as the ratio of the mean hole energy and the local activation energy. Functional relationships are presented to show that the structural parameters in Tool's equation should not be constants but a function of β and temperature. The study improves our understanding that the physical aging in polymer glasses is dominated by the nonequilibrium structural dependent part of the relaxation time.

Introduction

The phenomenon of physical aging that occurs in amorphous materials annealed below the glass transition temperature (T_g), and exhibits sensitive and complicated nonequilibrium characteristics, has been extensively investigated in recent years.[1-10] Attributing the volume relaxation in amorphous polymers near the glass transition to free volume collapse, a molecular kinetic theory[1] based on the existence of free volume distribution has been recently developed to provide a coherent interpretation of some recent models. They include the molecular theories advanced by Robertson[3] and Curro, Lagasse, and Simha[4] and the phenomenological model developed by Kovacs and co-workers.[8] The kinetics of free volume are regarded as a series of relaxational processes in the present statistical theory. The departure from equilibrium is treated by a nonequilibrium transition-state theory where the structural contributions to the relaxation times are considered as the result of nonequilibrium fluctuations of the system and are related to the change of entropy.[1] The present theory can readily be extended to include the effects of stress and stress rate[2] and be incorporated in a nonequilibrium criterion[11] for the determination of T_g in a self-consistent manner.

In this paper, a calculation based on the molecular kinetic theory[1] is made and is compared with the well-known data[7] on volume recovery of poly(vinyl acetate). The equilibrium free volume fraction defines the equation of state. The mean energy of hole formation, the reference free volume fraction, and the coefficient of free volume

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expansion are determined from the experimental *PVT* data above T_g. The physical aging processes are then calculated as the departure from the equilibrium described by the molecular kinetic equations. In addition to the equilibrium parameters, the general solution is expressed in terms of a distribution of relaxation times which is characterized by the Williams–Watts[12] parameter, β. After the detailed comparisons between theory and experiment, we will discuss the apparent relaxation time, its activation energy, and its dependence on the deviation from equilibrium in terms of the parameters of the phenomenological models.

Equation of State

Consider a system of n_x polymer molecules and n holes or free volumes where the change of free volume determines the volume relaxation process near the glass transition. Given that the system has hole energy states represented by $\epsilon_1, \epsilon_2, ..., \epsilon_i, ..., \epsilon_L$, the problem reduces to determining the distribution of the ensemble characterized by the set of hole numbers $n_1, n_2, ... n_i, ..., n_L$ with $\sum_i n_i = n$. Consider a lattice model consisting of $N = n + xn_x$ cells where x is the ratio of the volume of a polymer molecule to that of a hole and associate each site with a unit cell of volume v. Minimizing the excess Gibbs free energy due to hole introduction with respect to n_i, the equilibrium free volume distribution is obtained[1]

$$\bar{n}_i = (\bar{N}/c)\exp[-(\epsilon_i + pv)/kT] \qquad (i = 1, ..., L) \quad (1)$$

where $c = \exp(1 - 1/x - S_h/k)$, k is Boltzmann's constant, S_h is the internal entropy associated with a hole, $\bar{N} = \bar{n} + xn_x$, p is pressure, and T is temperature. The ratio of $n_1/N = f_i$ is defined as the ith contribution to the free volume fraction (f) with its equilibrium value

$$\bar{f} = \sum_i \bar{f}_i = \bar{f}_r \exp[-(\bar{\epsilon} + pv)(T^{-1} - T_r^{-1})/k] \quad (2)$$

where $\bar{f}_r$ is the reference free volume fraction at the reference temperature T_r which is usually taken to be the glass transition temperature.

In this paper, where we consider only systems under no external pressure, $p = 0$, and the mean energy of the hole formation is

$$\bar{\epsilon} = \sum_i \epsilon_i \bar{f}_i / \bar{f} \quad (3)$$

which characterizes the intermolecular interaction. The equilibrium total volume ($\bar{V}$) of the system is given by

$$\bar{V} \equiv v\bar{N} = V_r[1 + \alpha_v(T - T_r)]/(1 - \bar{f}) \quad (4)$$

where $V_r = xn_x v_r$, v_r is the volume of a lattice site at T_r, and $\alpha_v = (1/v)(\partial v/\partial T)_p$ is the thermal expansion coefficient for the "occupied" volume. The equilibrium free volume fraction, eq 2, defines the equation of state, eq 4. When experimental V–T data[7] on poly(vinyl acetate) (PVAc) above $T_r = 308$ K at atmospheric pressure are used, eq 2 and 4 give $V_r = 0.817$ cm^3/gm, $\alpha_v = 2.1 \times 10^{-4}$ K^{-1}, $N_A\bar{\epsilon} = 2.51$ kcal/mol, and $\bar{f}_r = 0.0336$, where N_A is Avogadro's number. The slope of V–T data equals $\alpha_v + \alpha_f$ and determines the average coefficient of expansion of the free volume $\alpha_f = 4.7 \times 10^{-4}$ K. A comparison between the present equation of state, eq 4, Simha's theory,[13] and experimental data on PVAc are shown in Figure 1 where the equilibrium free volume fraction is also plotted. Its values below T_r will be used in the later physical aging calculation.

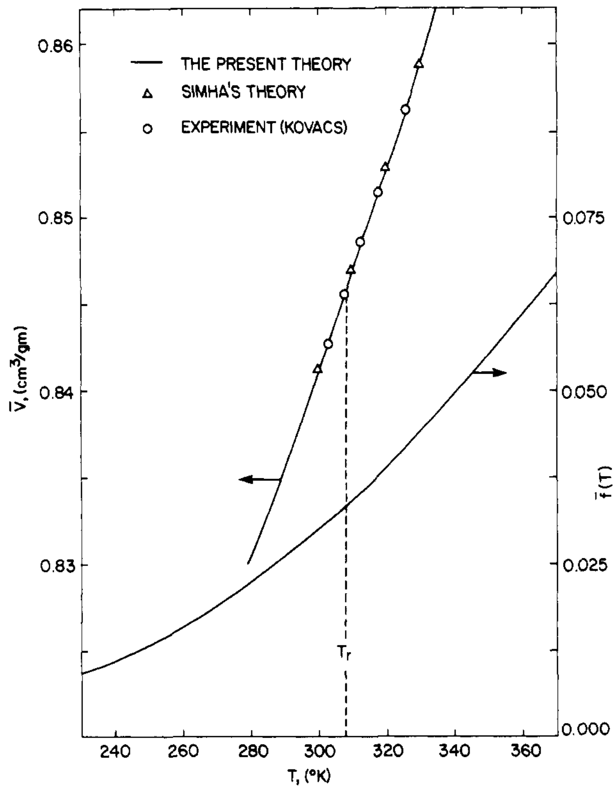

Figure 1. Plots of the equilibrium volume and free volume fraction vs. temperature for PVAc.

Nonequilibrium Equations

The nonequilibrium nature of the glass transition can be described by a nondimensional parameter $\delta = \sum_i \delta_i$, which measures the departure from equilibrium volume of a system. Each individual contribution to the departure from equilibrium is

$$\delta_i(t) = f_i(t) - \bar{f}_i \quad (5)$$

the time-dependent phenomenon is governed by the kinetic equations[1]

$$d\delta_i/dt = -\delta_i/\tau_i - \bar{\alpha}_i q \qquad (i = 1, ..., L) \quad (6)$$

where $q = dT/dt$, the experimental cooling ($q < 0$) or heating ($q > 0$) rate. Here the ith relaxation

$$\tau_i = \tau_{ir}\exp[-\epsilon_a(T - T_r)/kT_r^2 + \delta S/k\bar{N}] \equiv \tau_{ir}\lambda \quad (7)$$

where τ_{ir} is the ith relaxation time at T_r in equilibrium, ϵ_a is the activation energy, δS is the change of entropy related to the nonequilibrium fluctuations of a system, and λ is the shift factor. Using the concept of mean field theory, we have related the entropy change due to molecular fluctuations surrounding the ith local state to the well-known Dolittle equation and have found[1]

$$\epsilon_a/kT_r^2 = B\alpha_f/\bar{f}_r^2 \quad (8)$$

and

$$\delta S/k\bar{N} = -B(f - \bar{f})/\bar{f}_r^2 \quad (9)$$

To the first approximation, $\bar{f}_r \simeq B\bar{\epsilon}/\epsilon_a$ where $\bar{\epsilon}$ determines thermodynamic equilibrium and ϵ_a contributes to the local relaxation in glasses.[1] Instead of having a constant ith contribution to the excess thermal expansion coefficient ($\Delta\alpha_i$) used in the KAHR equations,[8] eq 6 explicitly incorporates a temperature-dependent thermal expansion coefficient ($\bar{\alpha}_i$) calculated from the equilibrium free volume distribution

$$\bar{\alpha}_i = (\partial\bar{f}_i/\partial T)_p = (\epsilon_i + pv)\bar{f}_i/kT^2 \quad (10)$$

and $\bar{\alpha} = \sum_i \bar{\alpha}_i = (\partial\bar{f}/\partial T)_p$ which is a slowly increasing function of temperature.

Introducing the normalized relaxation function

$$\varphi(t) = \sum_{i=1}^{L} g_i \exp(-t/\tau_{ir}\lambda) \tag{11}$$

and using eq 10, we obtain

$$g_i = \bar{\alpha}_i/\bar{\alpha} = \epsilon_i\bar{f}_i/\bar{\epsilon}\bar{f} \tag{12}$$

with

$$\sum_{i=1}^{L} g_i = 1$$

The probability of finding a state in a given energy level ϵ_i is $\bar{f}_i/\bar{f}$, and g_i can be interpreted as the statistical distribution of the hole energy at a given state. When a system is quenched from equilibrium, the general solution of eq 6 is[10]

$$\delta(t) = -\int_0^t \bar{\alpha} q \varphi(t,t')\, \mathrm{d}t' \tag{13}$$

In the case of volume recovery during isothermal annealing followed by quenching from a equilibrium temperature T_0 to T (i.e., $|q_0| \rightarrow \infty$ and $q_1 = 0$), eq 13 becomes

$$\delta(t) = -\varphi(t) \int_{T_0}^{T} \bar{\alpha}(T')\, \mathrm{d}T' = \varphi(t)[\bar{f}(T_0) - \bar{f}(T)] \tag{14}$$

For simplicity and self-consistency, we assume that the relaxation function follows the Williams–Watts function

$$\varphi(t) = \exp[-(t/\tau)^{\beta}] \tag{15}$$

where $0 < \beta \leq 1$ is a measure of the width of the distribution of relaxation times.[10] Our attempt at deriving eq 15 will be given elsewhere.[14] The apparent relaxation time of the whole system is

$$\tau = \tau_r a \tag{16}$$

where τ_r is the reference relaxation time and a is the apparent shift factor. The Laplace inversion[15] of the Williams–Watts function is $g(\tau)$ which has been shown[10] to be the continuous representation of g_i. The associated distribution of relaxation times[10] $G(\tau) = g(\tau)/\tau$ is plotted in Figure 2 and is characterized by a single parameter β. In order to satisfy eq 12 and 15 and Figure 2 simultaneously, β has to be a constant because the distribution of the hole energies is fixed for a given system. This will be verified experimentally in conjunction with the following analysis of linking the relaxation of a macrosystem to that of localized state.

The isothermal response has also been analyzed in terms of an effective relaxation time (τ_{eff}). From eq 14–16, one obtains

$$\tau^{-1}{}_{\mathrm{eff}} = -\mathrm{d} \ln \delta/\mathrm{d}t = \beta t^{\beta-1}/\tau_r{}^{\beta} a^{\beta} \tag{17}$$

Following eq 11, an alternative expression for the effective relaxation time can be written

$$\tau^{-1}{}_{\mathrm{eff}} = (1/\lambda)\sum_{i=1}^{L}(g_i/\tau_{ir}) \exp\{-a^{-\beta}[(a^{\beta}/\lambda)(t/\tau_{ir}) - (t/\tau_r)^{\beta}]\} \tag{18}$$

Applying a scaling argument[16,17] to eq 17 and 18, we find

$$a \sim \lambda^{1/\beta} \tag{19}$$

From eq 7–9, 16, and 19, the apparent relaxation time can be written more explicitly as

$$\tau = \tau_r \exp\{-B[\alpha_f(T - T_r) + \delta(t)]/\beta\bar{f}_r{}^2\} \tag{20}$$

and $B = 1$ will be assumed.[18] Equation 20 provides a new relationship between the relaxation in glasses, which is a highly cooperative process, and the material parameters related to the free volume fractions and distributions.

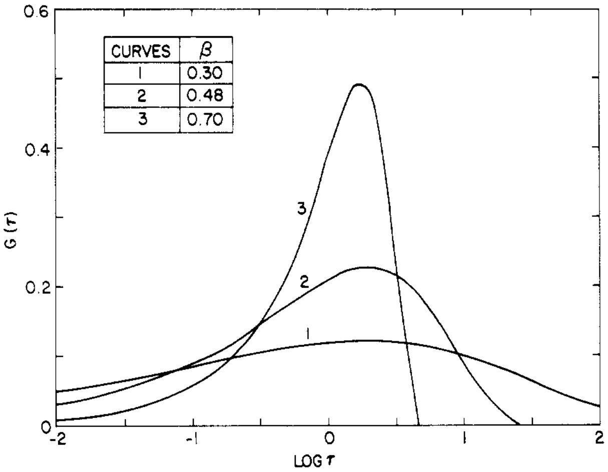

Figure 2. Distribution of relaxation times as a function of β. $\beta = 0.48$ is for PVAc.

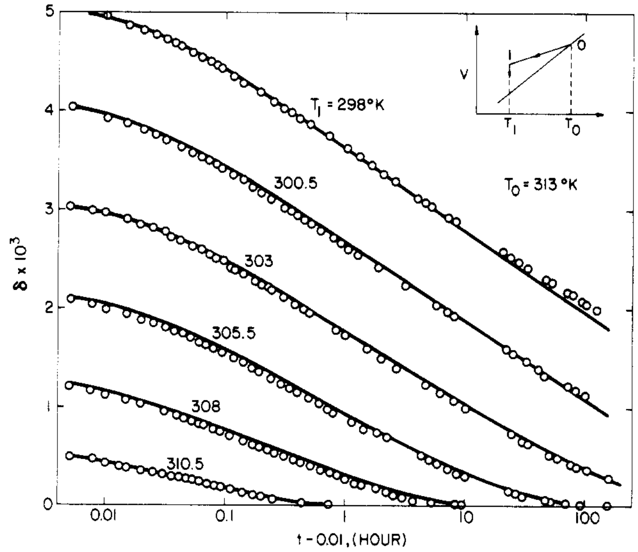

Figure 3. Comparison of isothermal annealing calculated from the present theory (curves) and measured[7] (circles) for PVAc quenched from T_0 to various T_1.

Experimental Comparison

Theoretical calculation of physical aging based on the equations presented in the last section will be put in detailed comparisons with the well-known experiment[7] on volume recovery of PVAc. In all the figures throughout the comparison between theory and experiment, the circles are Kovacs' data points and the solid curves represent the theoretical calculation using the input parameters:

$$\begin{aligned} &N_A\bar{\epsilon} = 2.51 \text{ kcal/mol} \qquad \bar{f}_r = 0.0336 \\ &\alpha_f = 4.7 \times 10^{-4}\ \mathrm{K}^{-1} \qquad \beta = 0.48 \qquad \tau_r = 25 \text{ min} \end{aligned} \tag{21}$$

The first three equilibrium parameters ($\bar{\epsilon}$, $\bar{f}_r$, α_f) have been determined earlier from the PVT data with $T_r = 308$ K. The remaining two parameters (β, τ_r) characterize the distribution of relaxation times.

A. Isothermal Annealing. The isothermal volume recovery of glass forming polymers following a single temperature jump from equilibrium can be calculated from eq 2, 14, 15, and 20. Figure 3 compares the calculated and measured variation of volume contraction for PVAc following quenches from equilibrium at $T_0 = 313$ K to several different annealing temperature (T_1) ranging from 298 to 310.5 K. The parameters $\beta = 0.48$ and $\tau_r = 25$ min were adopted to fix experimental data. The corresponding

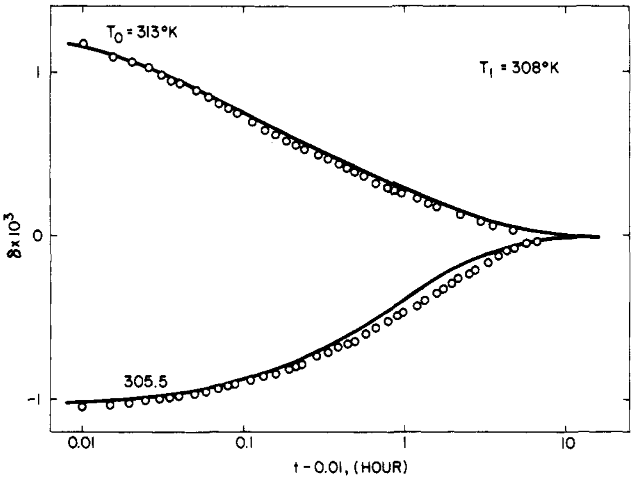

Figure 4. Isothermal approach of PVAc toward equilibrium by contraction and expansion. The curves are calculated and the circles are Kovacs' data.

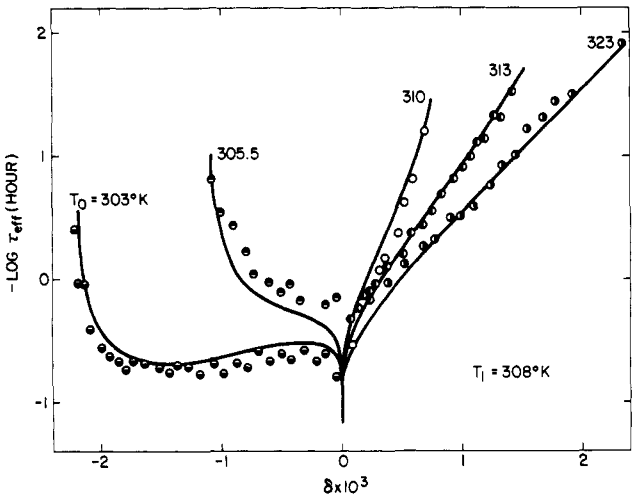

Figure 5. Comparison of log τ_{eff} vs. δ of PVAc predicted (curves) by eq 22 and measured (circles) by Kovacs.

distribution of relaxation times was plotted in Figure 2. Figure 3 also reveals that β is independent of temperature and its value is within the range (0.43–0.52) of what has been found from dielectric experiments.[19] The difference between the contraction and expansion isotherms quenched and rapid reheated, respectively, from different initial equilibrium temperatures T_0 to T_1 is shown in Figure 4.

B. Effective Relaxation Time. τ_{eff} plots contain all the salient features including nonlinear and asymmetric characteristics of volume recovery in polymer glasses and are severe tests for any theoretical treatment.[7] From eq 14, 15, and 17, we obtain

$$\log \tau_{\text{eff}} = \log (\tau/\beta) + [(1-\beta)/\beta] \log [-\ln \varphi(t)] \qquad (22)$$

A comparison of eq 22 and experimental data in terms of log τ_{eff} and δ is shown in Figure 5. There are five different initial temperatures (T_0) with a common annealing temperature $T_1 = 308$ K. Curves and data at $T_0 = 305.5$ and 313 K are related to those corresponding δ vs. log ($t - 0.01$) plots in Figure 4 by the definition $\tau_{\text{eff}}^{-1} = -\text{d} \ln \delta/\text{d}t$. The asymmetry in approaching equilibrium from $\delta > 0$ and $\delta < 0$ is known as one of the most characteristic features of the structural relaxation in polymer glasses.

C. Memory Effects. The memory effect is associated with two consecutive temperature jumps. The thermal history of the system involves quenching ($0 \rightarrow 1$), annealing ($1 \rightarrow 2$), and rapid reheating ($2 \rightarrow 3$), i.e., $q_0 \rightarrow -\infty$, $q_1 = 0$, and $q_2 \rightarrow \infty$. The volume recovery is calculated as a function of the elapsed time $t - t_3$ from eq 13 as

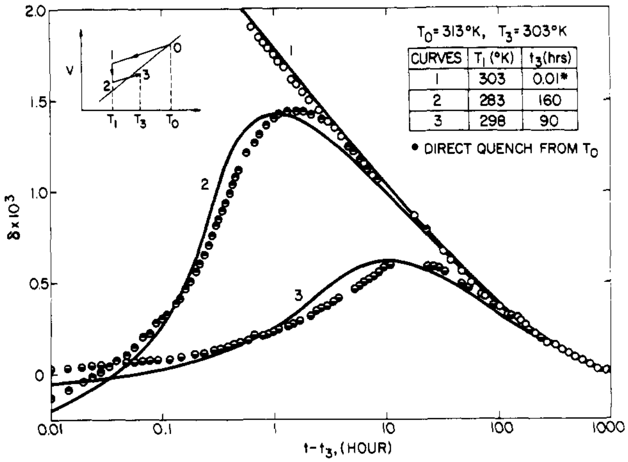

Figure 6. Comparison of memory effects predicted (curves) by eq 23 and measured[7] (circles) for PVAc.

$$\delta(t) = -\int_0^{t_1} \bar{\alpha} q_0 \varphi(t,t')\,\text{d}t' - \int_{t_2}^{t_3} \bar{\alpha} q_2 \varphi(t,t')\,\text{d}t' = [\bar{f}(T_0) - \bar{f}(T_1)]\varphi_1(t) - [\bar{f}(T_3) - \bar{f}(T_1)]\varphi_3(t) \qquad \text{for } t > t_3 \qquad (23)$$

where

$$\varphi_1(t) = \exp\{-[(-\ln \varphi(t_2 - t_1))^{1/\beta} + (t - t_3)/\tau(T_3,\delta)]^{\beta}\}$$

and

$$\varphi_3(t) = \exp\{-[(t - t_3)/\tau(T_3,\delta)]^{\beta}\}$$

We again use the parameters given by eq 21 to obtain the comparison shown in Figure 6 between the theoretical and experimental behavior. This plot is a much more severe test of the theory than the situation of a single temperature jump. Curve 1, the intrinsic isotherm obtained by direct quenching from $T_0 = 313$ K to $T_1 = 303$ K, has already been shown in Figure 3.

Apparent Relaxation Time

The temperature and structural dependence of the apparent relaxation time is usually written in accordance to the modified Tool equation:[20]

$$\tau = \tau_r \exp[-\theta(T - T_r)] \exp[-\theta(1 - X)(T_f - T)] \qquad (24)$$

where θ and X are structural parameters, and T_f is the fictive temperature. Equation 24 with constant θ and X has been used in all phenomenological models.[8-10] Comparing the above equation with eq 20 and 14, one can write

$$\theta = B\alpha_f/\beta \bar{f}_r^{\,2} \qquad (25)$$

and

$$X = 1 - [\bar{f}(T_0) - \bar{f}(T)]/\alpha_f(T_0 - T) \qquad (26)$$

This reveals that θ depends not only on the equilibrium parameters but also on the width of relaxation spectrum, and X is a decreasing function of annealing temperature. When $T_0 - T$ is getting smaller, eq 26 reduces to[1]

$$X = 1 - \bar{\epsilon}\bar{f}/\alpha_f k T^2 \qquad (27)$$

Substituting eq 21 into eq 8, 25, and 26, we also obtain

$$N_A\epsilon_a = 78.4 \text{ kcal/mol} \qquad \theta = 0.867 \text{ K}^{-1}$$
$$X(T_0 = 313 \text{ K}, T = 283 \text{ K}) = 0.113 \qquad (28)$$

which show that PVAc is a highly structural dependent nonlinear material.

Conclusion

The idea of free volume has been applied before[3-6] as the basis of the microscopic interpretation of relaxation in glasses. However, none of these theories has demonstrated the ability of predicting a variety of thermal histories over a broad time and temperature range without changing the input structural parameters. The search for quantitative prediction has been the focus of recent intensive investigations.[21] We have achieved for the first time a favorable comparison between the present molecular kinetic theory near the glass transition and experimental data on the isothermal annealing, τ_{eff}, and memory effects for PVAc. All the kinetic phenomena were calculated from the same set of five input parameters, eq 21.

The study reveals that the physical aging of PVAc is dominated by the nonequilibrium structure-dependent part of relaxation times and, in contrast to recent reports in the literature,[21] that the distribution of relaxation time is actually independent of temperature. This is consistent with eq 12 and Figure 2 which relate the distribution of relaxation times to the fixed distribution of hole energies of a given system. Therefore, it supports the idea of representing the relaxation spectrum by a single parameter β. Through detailed comparison between theory and experiment, the new equation for the apparent relaxation time, eq 20, and our basic physical picture of relating the glass relaxation to the mean energy of hole formation, its statistical distribution, and the reference conditions have received experimental verification.

There is a subtle difference between the KAHR equations and our molecular kinetic equations, eq 6, which explicitly incorporate temperature-dependent thermal expansion coefficients ($\bar{\alpha}_i$). The present study reveals that the structural parameters (θ, X) of Tool's equation should not be constants but a function of β or temperature. These may explain why the phenomenological models had difficulty[10,22] of predicting several experiments by one set of structural parameters.

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Osmotic Compressibility Measurements on Semidilute Polystyrene–Cyclohexane Solutions

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Received June 28, 1983

ABSTRACT: The thermodynamic properties of semidilute solutions of polystyrene of molecular weight ranging from 4.22×10^5 to 20.6×10^6 in cyclohexane are studied as a function of concentration ($2 \times 10^{-2} \lesssim C$ (g/cm^3) $\lesssim 0.1$) and temperature ($\Theta \leq T < 65$ °C) by intensity light scattering. The corresponding scaling laws for the inverse of the osmotic compressibility $\partial\pi/\partial C$ are verified.

1. Introduction

Using general concepts of scaling theory,[1,2] theoreticians and experimentalists have studied the thermodynamic properties and conformation of polymer chains in solution (see, e.g., ref 3–5). The results have led to the construction of the universal temperature–concentration diagram.[5] In this paper, we will be interested in a part of this diagram, namely, the semidilute Θ solutions and the transition from Θ to good solvent system. With respect to concentration, polymer solutions are classified as dilute or semidilute, the crossover between both regimes being located at the overlap concentration:[1,2]

$$C_{\mathrm{T}}^* \simeq M R_{\mathrm{G}}^{-3}(T) \sim M^{1-3\nu} \qquad (1)$$

R_{G}, the radius of gyration of a single coil, is linked to the molecular weight of the polymer M by the relation $R_{\mathrm{G}} \sim M^{\nu}$. At the Θ temperature ($\nu = {}^1/_2$) we have

$$C_{\Theta}^* \sim M^{-1/2} \qquad (2)$$

In the semidilute regime, the diagram is divided into good solvent and Θ regions, with the boundary[5] located at $\tau^{**} \sim C$, where τ is the reduced temperature ($\tau = (T - \Theta)/\Theta$, $\tau > 0$).

The thermodynamic state of the system is characterized by the osmotic pressure π. Two predictions of the scaling theory for good solvent semidilute solutions have already been confirmed:[6,7] (a) π is independent of molecular weight and (b) π scales as $\pi \sim C^{2.32}$.

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0024-9297/84/2217-2340$01.50/0