Numerical Calculation of the Relaxation Spectrum from the Correlation Function†

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It has been shown that the distribution of relaxation times, H(lnτ), in semi-logarithmic time scale can easily be calculated numerically from the derivative of the relaxation function in semilogarithmic scale. In that, ln τ, the abscissa, is divided into N different segments of equal size, then H is considered to be a linear function of ln τ within each segment. The technique has been applied to a Williams-Watts function as well as to the relaxation function obtained by photon correlation spectroscopy from atactic polystyrene glass. It has been demonstrated that the relaxation functions can be precisely reproduced from the calculated distribution functions.

Introduction

Recent development in light scattering technique has made it possible to investigate the relaxational behavior of amorphous polymers.[1-6] The result of a light scattering experiment is usually obtained in the form of the correlation function which can be expressed in terms of the relaxation function.[1,2] However it has always been the most tricky problem how to extract the relaxation spectrum, *i.e.* the distribution of the relaxation times, from the relaxation function. There are many equations suggested for expressing the approximate distribution of the relaxation times.[7-16] Some of these equations work better on relaxation functions with narrow spectrum and others work better on relaxation functions with broad spectrum. There are also some numerical methods proposed.[17] Most of the numerical methods are too complicated to be used practically. In this paper, using linear regession analysis technique, a new method for numerical calculation of the relaxation spectrum from the relaxation function is proposed.

Theoretical

The distribution of relaxation times, or the relaxation spectrum, in semi-logarithmic scale can be expressed in the following form[8]:

$$G(t) = G_e + \int_{-\infty}^{\infty} H(\ln \tau)\ \exp(-t/\tau)\ d\ln\tau \tag{1}$$

where G(t) is the relaxation function, G_e is the equilibrium value of G(t), H(ln τ) is the distribution function of the relaxation times, τ is the relaxation time, and t is the time. According to Andrews[12], the approximate distribution function can be obtained by computing the derivative of the relaxation function:

$$H(\ln \tau) = -\left.\frac{dG(t)}{d\ln t}\right)_{t=\tau} \tag{2}$$

The common shapes of G(t) and H(ln τ) are shown in Figure 1. By differentiating eq (1) with respect to ln t, one can obtain the following:

$$D(t) = -\frac{dG(t)}{d\ln t} \tag{3}$$

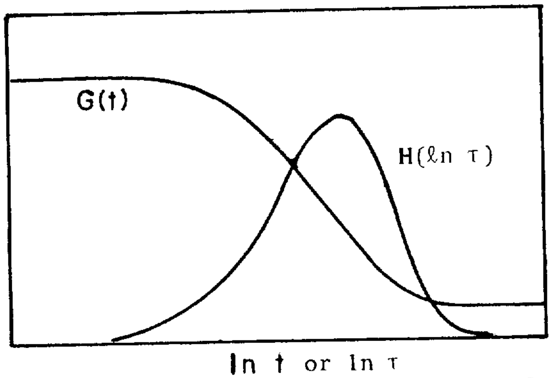

Figure 1. Common shapes of the relaxation function G(t) (see eq.(1)) and the distribution function H(ln τ).

$$= -\frac{dG(t)}{dt} \cdot \frac{dt}{d\ln t} \tag{4}$$

$$\left.\begin{aligned} &= \int_{-\infty}^{\infty} \left(\frac{t}{\tau}\right) H\ e^{-t/\tau}\, d\ln\tau \\ &= \int_{-\infty}^{\infty} H\ f(x,t)\, dx \end{aligned}\right\} \tag{5}$$

where

$$x = \ln\tau,$$

and

$$f(x,t) = \frac{t}{\tau} e^{-t/\tau}$$

One can expect that it would be easier to extract the distribution function from the derivative, D(t), rather than directly from the relaxation function. Since D(t) already has approximately the same shape as the distribution function, it should be more sensitive to the change of the distribution than the relaxation function is.

The numerical values of H can be calculated by fitting eq. (5) to the experimental values of D(t). One way of doing it is to divide $x(=\ln\tau)$, the abscissa, into N different segments of equal size and assume that H varies linearly within each segment as shown in Figure 2. Thus,

$$\begin{aligned} D(t) &= \sum_{j=1}^{N} \int_{x_j}^{x_{j+1}} [H_j + \frac{H_{j+1}-H_j}{\Delta x}(x-x_j))] f(x,t)\,dx \\ &= \sum_{j=1}^{N} [H_j - \frac{H_{j+1}-H_j}{\Delta x} x_j] F_j(t) + \sum_{j=1}^{N} [\frac{H_{j+1}-H_j}{\Delta x}] I_j(t) \end{aligned} \tag{6}$$

where

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† On the occasion of 60th birthday of Professor Nung Min Yoon to honor his distinguished work and devotion in organic chemistry and in education.

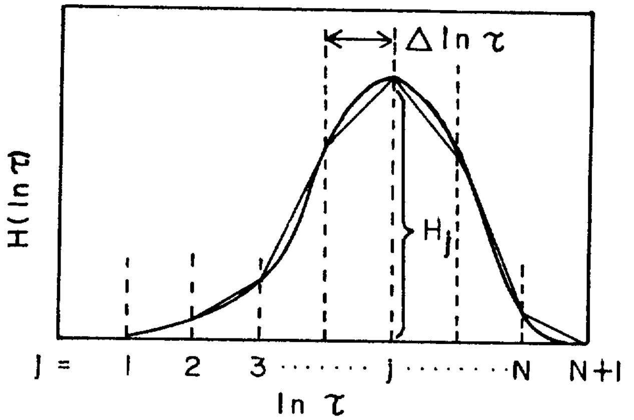

Figure 2. The distribution function of the relaxation times, $H(\ln \tau)$. The abscissa, $x = \ln \tau$, is divided into N segments of equal size, $\Delta x = \Delta \ln \tau$, and H is assumed to vary linearly within each segment.

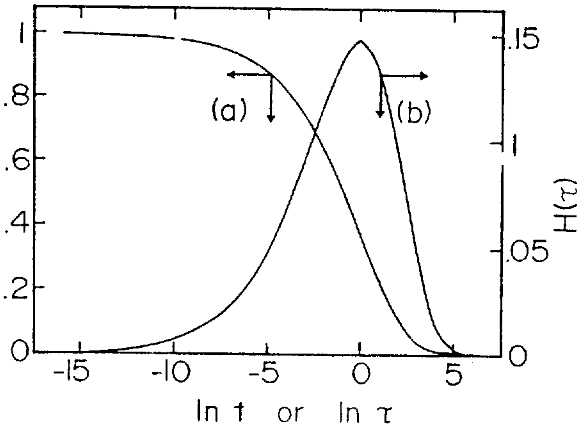

Figure 3. (a) Williams-Watts function. (b) The shape of the distribution function calculated from the Williams-Water function.

$$F_j(t) = \int_{x_j}^{x_{j+1}} f(x, t)\,dx, \tag{7}$$

$$I_j(t) = \int_{x_j}^{x_{j+1}} x\, f(x, t)\,dx, \tag{8}$$

Δx is the width of each segment of x, x_j is the lower boundary of the j-th segment of x, and H_j is the magnitude of the distribution function at $x = x_j$. In equation (6) it is assumed that the distribution function H(x) has a finite width and the magnigude is significant only in the region of $x_1 < x < x_{N+1}$. By rearranging eq. (6) the following expression can be obtained casily.

$$\begin{aligned} D(t) &= H_1 \{F_1(t) + \frac{1}{\Delta x} x_1 F_1(t) - \frac{1}{\Delta x} x_1 F_1(t) - \frac{1}{\Delta x} I_j(t)\} \\ &+ \sum_{i=2}^{N} H_j \{F_j(t) + \frac{1}{\Delta x}[x_j F_j(t) - x_{j-1} F_{j-1}(t)] \\ &- \frac{1}{\Delta x}[I_j(t) - I_{j-1}(t)]\} + H_{N+1}\{ - \frac{1}{\Delta x} X_N F_N(t) + \frac{1}{\Delta x} I_N(t)\} \end{aligned} \tag{9}$$

The relaxation function, G(t) is determined experimentally. The approximate values of D(t) can be obtained from G(t) by means of eq. (3), *i.e.*,

$$D(t) \cong -\frac{\Delta G(t)}{\Delta (\ln t)} \tag{10}$$

$F_j(t)$'s and $I_j(t)$'s are evaluated by means of equations (7) and (8). Therefore, H_j's are the only unknowns to be determined in eq. (9). Since D(t) is a linear function of H_j's, linear regression technique can be applied to determine the magnitude of H_j's. For this calculation a computer program has been written in APL (a program language).

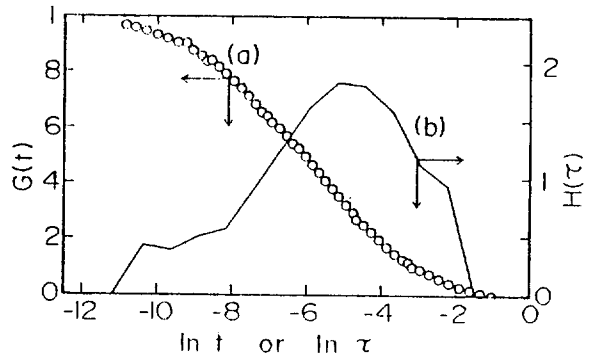

Figure 4. (a) The relaxation function of atactic polystyrene at 97°C (quoted from ref. 5) (b) The distribution function calculated from the experimental relaxation function of (a).

Results and Discussion

The common shape of relaxation functions of polymers with a broad distribution of relaxation times may be expressed by the empirical equation of Williams and Watts[8],

$$\phi(t) = \phi(0)\, e^{-(\frac{t}{\tau_0})^{\beta}} \qquad (0 < \beta \leq 1) \tag{11}$$

where τ_0 is the characteristic relaxation time, $\phi(o)$ is the relaxation amplitude, and β is a constant which determines the width of the distribution of the relaxation times. The technique has been tested on a Williams-Watts function as shown in Figure 3. The shape of G(t) in Figure 3(a) is the Williams-Watts function, and the shape of the distribution function calculated from the Williams-Watts function is shown in Figure 3(b). In order to obtain the distribution function in Figure 3(b), the range of ln τ axis from (ln τ_0–16) to (ln τ_0+7) has been devided into 20 segments, and the linear regression technique has been applied to find H_j's of eq. (9). It is appreciated that the 20-segment-fit gives so smooth a curve that one can hardly recognize the discontinuity at the boundaries between the segments. When the relaxation function is regenerated from the calculated H_j's, it overlaps precisely on the curve in Figure 3(a).

The technique has also been applied to a real polymer system. The relaxation function of atactic polystyrene shown in Figure 4(a) is quoted from Lee *et al*'s work[5] in which photon correlation spectroscopy was used. The distribution function, H(ln τ), calculated from the relaxation function is shown in Figure 4(b). In this calculation the range of ln τ axis from –11.2 to 0 has been divided into 14 segments and linear regression technique has been applied to obtain H_j's in eq. (9). It is interesting to note that the distribution function has a small shoulder on the left end of the curve. This is due to the fast relaxational process which is discussed in Lee *et al*'s original work[5]. The relaxation function regenerated from the calculated values of H_j's overlaps precisely on top of the experimental relaxation function.

This technique is very similar to the histogram method developed by Chu *et al*[19] for the calculation of the distribution of the diffusion coefficients. The main difference of this technique from Chu *et al*'s is in the idea that the distribution function H be calculated from the derivative of the relaxation function, *i.e.* from eq. (3), but not from eq. (1). It should be pointed out that this technique, just like the histogram method of Chu *et al*[19], can also be applied to the calculation of the distribution of the diffusion coefficients in solution.

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Kinetic Studies on Bromine-Exchange Reactions of Antimony Tribromide with α-Phenyl-n-butyl and α-Phenyl-i-butyl Bromides in Nitrobenzene†

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The rate of bromine-exchange reaction between antimony tribromide and α-phenyl-n-butyl bromide in nitrobenzene has been determined, using antimony tribromide labelled with Br-82. The results indicate that the exchange reaction follows the first-order kinetics with respect to the organic bromide, and either the second- or first-order kinetics with respect to antimony tribromide depending on its concentration. The third-order rate constant obtained was 7.50×10^{-2} $l^2mol^{-2}s^{-1}$ at 28°C. Similar study on the bromine-exchange reaction between antimony tribromide and α-phenyl-i-butyl bromide has also been carried out. The results of the study show the same kinetic orders as the ones observed with α-phenyl-n-butyl bromide. The third-order rate constant observed was 2.40×10^{-2} $l^2mol^{-2}s^{-1}$ at 28°C. The activation energy, the enthalpy of activation and the entropy of activation for the two exchange reactions mentioned above have been determined. The reaction mechanisms for the exchange reactions are discussed.

Introduction

In the previous papers of this series,[1-6] we reported the results of kinetic studies on the bromine-exchange reactions between gallium bromide and alkyl bromides in nitrobenzene. The alkyl bromides(RBr) examined were methyl, ethyl, n-propyl, i-propyl, n-butyl and i-butyl bromides. From the results of these studies, it was concluded that all the bromine-exchange reactions followed the second-order kinetics with respect to gallium bromide and the first-order kinetics with respect to the alkyl bromides examined.

$$\text{Rate} = k_3[GaBr_3]^2[RBr]$$

It was assumed that the exchange reactions between gallium bromide and the alkyl bromides took place through the following reaction schemes (S denotes the solvent molecule):

$$S + Ga_2Br_6 \rightleftharpoons S\colon Ga_2Br_6$$

$$S + S\colon Ga_2Br_6 \rightleftharpoons 2\ S\colon GaBr_3$$

$$RBr + S\colon GaBr_3 \rightleftharpoons R^{\sigma+}Br^{\sigma-}\colon GaBr_3 + S$$

$$R^{\sigma+}Br^{\sigma-}\colon GaBr_3 + S\colon GaBr_3 \xrightarrow{\text{slow}} R^+Ga_2Br_7^- + S$$

$$S + R^+Ga_2Br_7^- \rightleftharpoons RBr + S\colon Ga_2Br_6$$

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