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Damping Function of the Shear Relaxation Modulus and the Chain Retraction Process of Entangled Polymers

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ABSTRACT: The shear relaxation modulus, $G(t,\gamma)$, of entangled polymers decreases with increasing magnitude of shear, γ. A damping function defined as $h(t,\gamma) = G(t,\gamma)/G(t,0)$ decreases with time and approaches a finite value, $h(\gamma)$, at long times. In the tube model theory, the relaxation of $G(t,0)$ is attributed to the reptation process and that of $h(t,\gamma)$ is attributed to the retraction along the tube of a chain extended according to the large deformation of the material. We examine, in view of experimental results, an expression $h(t,\gamma)/h(\gamma) = [1 + A(t,\gamma)]^2$ derived from a theory of Doi. Here, $1 + A(t,\gamma)$ is an average elongation ratio of a chain contour in the tube. At γ less than about 7, the function $A(t,\gamma)$ was factorizable into functions of t and γ, respectively: the reptation process and the retraction process are not coupled in this case. At higher strains, $A(t,\gamma)$ is not factorizable and is dominated by modes of shorter relaxation times. Possibly the limited extensibility of chain portions of the order of the entanglement spacing changes the nature of the tube at large deformations. For branched polymers, the fast relaxation modes become dominant even at $\gamma = 5$. This may be in accord with the well-established theory for branched polymers that stress relaxation at vanishing γ requires the retraction of the chain end along the contour of the chain. This process is essentially the same as the retraction process at large strain, and these two relaxation processes cannot occur independently of each other.

Introduction

The shear relaxation modulus of entangled polymers decreases with increasing magnitude of shear, γ. In the tube model theory of Doi and Edwards, the effect of finite strain is attributed to the retraction along the tube of a chain extended in the large deformation.[1,2] To investigate the process of retraction in detail, we define a damping function, $h(t,\gamma)$, as the ratio of the relaxation modulus at finite strain, $G(t,\gamma)$, to that at the limit of zero strain, $G(t)$. The definition is an extension of the traditional damping function defined as the limiting value at long times, $h(\gamma) = h(\infty,\gamma)$.

The characteristic features of the function $h(t,\gamma)$ exhibited in the few reports[3−8] available are as follows. At a fixed time, it decreases with increasing γ. At a fixed value of γ, it is close to 1 at short times, decreases with time, and levels off at a certain time, τ_k. The limiting value, $h(\gamma)$, is a common function for various polymers and is in accord with the value derived from the concept of retraction in the tube model theory. The time τ_k is independent of γ for melts and solutions of polymers with sharp molecular weight distribution. It is found to be proportional to the square of the molecular weight, M, for semidilute solutions of polystyrene and poly(α-methyl styrene) and is believed to be related to the conformational relaxation time in the tube of the chain regarded as a Rouse model.[9] The function $h(t,\gamma)$, if plotted against a reduced time t/τ_k, is independent of the molecular weight or concentration for semidilute solutions of polystyrene and poly(α-methyl styrene). This result is reproduced in Figure 1. The dashed curves represent the results for solutions of four-armed star-branched polystyrenes. As in the case of linear polymers, the curves for several solutions of the branched polymers overlap to form the dashed curves on the reduced time scale t/τ_k. It may be noted that $h(t,\gamma)$ as a function of t/τ_k varies with the geometry of the polymer chain.

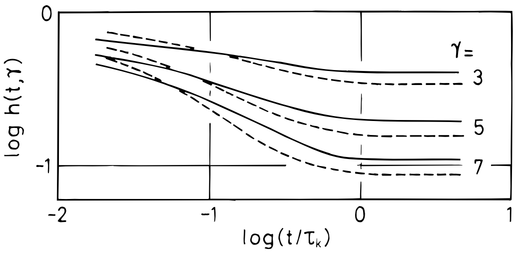

Figure 1. Damping function $h(t,\gamma)$ for semidilute solutions of linear (solid lines) and star-branched (dashed lines) polystyrenes. γ = 3, 5, and 7, from top to bottom.

Doi investigated the time variation of the function $h(t,\gamma)$ on the basis of a tube model with the independent alignment assumption and derived an expression,[10]

$$h(t,\gamma)/h(\gamma) = \langle[1 + \langle A_n(t,\gamma)\rangle_e]^2\rangle_n \tag{1a}$$

$$= \sum\nolimits_{\mathrm{p:odd}}(8/\pi^2p^2) \times [1 + a(\gamma)\exp(-tp^2/\tau_{eq})]^2 \tag{1b}$$

Here, the quantity inside the square brackets in the first line is the extension ratio of the chain contour length at the nth tube segment of a chain, and the function $A_n(t,\gamma)$ represents the excess extension ratio. The set of brackets with subscript e implies the ensemble average, and that with subscript n implies the average over n. The quantity τ_{eq} represents the conformational relaxation time of the chain, modeled as a Rouse chain allowed to move along the tube. The quantity $a(\gamma)$ is equal to the value of A_n at $t = 0$, which is assumed to be the value corresponding to the affine deformation of each part of the chain contour.

$$\begin{aligned} A_n(0,\gamma) &= [h(\gamma)]^{-1/2} - 1 \\ &= a(\gamma) \end{aligned} \tag{2}$$

Takahashi et al. proposed that the Doi equation is approximated by the following equation at long times:[8]

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$$h(t,\gamma)/h(\gamma) = [1 + a(\gamma)\exp(-t/\tau_{\mathrm{eq}})]^2 \qquad (3)$$

They examined the $h(t,\gamma)$ for a polystyrene melt and observed that the τ_{eq} thus evaluated from $h(t,\gamma)$ was independent of γ and was about $\tau_{\mathrm{k}}/4$. This result seems to offer some justification for the expression of eq 1. The factor $a(\gamma)$ determined from eq 3 was about 45% of the value determined from $h(\gamma)$ by eq 2. Thus, the theory is not in quantitative agreement with the observations, and the deviation is not due to the omission of higher order terms in deriving eq 3.

The goal of this study is to examine the chain retraction mechanism proposed by Doi, which is designed to account for the absence of time-strain factorizability that is typically observed in the shear relaxation modulus at early times, and which is not predicted by the original Doi−Edwards model.

Method

We wish to compare eq 1 with published experimental data. One can derive a good approximation to eq 1, more precise than eq 3, at long times by assuming that $\exp(-tp^2/\tau_{\mathrm{eq}}) = 0$ for p larger than 3:

$$h(t,\gamma)/h(\gamma) = 1 - (8/\pi^2) + (8/\pi^2)[1 + a(\gamma)\exp(-t/\tau_{\mathrm{eq}})]^2 \qquad (4)$$

The quantities $a(\gamma)$ and τ_{eq} can be estimated from data for $h(t,\gamma)/h(\gamma)$ by a semilogarithmic plot of $[(\pi^2/8)h(t,\gamma)/h(\gamma) + 1 - (\pi^2/8)]^{1/2} - 1$ vs t. As is shown later, the $a(\gamma)$ value thus obtained is about 55% of the theoretical value of eq 2. This value is to be compared with the value 45%, obtained with eq 3. Thus, the discrepancy between theory and experiment decreases only slightly with an improved approximation to eq 1.

Since we cannot expect complete agreement as mentioned above, we employ the following equation to examine the overall features of $h(t,\gamma)$:

$$h(t,\gamma)/h(\gamma) = [1 + A(t,\gamma)]^2 \qquad (5)$$

Equation 5 may be regarded as an approximation (i.e., a preaveraging approximation) of eq 1, and the quantity $1 + A(t,\gamma)$ may be regarded as a certain average of the extension ratio of the chain contour. The quantity $A(t,\gamma)$ will be extracted from the data of $h(t,\gamma)$ and its properties investigated.

A reduced function, $B(t,\gamma)$, is defined as follows:

$$\begin{aligned} B(t,\gamma) &= A(t,\gamma)/A(0,\gamma) \\ &= A(t,\gamma)/\{[h(\gamma)]^{-1/2} - 1\} \qquad (6) \end{aligned}$$

This function will be independent of γ if the function $A(t,\gamma)$ is factorizable into functions of t and γ, respectively.

For the present purpose, we looked for published data of $h(t,\gamma)$ taken over a sufficiently wide range of time for polymers with sharp molecular weight distributions. Such data are scarce in spite of a large amount of data for the damping function at long times.[2] The available data under these conditions are as follows: (A) 20% polystyrene solution in Aroclor,[3] $M_{\mathrm{w}} = 1.8 \times 10^6$, 30 °C, highest $\gamma = 25.6$; (B) 8% polystyrene solution in Aroclor,[4] $M_{\mathrm{w}} = 3.0 \times 10^6$, 30 °C, highest $\gamma = 31$; (C) 32% polystyrene solution in Aroclor,[5] $M_{\mathrm{w}} = 6.7 \times 10^5$, 30 °C, highest $\gamma = 4$; (D) polystyrene solutions in Aroclor,[6,7] $M_{\mathrm{w}} = 2.89 \times 10^6$ and 8.42×10^6, 3−10%, 30 °C, highest $\gamma = 7$; (E) solutions of poly(α-methyl styrene) in Aroclor,[6,7] $M_{\mathrm{w}} = 2.71 \times 10^6$ and 6.85×10^6, 3.9−13.9%, 30 °C, highest $\gamma = 7$; (F) solutions of four-arm star-branched polystyrene in Aroclor,[7] $M_{\mathrm{w}} = 7.36 \times 10^5$, 1.24×10^6, and 2.65×10^6, 9−30%, highest $\gamma = 7$; (G) Polystyrene melt,[8] $M_{\mathrm{w}} = 2.5 \times 10^5$, 160 °C, highest $\gamma = 6$.

The precision of the first two sets of data, A and B, may be a little lower than that of the other sets because the A and B data were obtained over a very wide range of γ with one apparatus. However, they were included to cover the range of high γ. The quantity $h(\gamma)$ is shown in Figure 2. The observed results, except for the sets A and B, are quite close to the prediction of Doi−Edwards theory.[1]

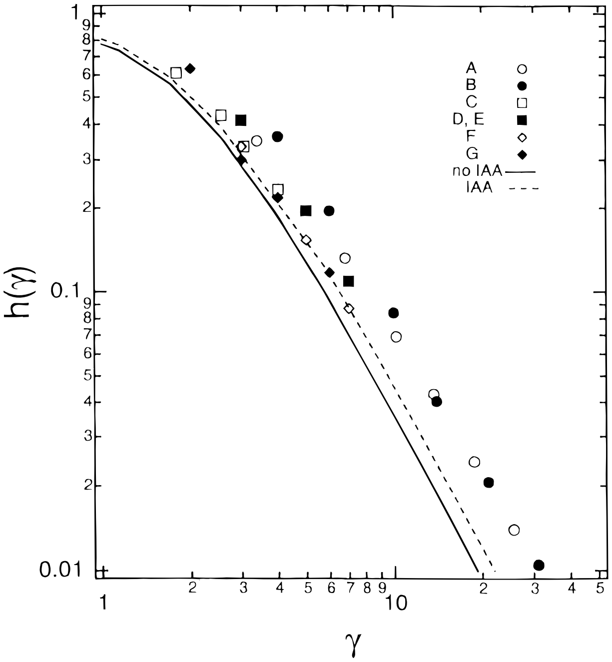

Figure 2. Damping function at long time, $h(\gamma)$, for the polymeric systems studied. Lines indicate Doi−Edwards prediction with independent alignment assumption (IAA) and without IAA.

Results

Linear Polymers at Low Strains. The results of the analysis at γ not higher than 7 were the same for all the linear polymers investigated, apart from the differences in the material constant τ_{k}. A test of eq 4 is shown in Figure 3 for the semidilute polystyrene solutions (data set D).[7] The logarithm of the following quantity,

$$\begin{aligned} F(t,\gamma) = \{[(\pi^2/8)h(t,\gamma)/h(\gamma) + {} \\ 1 - (\pi^2/8)]^{1/2} - 1\}/\{[h(\gamma)]^{-1/2} - 1\} \quad (7) \end{aligned}$$

is plotted against time. Equation 4 predicts a straight line at long times, and its extrapolation to $t = 0$ gives the intercept 1 for any γ value. This is valid in Figure 3, except that the intercept is about 0.53. The slope of the line corresponds to $\tau_{\mathrm{eq}} = 0.22\tau_{\mathrm{k}}$. The intercept was 0.5−0.55, and the ratio $\tau_{\mathrm{k}}/\tau_{\mathrm{eq}}$ was 4−5 for all cases of linear polymers at γ not higher than 7.

The quantities $A(t,\gamma)$ and $B(t,\gamma)$ defined by eqs 5 and 6, respectively, are plotted against time in semilogarithmic scales in Figure 4 for the semidilute polystyrene solutions (data set D). The graph of $B(t,\gamma)$ is almost the same as Figure 3. The difference is that the intercept at $t = 0$ of the extrapolated line is about 0.45. The same was true for all the linear polymers at low strains (data sets A−E, G).

Linear Polymers at High Strains. The quantities $A(t,\gamma)$ and $B(t,\gamma)$ for the 8% polystyrene solution (data set B) are shown in Figure 5. The graph of the quantity F of eq 7 is not shown because its behavior is essentially the same as that of $B(t,\gamma)$. The reduced quantity B

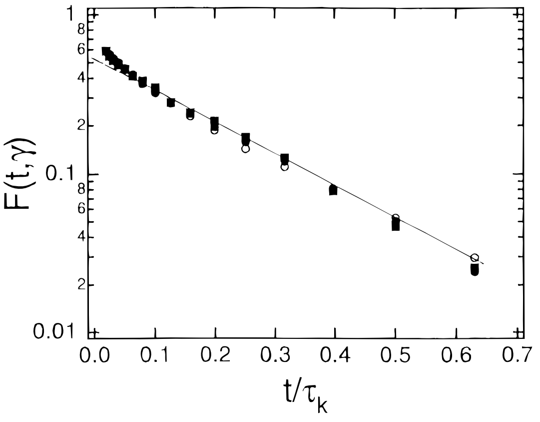

Figure 3. $F(t,\gamma)$ of eq 7 for semidilute polystyrene solutions (data set D). $\gamma = 3$ (■), 5 (○), and 7 (●).

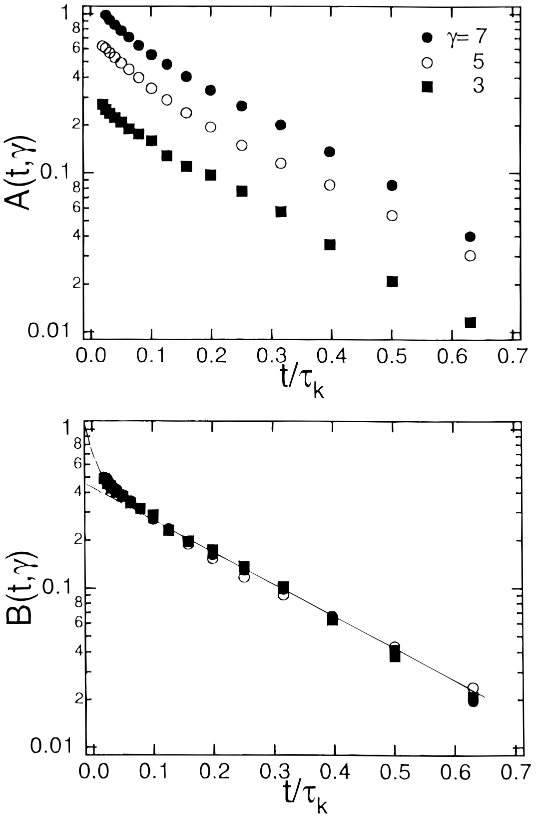

Figure 4. $A(t,\gamma)$ and $B(t,\gamma)$ for semidilute polystyrene solutions (data set D). $\gamma = 3$ (■), 5 (○), and 7 (●). Almost the same results were obtained for linear polymers at low strains (data sets A, B, C, E, and G).

decreases with the strain at high strains, i.e., γ higher than about 10. One may fit the data points at long times with straight lines with a slope independent of γ. It may be noted that the quantity $A(t,\gamma)$ at high γ does not vary much with γ; possibly the quantity A approaches some limit at high strains.

Qualitatively, the same result was obtained for the 20% polystyrene solution (data set A).

Branched Polymers at Low Strains. Figure 6 represents the result for the branched polymers at relatively low γ values (data set F). In contrast with Figure 4 for linear polymers, the function $B(t,\gamma)$ decreases with increasing γ. On the other hand, $A(t,\gamma)$ at long t is affected little with increasing γ, even in the range of $\gamma = 3-7$. This behavior is similar to that observed for linear polymers at much higher γ values.

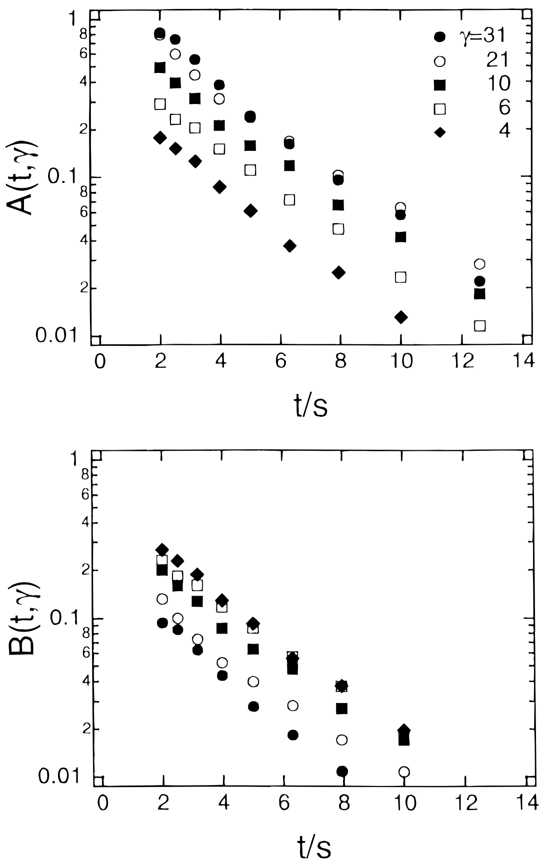

Figure 5. $A(t,\gamma)$ and $B(t,\gamma)$ for 8% polystyrene solution (data set B). $\gamma = 4$ (◆), 6 (□), 10 (■), 21 (○), and 31 (●). Almost the same result was obtained for data set A.

Discussion

Relaxation Time. In all the cases, the semilogarithmic plot of $A(t,\gamma)$ or $B(t,\gamma)$ against time can be approximated at long times with straight lines of slopes independent of γ. If an exponential decay like eq 3 is assumed, the slope gives a relaxation time 4−5 times smaller than the τ_k, defined as the time where $h(t,\gamma)$ levels off. One can expect this result provided that the decay at long times is dominated by an exponential function; since $\exp(4.5) = 90$, τ_k will correspond to the time where $h(t,\gamma)$ is about 1% higher than the limiting value, a reasonable criterion for the point of leveling off. The τ_k is reported to be independent of γ for all the data treated here; accordingly, the slope of the curves at long times is independent of γ. The relaxation time about 4.5 times smaller than τ_k corresponds to the previously proposed conformational relaxation time of a chain[6] regarded as a Rouse model.[9] This problem will be treated in a future publication.

Behavior of Linear Polymers at Low γ. At small strains, the function $B(t,\gamma)$ is independent of γ: $A(t,\gamma)$ is factorizable into functions of t and γ, respectively. This result is expected, provided that the retraction process and the reptation process are independent of each other and that the deformation does not change the nature of the tube so much as to affect the equation of motion of the chain in the tube. The theory of Doi[10] leading to eqs 1 and 2 is based on this assumptions. The present result is in accord with the theoretical result up to the point that $A(t,\gamma)$ is factorizable. The examination of eq 7 in Figure 3 indicates that the value of $a(t,\gamma)$ derived from the time dependence of $h(t,\gamma)$ at long times is about 50−55% of the value evaluated from $h(\gamma)$ by eq

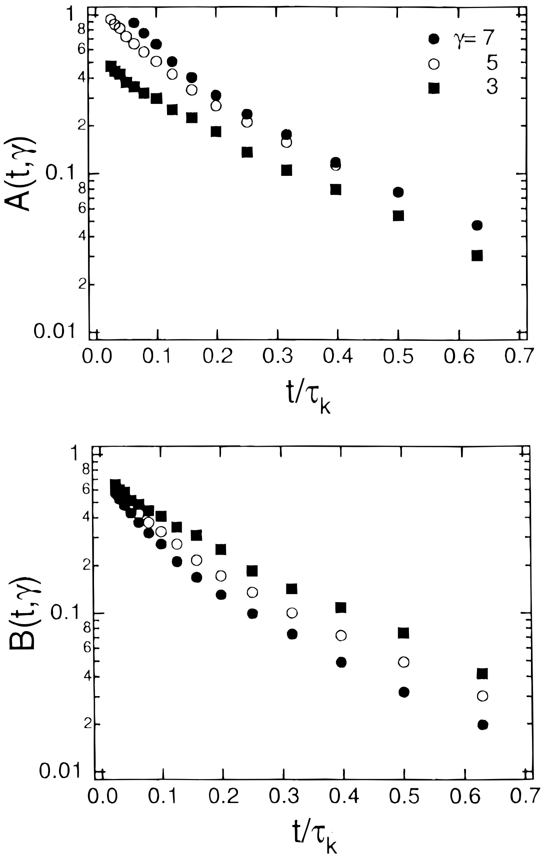

Figure 6. $A(t,\gamma)$ and $B(t,\gamma)$ for semidilute solutions of star-branched polystyrenes (data set F). $\gamma = 3$ (■), 5 (○), and 7 (●).

2. Obviously, the relaxation of $h(t,\gamma)$ is affected more by modes of shorter relaxation times than predicted by eq 1.

The upper bound of γ for factorizable $A(t,\gamma)$ is in between 7 and 10. The tube model assumes that the end-to-end vector of any fraction of a chain longer than the entanglement molecular weight, M_e, is approximated as a Gaussian chain and that it stretches in an affine manner in accord with the macroscopic deformation. This assumption will be violated for short chains in large deformation. For example, M_e for polystyrene is 1.8×10^4, and the molecular weight of the Kuhn segment, M_K, is about 10^3; the ratio of the fully stretched end-to-end length to the equilibrium length of the chain for entanglement spacing is $(M_e/M_K)^{1/2} = 4.2$.[11] This end-to-end length corresponds to $\gamma = 7$ if an affine deformation of a Gaussian chain is assumed for a rough estimate. Thus, the assumption of affine deformation of a Gaussian chain may be readily violated for a chain segment of the size of M_e. Since M_e increases with decreasing concentration, the assumption may be valid up to higher strains for semidilute solutions.

Behavior of Linear Polymers at High γ. It is likely that the nature of the tube and the equation of motion change when the strain is too high. The distribution of relaxation times for the retraction process changes, and the relaxation at short times becomes more important. On the other hand, the last part of the relaxation proceeds with the same time constant as at low strains. Possibly, the nature of the tube may return to that of the equilibrium state with the progress of the retraction process.

Branched Polymers. The behavior of branched polymers at relatively small strains is similar to that of linear polymers at large strains. One may be tempted to assume that chains of branched polymers are more easily extended than linear chains in deformation. However, the portion of chain as short as M_e is not likely to be affected by the branch point unless it is located very close to the branch point. Thus, the similarity mentioned above may be fortuitous.

It is well established that the stress relaxation of the star-branched polymers cannot proceed through reptation, i.e., the sliding of the chain as a whole along the tube.[12] The end of each branch has to retract back along its contour for relaxation to occur. This process is almost equivalent to the retraction process in large deformations. Thus, in the case of branched polymers, the shrinking process cannot be independent of stress relaxation at vanishing strain. The application of relatively small strains, like 3−5, seems to accelerate the relaxation process in excess of what is expected from the relaxation at vanishing strains and the retraction process independently considered.

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