Flow Properties of Polymer Solutions. III. Non-Newtonian Viscosity and Relaxation Mechanisms with Long Relaxation Times*

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ABSTRACT: Contributions of relaxation mechanisms with long relaxation times were examined for the shear stress $\kappa\tilde{\eta}(t, \kappa)$ after a sudden stop of steady shear flow of a 20-% polystyrene solution in chlorinated biphenyl, where κ is the rate of shear and t is the time of stress decay. The longest relaxation time $\tau_m(\kappa)$ and the corresponding strength $\eta_m(\kappa)$ were evaluated from the slope and the intercept at $t=0$, respectively, of the asymptotic straight line at large t in the plot of $\log \tilde{\eta}(t, \kappa)$ vs. t. Those for the second longest relaxation time, $\tau_{m-1}(\kappa)$ and $\eta_{m-1}(\kappa)$, were obtained in a similar manner from the plot of $\log [\tilde{\eta}(t, \kappa) - \eta_m e^{-t/\tau_m}]$ vs. t. The relaxation times $\tau_m(\kappa)$ and $\tau_{m-1}(\kappa)$ were found to be independent of κ and the ratio $\tau_m(\kappa)/\tau_{m-1}(\kappa)$ was about 3. At the limit of zero rate of shear, $\eta_m(\kappa)$ and $\eta_{m-1}(\kappa)$ were approximately 30 and 45%, respectively, of the zero shear viscosity η^0. As κ increased, $\eta_m(\kappa)$ and $\eta_{m-1}(\kappa)$ decreased more rapidly than the steady shear viscosity $\eta(\kappa)$ did; the difference $\eta(\kappa) - \eta_m(\kappa) - \eta_{m-1}(\kappa)$ was almost independent of κ. It was concluded that the nonlinear behavior, such as the shear-dependent viscosity of the polymer solution, is mainly due to the nonlinear behavior of the few relaxation mechanisms with long relaxation times.

KEY WORDS Steady Shear / Stress Decay / Relaxation Time / Non-Newtonian Viscosity / Constitutive Equation /

Tobolsky and Murakami have pointed out the importance of the relaxation mechanism corresponding to the longest relaxation time (the longest relaxation mechanism for short) in the study of flow properties of polymers at the limit of small strain.[1,2] They have examined the contributions of mechanisms of long relaxation times to the relaxation moduli for undiluted polystyrene and shown that about 70% of the zero shear viscosity is due to the longest relaxation mechanism. Recently we have suggested that the strength of the longest relaxation mechanism is proportional to the third power

of concentration for concentrated polystyrene solutions while those corresponding to the time scale of the rubbery plateau region are proportional to the second power.[3,4,5]

In the case of large strain, the contribution of the longest relaxation mechanism has been investigated for the strain-dependent relaxation modulus of a concentrated polystyrene solution.[6] It was found that the longest relaxation time is not affected by varying the strain, while the strength decreases very rapidly with increasing strain.

In the present paper, the contribution of the longest relaxation mechanism is examined for the shear stress after a sudden stop of steady shear flow in a polymer solution. The purposes of this study are to show that the contribution may be evaluated over a wide range of rate of shear and to examine the detailed nature of the rate-dependent shear viscosity for a typical polymer solution.

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METHOD

The stress decay function $\tilde{\eta}(t, \kappa)$ we are concerned with here is the ratio of the shear stress to the rate of shear after time t following a sudden stop of steady shear flow of rate of shear κ. This function may be expanded in a series of exponential functions as

$$\tilde{\eta}(t, \kappa) = \sum_p \eta_p(\kappa) e^{-t/\tau_p(\kappa)} , \quad (\tau_m > \tau_{m-1} > \cdots) \quad (1)$$

where η_p and τ_p are functions of κ. When κ is very small, the relation of linear viscoelasticity applies

$$\eta_p = \tau_p G_p \quad (\kappa \text{ small}) \quad (2)$$

where G_p is the strength of p-th relaxation mechanism; τ_p and G_p are independent of κ in this case. On the other hand, $\tilde{\eta}(t, \kappa)$ reduces to the viscosity $\eta(\kappa)$ at the limit of $t \to 0$,

$$\eta(\kappa) = \sum_p \eta_p(\kappa) \quad (3)$$

The contribution of the longest relaxation mechanism may be estimated with a simple method provided that the longest relaxation time τ_m is much longer than the next longest τ_{m-1} and that η_m is not much smaller than η_{m-1}. Under these conditions, the single term $\eta_m(\kappa) e^{-t/\tau_m(\kappa)}$ due to the longest relaxation mechanism is much larger than the sum of the rest of the terms on the right hand side of eq 1 in the range of large t. The plot of $\log \tilde{\eta}(t, \kappa)$ vs. t gives a straight line in this time scale. The intercept of the straight line at $t=0$ gives $\eta_m(\kappa)$ and the slope, $-2.303/\tau_m(\kappa)$, gives $\tau_m(\kappa)$. The contribution of the second longest relaxation mechanism may be estimated in a similar manner provided that τ_{m-1} is much longer than τ_{m-2} and that η_{m-1} is not much smaller than η_{m-2}. In this case, $\log [\tilde{\eta}(t, \kappa) - \eta_m(\kappa) e^{-t/\tau_m(\kappa)}]$ is to be plotted against t. Detailed criteria for this method have been given by Tobolsky and Murakami,[1,2] who applied the method to the relaxation modulus $G(t)$ in linear viscoelasticity. It may be noted that $\tilde{\eta}(t) (= \lim_{\kappa \to 0} \tilde{\eta}(t, \kappa))$ is in principle more suitable than $G(t)$ is for evaluation of τ_m and G_m in linear viscoelasticity because η_m/η_{m-1} is always larger than G_m/G_{m-1}, according to eq 2.

Contributions of relaxation mechanisms of long relaxation times to $\tilde{\eta}(t, \kappa)$ were evaluated from previous data obtained for a 20-% solution of polystyrene (standary sample 14a from Pressure Chemical Company) in Aroclor 1248 (partially chlorinated biphenyl from Monsanto Chemical Company).[7]

RESULTS

Examples of the plot of $\log \tilde{\eta}(t, \kappa)$ vs. t are shown with open circles in Figure 1 for the data of $\tilde{\eta}(t, \kappa)$ at variovs rate of shear obtained at 35°C. Apparently, the data points at long times ($t > 1500$ sec) lie on a straight line at each rate of shear. The straight lines corresponding to various rates of shear are approximately parallel to each other, indicating that the maximum relaxation time is not affected by the varying rates of shear. On the other hand, the intercept at $t=0$, or $\eta_m(\kappa)$, decreases as κ increases. The filled circles in Figure 1 represent the plot of $\log [\tilde{\eta}(t, \kappa) - \eta_m(\kappa) e^{-t/\tau_m(\kappa)}]$ vs. t, where values of $\eta_m(\kappa) e^{-t/\tau_m(\kappa)}$ are evaluated from the straight lines mentioned above. The points at relatively long times ($t > 350$ sec) seem to lie on a straight line at each rate of shear. Again the straight lines corresponding to various rates of shear are approximately parallel to each other and the intercept at $t=0$ decreases with increasing rate of shear. This result indicates that the second longest relaxation time $\tau_{m-1}(\kappa)$ is independent of κ, while $\eta_{m-1}(\kappa)$ is a decreasing function of κ.
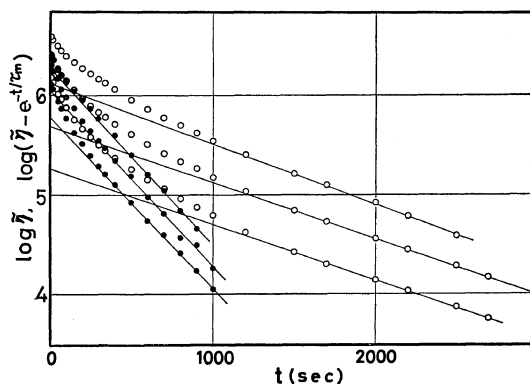

Figure 1. $\log \tilde{\eta}$ (open circles) and $\log (\tilde{\eta} - e^{-t/\tau_m})$ (closed circles) plotted against time t for 20-% polystyrene solution in chlorinated biphenyl at 35°C. Rates of shear are 4.60×10^{-4}, 3.61×10^{-3}, and 8.86×10^{-3} sec^{-1} from top to bottom.

Table I. Steady shear viscosity η, the longest relaxation time τ_m, corresponding relaxation strength η_m, and those for the next longest relaxation time, τ_{m-1} and η_{m-1}, for 20-% polystyrene solution in chlorinated biphenyl

κ, sec^{-1}	η, poise	τ_m, sec	η_m, poise	τ_{m-1}, sec	η_{m-1}, poise
(30°C)					
4.60×10^{-4}	4.3×10^6	722	1.3×10^6	242	1.95×10^6
8.65×10^{-4}	4.3×10^6	718	1.25×10^6	242	1.95×10^6
2.30×10^{-3}	3.3×10^6	773	7.8×10^5	254	1.3×10^6
3.61×10^{-3}	2.8×10^6	767	4.9×10^5	246	1.15×10^6
8.86×10^{-6}	1.9×10^6	772	1.85×10^5	252	6.1×10^5
(40°C)					
8.65×10^{-4}	2.05×10^6	398	6.6×10^5	—	—
1.92×10^{-3}	1.90×10^5	352	5.3×10^5	124	8.8×10^5
3.61×10^{-3}	1.70×10^6	346	4.0×10^5	126	7.1×10^5
8.86×10^{-3}	1.25×10^6	348	1.65×10^5	129	5.0×10^5
1.95×10^{-2}	9.2×10^5	352	8.5×10^4	125	2.6×10^5
3.67×10^{-2}	5.7×10^5	328	4.7×10^4	115	1.45×10^5

Figure 2. Reduced relaxation times τ_m/η^0 and τ_{m-1}/η^0 plotted against reduced rate of shear κa_T for 20-% polystyrene solution in chlorinated biphenyl. Reference temperature is 30°C and directions of pips indicate temperature of measurement; pip up, 35°C, and pip right, 40°C.

Similar figures are obtained for $\bar{\eta}(t, \kappa)$ at other rates of shear at 35°C and also for those obtained at 40°C. The results for η_m, τ_m, η_{m-1}, and τ_{m-1} are shown in Table I. At 45°C and 50°C, the precision of $\bar{\eta}(t, \kappa)$ is not high enough to allow the evaluation of $\tau_{m-1}(\kappa)$ and $\eta_{m-1}(\kappa)$, because of the very low shear stress in the measurements of $\bar{\eta}(t, \kappa)$. The results of $\bar{\eta}(t, \kappa)$ at 30°C turned out to include slight errors at long times due to the poor stability of the recorder employed in the measurements; thus unique straight lines were not obtained in the plot of $\log \bar{\eta}(t, \kappa)$ vs. t. The results given in Table I may be reduced to these temperatures, if desired, with the method of reduced variables[7] for $\bar{\eta}(t, \kappa)$: zero shear viscosities η^0 at 30, 35, 40, 45, and 50°C are 1.05×10^7, 4.3×10^6, 2.05×10^6, 1.4×10^6, and 8.0×10^5 poise, respectively.

Figure 2 shows the plots of $\tau_m(\kappa)/\eta^0$ and $\tau_{m-1}(\kappa)/\eta^0$ vs. rate of shear reduced to 30°C, $\kappa a_T = \kappa \eta^0/\eta^0(30°C)$. It is seen that $\tau_m(\kappa)/\eta^0$ and $\tau_{m-1}(\kappa)/\eta^0$ are not affected by varying the temperature. This result is consistent with the time—shear rate—temperature reduction rule reported for $\bar{\eta}(t, \kappa)$ in a previous paper.[7] It is also observed that $\tau_m(\kappa)$ and $\tau_{m-1}(\kappa)$ are independent of κ and the ratio $\tau_m(\kappa)/\tau_{m-1}(\kappa)$ is about 3.

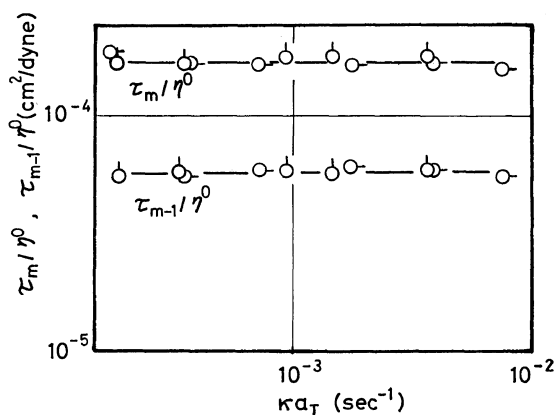Figure 3 shows $\eta(\kappa)/\eta^0$, $\eta_m(\kappa)/\eta^0$, and $\eta_{m-1}(\kappa)/\eta^0$

Figure 3. η/η^0, η_m/η^0, and η_{m-1}/η^0 plotted againit reduced rate of shear κa_T for 20-% polystyrene solution in chlorinated biphenyl. Reference temperature is 30°C and direction of pips indicates tempe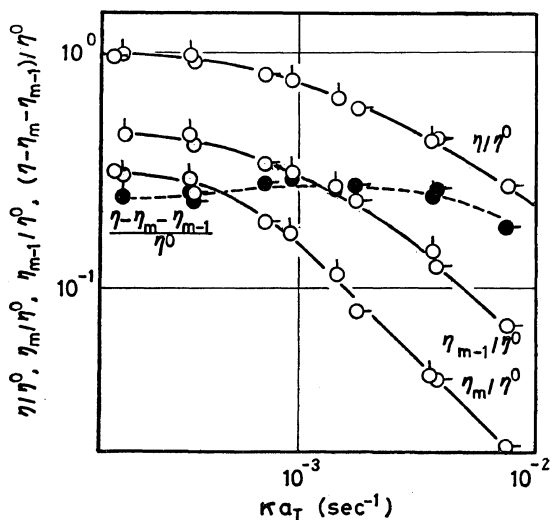rature of measurement; pip up, 35°C, and pip right, 40°C. Closed circles represent contribution of short relaxation mechanisms $(\eta - \eta_m - \eta_{m-1})/\eta^0$ to steady shear viscosity.

plotted against rate of shear κa_T reduced to 30°C. The shear rate—temperature reduction rule is apparently applicable to $\eta_m(\kappa)$ and $\eta_{m-1}(\kappa)$

in agreement with the previous result for $\bar{\eta}(t, \kappa)$.[7] At the limit of $\kappa \to 0$, $\eta_\mathrm{m}(\kappa)/\eta^0$ and $\eta_{\mathrm{m}-1}(\kappa)/\eta^0$ are about 0.3 and 0.45, respectively. As κ increases, $\eta(\kappa)$, $\eta_\mathrm{m}(\kappa)$, and $\eta_{\mathrm{m}-1}(\kappa)$ all decrease. The relative rate of decrease of $\eta_\mathrm{m}(\kappa)$ is the largest and that of $\eta(\kappa)$ the smallest. The difference $[\eta(\kappa)-\eta_\mathrm{m}(\kappa)-\eta_{\mathrm{m}-1}(\kappa)]$ represented with filled circles is almost independent of the rate of shear, indicating that the dependence of the viscosity on the rate of shear is mostly due to the large dependences of $\eta_\mathrm{m}(\kappa)$ and $\eta_{\mathrm{m}-1}(\kappa)$ on κ.

DISCUSSION

Strengths of Relaxation Mechanisms

As seen above, $\tau_\mathrm{m}/\tau_{\mathrm{m}-1}$ and $\eta_\mathrm{m}/\eta_{\mathrm{m}-1}$ are approximately 3 and 2/3, respectively, at the limit of $\kappa \to 0$ for the present solution. These values seem large enough to assure the appropriateness of the estimation of the longest relaxation mechanism. In fact almost the same set of values were obtained for $\eta_\mathrm{m}(\kappa)$, $\tau_\mathrm{m}(\kappa)$, $\eta_{\mathrm{m}-1}(\kappa)$, and $\eta_{\mathrm{m}-1}(\kappa)$ when the extrapolation procedure of Figure 1 was performed independently by several persons. However, the ratio $G_\mathrm{m}/G_{\mathrm{m}-1} \simeq$ 2/9 as calculated with eq 2 is not very large so that evaluations of G_m and τ_m from the relaxation modulue $G(t)$ are apt to involve large errors. Actually, previous values[6] for G_m and τ_m obtained from $G(t)$ are respectively about 2 and 0.6 times as large as the present values obtained from $\bar{\eta}(t, \kappa)$. The large errors of the previous result may be due partly to the small value of $G_\mathrm{m}/G_{\mathrm{m}-1}$ and partly to the instability of the recorder at long times, as mentioned above.

For the present system, $\eta_\mathrm{m}(\kappa)$ and $\eta_{\mathrm{m}-1}(\kappa)$ are approximately 30 and 45%, respectively, of η^0 at the limit of $\kappa \to 0$. This result is in sharp contrast with that of Tobolsky and Murakami, whose η_m is as large as 70% of η^0 for undiluted polystyrenes.[1,2] This discrepancy probably represents the difference in shape of a box-type relaxation spectra for an undiluted polymer and a concentrated polymer solution: The spectrum for a concentrated solution decreases gradually as the relaxation time increases in the long time range while that for an undiluted polymer is approximately constant until it drops sharply when the relaxation time exceeds the longest relaxation time.[4] This difference may be caused

by the very strong concentration dependence of the strengths of the long relaxation mechanisms, as reported earlier.[3,4,5] However, further studies are required for a definite conclusion since a weak relaxation mechanism of very long relaxation time might originate from a contamination of the polymer with a small amount of high molecular weight component.

Effect of High Rate of Shear

It is evident from the results given above that the study of long-time relaxation mechanisms is very important in the investigation of nonlinear behaviors of polymers. In a previous study[6] we have examined the effect of shear strain s on the longest relaxation mechanism of the shear relaxation modulus $G(t, s)$ for this polymer solution. Here we will compare the effect of κ and of s on the longest relaxation mechanisms of $\bar{\eta}(t, \kappa)$ and $G(t, s)$, respectively. The results obtained so far may be summarized as follows:

(i) The longest relaxation time $\tau_\mathrm{m}(s)$ evaluated from $G(t, s)$ is independent of strain s and $\tau_\mathrm{m}(\kappa)$ evaluated from $\bar{\eta}(t, \kappa)$ is independent of κ.[6]

(ii) For this polymer solution[6] the relaxation
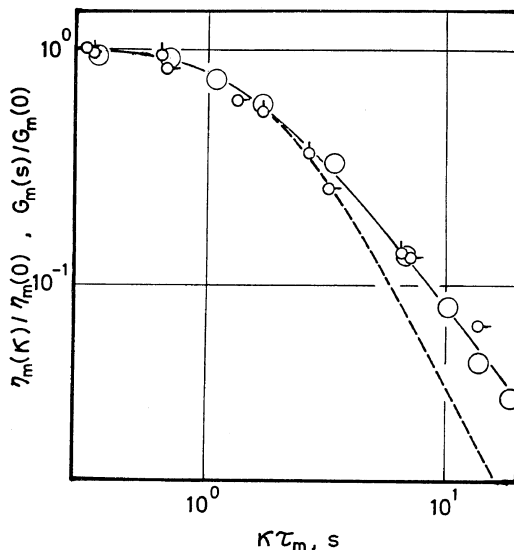
Figure 4. $\eta_\mathrm{m}(\kappa)/\eta_\mathrm{m}(0)$ (small circles) and $G_\mathrm{m}(s)/G_\mathrm{m}(0)$ (large circles) plotted against $\kappa\tau_\mathrm{m}$ and s, respectively, on the same scale for 20-% polystyrene solution in chlorinated biphenyl. Dashed line represents the relation $G_\mathrm{m}(s)/G_\mathrm{m}(0)=1/[1+(\alpha s)^2]$ with $\alpha=0.5$.

strength $G_m(s)$ as obtained from $G(t, s)$ is a decreasing function of s and when s is large the decrease is proportional to $s^{-1.66}$.

(iii) The quantity $\eta_m(\kappa)$ is a decreasing function of κ.

Figure 4 compares the effects of varying s and κ on $G_m(s)$ and $\eta_m(\kappa)$, respectively. In this figure $G_m(s)/G_m(0)$ (large circles) and $\eta_m(\kappa)/\eta_m(0)$ (small circles) are plotted against s and $\kappa\tau_m$, respectively. As mentioned above, reported values of $G_m(s)$ include large errors. However, the ratio $G_m(s)/G_m(0)$ is expected to be fairly precise because it has been found approximately equal to $G(t, s)/G(t)$ over a wide range of long times for this polymer solution.[6] It follows that ratios $G_p(s)/G_p(0)$ for a few long relaxation mechanisms are approximately equal to one another and the evaluated ratio $G_m(s)/G_m(0)$ may not involve serious error. A reduced rate of shear $\kappa\tau_m$ is employed in order to bring two types of data in the same range on the same abscissa. It may be seen that $\eta_m(\kappa)/\eta_m(0)$ as a function of $\kappa\tau_m$ is approximately identical with $G_m(s)/G_m(0)$ as a function of s. The dashed line represents a function of a form

$$G_m(s)/G_m(0)=1/[1+(\alpha s)^2] \qquad (4a)$$

or

$$\eta_m(\kappa)/\eta_m(0)=1/[1+(\alpha\tau_m\kappa)^2] \qquad (4b)$$

which is often employed in constitutive equations.[8] The parameter α is chosen as 0.5 to attain a good fit of the curve to the data for relatively small s values. It may be obvious that $G_m(s)$ or $\eta_m(\kappa)$ does not decrease as rapidly as in eq 4 does with increasing s or κ, respectively.

On Constitutive Equations

A most promising group of constitutive equations for polymer concentrates are of a single integral type written as

$$\boldsymbol{\sigma}(t)=\int_{-\infty}^{t} \mu(t, t')\mathbf{S}(t') \, dt' \qquad (5)$$

where $\boldsymbol{\sigma}(t)$ is the stress tensor at time t and $\mathbf{S}(t')$ is a tensor derived from the strain tensor at t' defined in reference to the state at t. Various forms have been proposed for the memory function $\mu(t, t')$.[8] The simplest function that can describe nonlinear behaviors of polymers to some extent is of the type[8]

$$\mu(t, t')=\mu(t-t', A(t'; t)) \qquad (6)$$

Here $A(t'; t)$ is a scalar derived from the tensors of rate of strain at time t' or of strain at t' defined in reference to the state at t. This type of memory function is very simple in the sense that the value of $\mu(t, t')$ is determined if only one state t' is specified in addition to the state at t. It has been found that the memory function of eq 6 with $A(t'; t)$ derived from the tensor of strain is able to describe interrelations among the strain-dependent relaxation modulus $G(t, s)$, the stress relaxation after application of double-step strain, and the stress development function $\bar{\eta}(t, \kappa)$ in the ranges of relatively small strain and rate of shear.[7,9]

The result of Figure 4 may be obtained from

$$\mu_m(t, t')=[G_m(s(t'))/\tau_m]e^{-(t-t')/\tau_m} \qquad (7)$$

where $\mu_m(t', t)$ is the part of the memory function corresponding to the longest relaxation mechanism, τ_m is a constant, and $G_m(s(t'))$ is a function of $s(t')$, the shear strain at t' defined in reference to t. $s(t')$ may be derived from the invariant of strain. It may be remarked that, when expanded in terms of exponential functions, eq 7 is an almost unique function of the type of eq 6 which is consistent with the result of Figure 4 and the properties (i), (ii), and (iii) shown in the preceding subsection.

Recently Takahashi and coworkers examined memory functions of the form[10]

$$\mu(t, t')=\sum_{p} [G_p f_p(A(t'; t))/\tau_p]$$
$$\times\exp\left[-\int_{t'}^{t} dt''/\tau_p g_p(B(t''; t'))\right] \qquad (8)$$

where G_p and τ_p are constants and f_p and g_p are functions of $A(t'; t)$ and $B(t''; t')$, respectively. Here $A(t'; t)$ has the same meaning as above and $B(t''; t')$ is a scalar derived from the tensor of rate of strain at t'' or of strain at t'' defined in reference to the state at t'. It may be noted that all the states for the period of time $t'\leq t''\leq t$ have to be specified to determine a value of $\mu(t, t')$ in this case. This type of function may represent one reasonable method to extend the very simple form of eq 6. In fact it includes almost any current constitutive equations[8] as special cases. The nonlinear behaviors of $G_m(s)$, $\eta_m(\kappa)$, $\tau_m(s)$, and $\tau_m(\kappa)$ as

mentioned in the preceding subsection are consistent with eq 8 only when $A(t'; t)$ is derived from the strain tensor and $B(t''; t')$ from the rate-of-strain tensor, according to the results of Takahashi, et al.[10] The result of Figure 4 is not obtained if $A(t'; t)$ includes κ; τ_m depends on s or κ if $B(t''; t')$ includes s. In this case, however, eq 8 is no more able than eq 6 is to describe the stress relaxation after application of a double-step shear strain.[9,10]

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