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Experimental Appraisal of the Doi–Edwards Theory for Polymer Rheology Based on the Data for Polystyrene Solutions

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ABSTRACT: The molecular theory of Doi and Edwards on viscoelasticity of polymer concentrates was tested on the basis of stress-relaxation data for polystyrene solutions. At relatively low molecular weights or concentrations, $cM < 10^6$ g/cm^3, the relaxation modulus $G(t,\gamma)$ was separable into two factors, one a function of time t and the other of strain γ, at times longer than a certain critical time τ_k. The strain-dependent factor agreed well with the predicted function. The shear stress in double-step shear strains was excellently predicted by the theory. In the range where $cM > 10^6$ g/cm^3, the observed results were not in agreement with the theory. At any molecular weights and concentrations, the stress appeared to relax through two types of processes: one, of the stronger strain dependence, characterized by the maximum relaxation time and the other by τ_k. The latter may correspond to the characteristic time T_{eq} of the chain reptation in the de Gennes tube model.

Recently Doi and Edwards developed a theory to describe viscoelastic properties of melts and concentrated solutions of polymers.[1-4] It is based on the tube model of de Gennes,[5] which, at present, is probably the best model for describing the topological constraint on the motion of molecular chains or the so-called entanglement coupling.[6] The theory predicts a strong dependence of viscosity on molecular weight, although not in precise agreement with the experimental results and qualitative features of the relaxation spectrum. Introducing a mathematical assumption of "independent alignment", Doi and Edwards succeeded in deducing a constitutive equation, in a closed form, with a strain-dependent memory function to describe the nonlinear viscoelasticity. The strain dependence of the memory function seems to be in accord with experimental results as far as the data referred to in their paper are concerned. We believe the theory is extremely important because it is based on a plausible model for entangled systems and on simple assumptions and because it leads to a constitutive equation which may be regarded as a particular form of the phenomenological strain-dependent model of Bernstein, Kearsley, and Zapas, the BKZ model;[7] this model is capable of describing many important rheological properties of polymeric liquids provided that appropriate memory functions are given.[8-12] Very recently Doi showed[13] that the theory, by eliminating the assumption of independent alignment, may even give an improvement over the BKZ phenomenological model in the case of double-step shear strains, for which the latter has failed in predicting the stress.[14,15]

On the other hand, the present authors have performed rheological measurements on a series of polystyrene solutions of various molecular weights and concentrations.[15-21] Polystyrene samples of narrow molecular weight distributions were used. The experiments included the stress relaxation on application of single-[16,19] or double-step[15,17] shear strains as well as stress measurements at the start[21] and on the cessation[20] of steady shear flow. The data may be quite appropriate for testing the validity of the Doi–Edwards theory because of the well-characterized samples and the appropriate types of flow histories examined, especially the step-shear strains. As a matter of fact, a part of the results were referred to by Doi and Edwards to substantiate the theory. However, there was a group of data which are in strong conflict with the theory. In view of the importance of the theory, we believe it necessary to compare the theory with the experiments more fully and to determine to what extent the theory may be applicable. We also examine the newest version of the theory concerning the stress relaxation in double-step shear strains.

Summaries of the Theory and Experiments

The Doi–Edwards Theory. The theory[1] is based on the de Gennes tube model, or reptating chain model,[5] which represents the interchain topological constraint of entangled polymeric materials. According to the theory of de Gennes, the polymer chain can wriggle rapidly along itself inside the tube so that any local tension or compression of the chain may diffuse out in a short time T_{eq}, which is proportional to the square of the molecular weight. In order for the chain to change shape completely from any particular shape, it has to go completely out of the tube corresponding to the original shape by random wriggling motions back and forth. So the process of shape change takes a long time T_d, which is proportional to the cube of the molecular weight.

The nonlinear rheological behavior at long times is attributed to the partial loss of stress due to the fast relaxation process in the Doi–Edwards theory. On application of an instantaneous deformation to the material,[1,2] it is assumed that the tube, together with the chain, changes shape affinely in accord with the macroscopic deformation. The local tension and compression of the chain due to the deformation then disappear in T_{eq}. The affinely deformed chain snaps back, so to speak, to the equilibrium contour length along the deformed tube. A part of the stress which is due to the extension of the chain is lost in this process of snapping back. The remaining part of the stress is due to the nonequilibrium shape of the tube, and its relaxation is caused by the renewal of the tube as the chain goes out of the deformed nonequilibrium tube. The process is slow and is associated with the relaxation time T_d. With the use of the diffusion equation for this process, the stresses corresponding to the step strains are obtained. Doi and Edwards show that the strain-dependent relaxation modulus $G(t,\gamma)$ can be factored as

$$G(t,\gamma) = G(\mathrm{t})\,h(\gamma) \tag{1}$$

in terms of the linear relaxation modulus $G(t)$ and a strain-dependent function $h(\gamma)$. Here t is the time and γ is the magnitude of shear. The theory gives explicit expressions for $G(t)$ and $h(\gamma)$. A remarkable result is that the function $h(\gamma)$ should not depend on the material but should be a unique function of γ. Later Doi obtained[13] the relation to describe the stress in double-step strains in terms of $G(t,\gamma)$.

In order to calculate the stresses for arbitrary strain histories, Doi and Edwards employed a mathematical assumption of "independent alignment".[2,3] The assumption states that the direction (tangent) of each part of the chain does not change in the instantaneous process of snapping

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back from the affinely deformed configuration to the configuration of the equilibrium contour length. By introducing this assumption, they derived a constitutive equation of the single integral type with a strain-dependent memory function.[3,4] They hoped that the independent alignment assumption is not too drastic at least when the direction and the sense of deformation remain constant. In fact the strain-dependent function[2] $h(\gamma)$ and the stress in double-step strains in the same sense[13] are scarcely affected by introduction of the assumption. On the other hand, the stress for double-step strains in the opposite senses is affected to a large extent.[13]

In the following, we use the notation "DE theory" to represent the theory developed without the use of the independent alignment assumption.[1,2] We include under the same notation the recent development made by Doi.[13] We denote the theory with the independent alignment assumption as DEIA.[2-4] The DEIA theory is equivalent to a BKZ phenomenological model[7] with a particular form of the memory function.

Experiments. The data[15-21] compared with that of the theory are the shear stresses in various flow histories of a series of polystyrene solutions, mostly in diethyl phthalate.[15,18-21] The molecular weights of polystyrene samples supplied by Toyo Soda Manufacturing Co. were 1.23×10^6, 2.24×10^6, 3.10×10^6, 5.53×10^6, and 7.62×10^6. The molecular weight distributions were quite narrow. Recent NMR studies revealed that the tacticity of the polymers probably does not depend on the molecular weight.[22] The investigated range of concentration varied with the molecular weight; a typical range was from 0.166 to 0.329 g/cm^3 for $M = 3.10 \times 10^6$. One solution in chlorinated biphenyl, Aroclor 1248 from Monsanto Chemical Co., was also investigated.[16,17] The polystyrene was the standard sample from Pressure Chemical Co. of $M = 1.80 \times 10^6$ and the concentration was 0.276 g/cm^3 at 30 °C.

Shear stresses were measured on application of a single-step shear strain,[16,19] double-step shear strains in the same[15,17] and in the opposite[15] senses, and on the sudden start[21] and on the cessation[20] of steady shear flow. Measurements were performed with cone-and-plate rheometers.[23,24] Various flow histories were produced by rotating the plate in appropriate ways. The step-shear strains were invoked by sudden rotations of the plate by hand or by the elastic restoring force of stretched rubber bands.

Most of the observed results were described well with the BKZ model or the single integral phenomenological model with strain-dependent memory functions.[21] Thus the shear stresses for most of the flow histories were quantitatively predicted from the model with the memory function determined from the relaxation modulus $G(t,\gamma)$. Only one exception was the result for the double-step shear strains in the opposite senses.[15] In this case the predicted values were far smaller than the observed values.

The Scheme of Comparison. With respect to the linear viscoelasticity, the Doi–Edwards theory gives a prediction that

$$\tau_1{}^0 = T_{\mathrm{d}} \propto M^3 \qquad (2)$$

$$H(\tau) \propto \tau^{1/2} \qquad (\tau < \tau_1{}^0) \qquad (3)$$

where $\tau_1{}^0$ is the maximum relaxation time and $H(\tau)$ is the distribution function of the relaxation time.[2,3] The observed results are in fair but not in full agreement with the prediction. For example, the maximum relaxation time for many polymeric systems satisfies[6]

$$\tau_1{}^0 \propto M^{3.5} \qquad (4)$$

rather than eq 2. In this paper we will examine only the nonlinear features of the theory and will not worry about the linear viscoelastic properties.[32]

One of the marked features of the Doi–Edwards theory is the existence of a time constant T_{eq} above which the relaxation modulus $G(t,\gamma)$ should be factored as in eq 1. The theory states that[2,25]

$$\tau_1{}^0/T_{\mathrm{eq}} = 3M/M_{\mathrm{e}} \qquad (5)$$

where M_{e} is the molecular weight corresponding to the entanglement spacing in the customary sense.[6] We now ask if there is any time constant to characterize nonlinear properties that may correspond to T_{eq} of the tube model.[5]

Another interesting prediction of the theory is that the strain-dependent function $h(\gamma)$ of eq 1 should be determined by the amount of shear γ alone and should not depend on the material.[2] We examine how the theoretical function $h(\gamma)$ compares with the strain dependence of polystyrene solutions.

The third point we examine is the stress relaxation on double-step shear strains. In this experiment, we apply a shear strain γ_1 at a past time $-t_1$ and then a second strain γ_2 of the same direction at $t = 0$. The shear stress at $t > 0$ will be designated as $\sigma(t,t_1,\gamma_1,\gamma_2)$. When we say "double-step shear strains in the opposite senses", we mean the particular case $-\gamma_1 = \gamma_2 \equiv \gamma$. The DE theory gives relations[13]

$$\sigma(t,t_1,\gamma_1,\gamma_2) = A(\beta)[\sigma(t + t_1,\gamma_1 + \gamma_2) - \sigma(t + t_1,\gamma_2)] + \sigma(t,\gamma_2) \qquad (6)$$

$$\sigma(t,t_1,-\gamma,\gamma) = \sigma(t,\gamma) - A(\beta)\sigma(t + t_1,\gamma) \qquad (7)$$

where $\sigma(t,\gamma)$ [$\equiv\gamma G(t,\gamma)$] represents the shear stress for a single-step shear strain and

$$\beta^2 = [3 + (\gamma_1 + \gamma_2)^2]/[3 + \gamma_1{}^2] \qquad (8)$$

$$A(\beta) = (4/\pi)\beta \cos(\pi\beta/2)/(1 - \beta^2) \qquad \beta < 1 \quad (9a)$$

$$A(\beta) = (4/\pi)\beta^2 \cos(\pi/2\beta)/(\beta^2 - 1) \qquad \beta > 1 \quad (9b)$$

The prediction of the DEIA theory or the BKZ theory is given by putting $A(\beta) = 1$ in eq 6 and 7. We will examined the validity of eq 6 and 7 for polystyrene solutions.

Comparison of Theory with Experiments

Relaxation Modulus—Separability into Functions of γ and t. It is revealed in a previous paper[21] that the contribution of the mode of the longest relaxation time to the relaxation modulus is separable into two functions, one of t and the other of γ, in the following sense. Suppose we write

$$G(t,\gamma) = \sum_p h_p(\gamma) G_1{}^0 \exp[-t/t_p(\gamma)] \qquad (\tau_1 > \tau_2 > \tau_3 \ldots) \qquad (10)$$

Then the experimental value of $\tau_1(\gamma)$ is independent of γ and is equal to the linear value $\tau_1{}^0$ for polystyrene solutions. This is not always the case for all the polymer solutions. For a solution of a block copolymer, for example, the longest relaxation time decreases with increasing shear.[26]

As shown in a previous paper,[21] measurements of strain-dependent relaxation modulus $G(t,\gamma)$ are restricted to the long time end of the relaxation spectrum for diethyl phthalate solutions of polystyrene at relatively low molecular weight or low concentration, i.e., $cM < 10^6$ g/cm^3 approximately. In these cases, the relaxation modulus is separable as eq 1 over almost the whole range of measurements and systematic deviation from eq 1 is scarcely

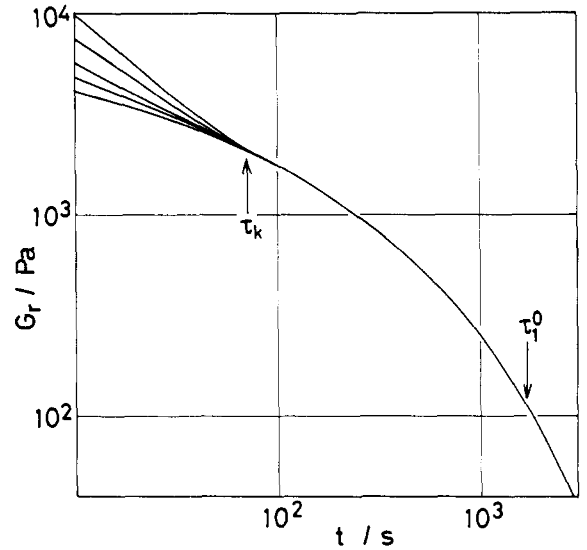

Figure 1. Reduced relaxation modulus $G_r(t,\gamma)$ plotted against time t for polystyrene solution in Aroclor at 30 °C;[16] the molecular weight of the polymer is 1.80×10^6 and the concentration is 0.276 g/cm^3. The bottom curve represents the linear relaxation modulus obtained for $\gamma \leq 0.68$. Magnitudes of shear for other curves are 2.4, 3.4, 6.8, and 13.7 upward.

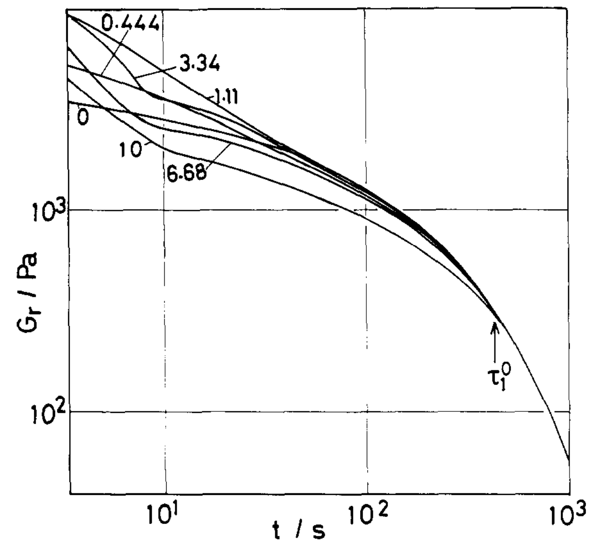

Figure 2. Reduced relaxation modulus $G_r(t,\gamma)$ plotted against time t for polystyrene solution in diethyl phthalate at 30 °C;[19] the molecular weight of the polymer is 5.53×10^6 and the concentration is 0.221 g/cm^3. Magnitudes of shear γ are indicated in the figure. The notation 0 represents the linear relaxation modulus obtained for $\gamma \leq 0.222$.

observed. In fact the time constant T_{eq} evaluated from eq 5, through a procedure given later, is of the order of 1 s or less, which is out of the range of measurements.

With the use of Aroclor, a solvent of higher viscosity, the relaxation spectrum moves to longer times and the relaxation modulus is measured over a wider range of time scale at a comparable molecular weight and concentration.[17] A reduced plot to examine the separability is given in Figure 1 for a solution of $M = 1.80 \times 10^6$ and $c = 0.276$ g/cm^3 in Aroclor at 30 °C. Here a reduced relaxation modulus

$$G_r(t,\gamma) = G(t,\gamma)/h_1(\gamma) \qquad (11)$$

is plotted against time, where the quantity $h_1(\gamma)$ represents the strain dependence of the relaxation strength corresponding to the longest relaxation time. It is seen that the reduced curves superimpose on one another over more than one decade of long times. The curves do not superimpose at times shorter than a certain time marked τ_k, 70 s in this case. The deviation of $G_r(t,\gamma)$ from $G(t)$ becomes larger with increasing shear strain γ. These features were pointed out in a previous paper.[27]

It may be interesting to compare the τ_k value with the time constant T_{eq} given by eq 5. In order to evaluate the entanglement spacing M_e, we assumed

$$M_e c = 2 \times 10^4 \text{ g cm}^{-3} \qquad (12)$$

This is in fair agreement with many experimental results for polystyrene solutions,[6,28,29] but not with the result of a scaling theory,[1] $M_e c^{3/4}$ = constant. For the solution of Figure 1, we obtain $M_e = 7.25 \times 10^4$ from eq 12 and $\tau_1^0 = 1700$ s, our earlier estimate,[17] and hence

$$T_{eq} = \tau_1^0(M_e/3M) = 22.8 \text{ s} \qquad (13)$$

It may be noted that the τ_k value, 70 s, is of the same order of magnitude as T_{eq} evaluated from eq 5; more precisely the former is larger than the latter by a factor of 3.

Figure 2 represents a reduced plot for a solution of relatively high molecular weight, $M = 5.53 \times 10^6$ and $c = 0.221$ g/cm^3, in diethyl phthalate.[19] In this case, good superposition of the reduced curves is attained in a very limited range of long times, approximately $t > \tau_1^0$. Over one decade just below this range of time scale, the dispersion of curves is not too large if the amount of shear is not too large, $\gamma < 7$ say. Thus the relaxation modulus $G(t,\gamma)$ is approximately separable over a certain range of γ and t for this solution of high molecular weight. It is to be noted, though, that the ranges of γ and t are much smaller than those of Figure 1. The series of curves in Figure 2 do not vary in a regular manner as in Figure 1 so that it is not possible to define a time constant τ_k from the deviating points of reduced curves. The qualitative features stated above are common to the solutions of high molecular weights or high concentrations,[19] i.e., of $cM > 10^6$ g/cm^3. Since this criterion of c and M corresponds to a marked change of rheological properties,[19-21] we divide the samples into two classes

$$\begin{array}{ll} \text{type I samples} & cM < 10^6 \text{ g/cm}^3 \\ \text{type II samples} & cM \geq 10^6 \text{ g/cm}^3 \end{array} \qquad (14)$$

for polystyrene solutions in diethyl phthalate. According to eq 12, one may say that the criterion corresponds to 50 entanglement points per molecule. Figures 1 and 2 represent type I and II samples, respectively.

For type II samples, the relaxation modulus $G(t,\gamma)$ for $3 < \gamma < 7$ shows marked two-step relaxations at relatively short times, i.e., the relaxation modulus decreases rapidly over a certain time range and then remains almost constant for a while.[19] Since the time corresponding to the break point, τ_b, seemed to be independent of γ and determined by the sample, it was suspected to be related to T_{eq} of the Doi–Edwards theory. Figure 3 shows how the time τ_b is determined from $G(t,\gamma)$. The curves of $G(t,\gamma)$ for $3 < \gamma < 7$ are smoothly extrapolated from both sides of the break point, and the time at the intercept of the extrapolated curves is defined as τ_b. The values of τ_b determined in this way are not affected by γ as seen in Figure 3. In Figure 4, the ratio τ_1^0/τ_b for three samples, for which the above procedure was feasible, is compared with the ratio M/M_e evaluated with the use of eq 12. The ratio τ_1^0/τ_k evaluated in Figure 1 is also included in Figure 4. It is seen that the ratios τ_1^0/τ_b and τ_1^0/τ_k are not only correlated strongly with but also are numerically close to the ratio M/M_e. Thus the values of τ_b or τ_k are larger than T_{eq} of eq 5 by

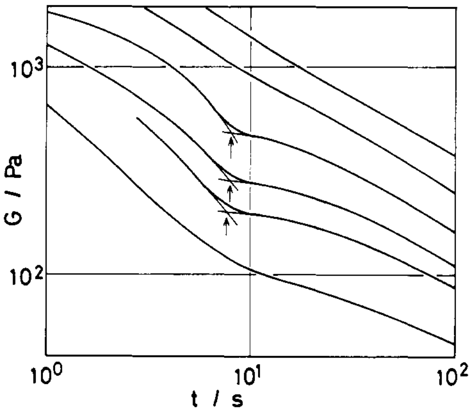

Figure 3. Relaxation modulus $G(t,\gamma)$ plotted against time t for the same polystyrene solution as in Figure 2.[19] Magnitudes of shear are 1.11, 1.88, 3.34, 5.22, 6.68, and 10.0 from top to bottom. Thin lines and arrows indicate how the time constant τ_b is determined.

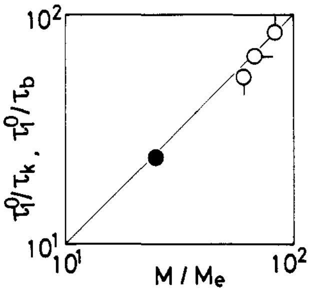

Figure 4. Ratios τ_1^0/τ_k and τ_1^0/τ_b, representing width in the time scale of the slow relaxation mechanism, plotted against M/M_e, the number of entanglement points for a polymer molecule. Solid circle represents τ_1^0/τ_k for a solution in Aroclor; $M = 1.80 \times 10^6$ and $c = 0.276$ g/cm^3. Open circles represent τ_1^0/τ_b for solutions in diethyl phthalate; pip up, $M = 7.62 \times 10^6$ and $c = 0.221$ g/cm^3; pip right, $M = 7.62 \times 10^6$ and $c = 0.176$ g/cm^3; pip down, $M = 5.53 \times 10^6$ and $c = 0.221$ g/cm^3.

a factor of 3. From our definition of τ_k or τ_b, it is likely that the value represents the long time end of the relaxation process located at the shorter time region. Thus we would propose a hypothesis

$$\tau_b \text{ or } \tau_k \simeq 3T_{eq} \tag{15}$$

The correspondence represented by Figure 4 or eq 15 may well be fortuitous and need further study.

Strain-Dependent Function $h(\gamma)$. Figure 5 shows the quantity $h_1(\gamma)$ which represents the strain dependence of the relaxation strength corresponding to the longest relaxation time,[19] see eq 10. The strain-dependent function $h(\gamma)$ of eq 1 of the DE theory[2] is also shown. As reported previously, the strain-dependent function $h_1(\gamma)$ is approximately common to the type I samples of relatively low molecular weights or concentrations. Most of the data for the type I samples, as well as that for the sample of Figure 1, lie within 10% of the curve denoted as I. The notation II indicates samples of type II, for which the function $h_1(\gamma)$ varies from sample to sample.

The fact that the $h_1(\gamma)$ is common to many samples such as type I samples is in accord with the prediction of the Doi–Edwards theory. Moreover, the values of $h_1(\gamma)$ are quite close to the theoretical values of $h(\gamma)$. At relatively small γ, $\gamma \leq 2$, they agree with each other to well within the experimental error. At large γ, the theoretical values are about 50% lower than those observed. One may still say the agreement is astonishingly good, considering the facts that the range of γ is large and that there are no adjustable parameters involved in the comparison. Incidentally, the discrepancy at large γ values could be due to the molecular weight distribution of the polymer. A larger discrepancy in the same sense, i.e., $h_1(\gamma) > h(\gamma)$, was observed for a sample of broad molecular weight distribution. The curve[30] marked as T in Figure 5 represents the strain dependence of a 0.21-g/cm^3 solution in chlorinated biphenyl at 30 °C of a thermally polymerized polystyrene. A GPC analysis showed that the weight-average molecular weight is 1.1×10^6 and $M_w/M_n = 4$ for this sample.

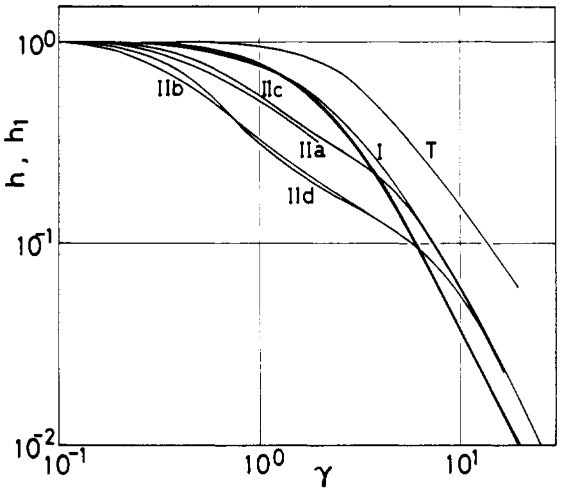

Figure 5. Strain-dependent functions $h(\gamma)$ and $h_1(\gamma)$.[19] The heavy line represents h due to the DE theory and the light lines represent experimental results of h_1 for polystyrene solutions. Notations I and II indicate type I and II samples, respectively; IIa, $M = 3.10 \times 10^6$ and $c = 0.329$ g/cm^3; IIb, $M = 5.53 \times 10^6$ and $c = 0.221$ g/cm^3; IIc and IId, $M = 7.62 \times 10^6$ and $c = 0.176$ and 0.221 g/cm^3, respectively. Notation T indicates thermally polymerized polystyrene in Aroclor; $M_w = 1.10 \times 10^6$, $M_w/M_n = 4$, and $c = 0.21$ g/cm^3.

On the other hand, the quantity $h_1(\gamma)$ for the type II samples varies with varying molecular weights and concentrations,[19] in contrast with the theoretical prediction. The shape of the curve for a type II sample in Figure 5 is quite different from that for the curve common to type I samples or from that of the theoretical curve. The deviation from the theoretical curve is large in the range of intermediate γ values and seems to diminish as γ increases. The discrepancy between the theory and the experiments for the strain dependence of type II samples is not likely to be due to the broadness of the molecular weight distribution of the polymer. The same polystyrene sample exhibits the behavior of the type I sample at lower concentrations.[19] The broadness of the molecular weight distribution will probably cause a discrepancy in the opposite sense, as represented by the curve for the thermal polystyrene in Figure 5.

Double-Step Shear Strains. We have revealed in previous reports that the shear stress on application of double-step shear strains in the same sense,[15,17] i.e., γ_1, $\gamma_2 > 0$, can be evaluated from the stresses in single-step shear strains with the use of the BKZ phenomenological relation. The relation is obtained by putting $A(\beta) = 1$ in eq 6. As shown by Doi,[13] the prediction of the DE theory is very close to that of the BKZ theory in the case of double-step strains in the same sense. In this case, the factor $A(\beta)$ is not far from unity and moreover the quantity in the square bracket of eq 6 is usually very small compared with the last term. Thus there is little point in comparing the predictions of the BKZ and the DE theories in this case.

On the other hand, the two theories give completely different predictions in the case of the double-step shear

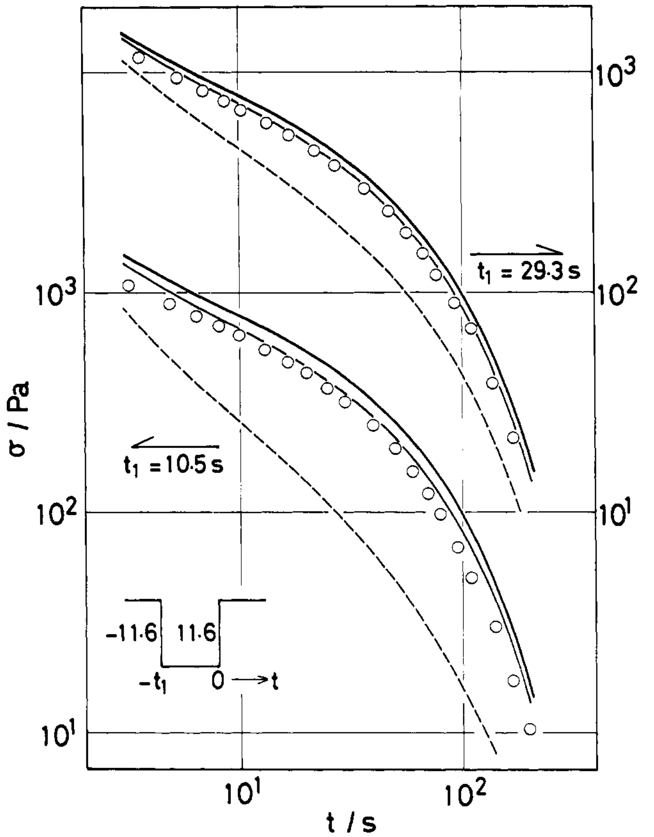

Figure 6. Shear stresses for double-step shear deformation of γ = 11.6 in opposite senses for polystyrene solution in diethyl phthalate;[15] M = 3.10 × 10^6 and c = 0.221 g/cm^3. The heavy lines represent stresses for single-step deformation. The light solid lines represent predictions of the DE theory and the light broken lines those of the BKZ theory.

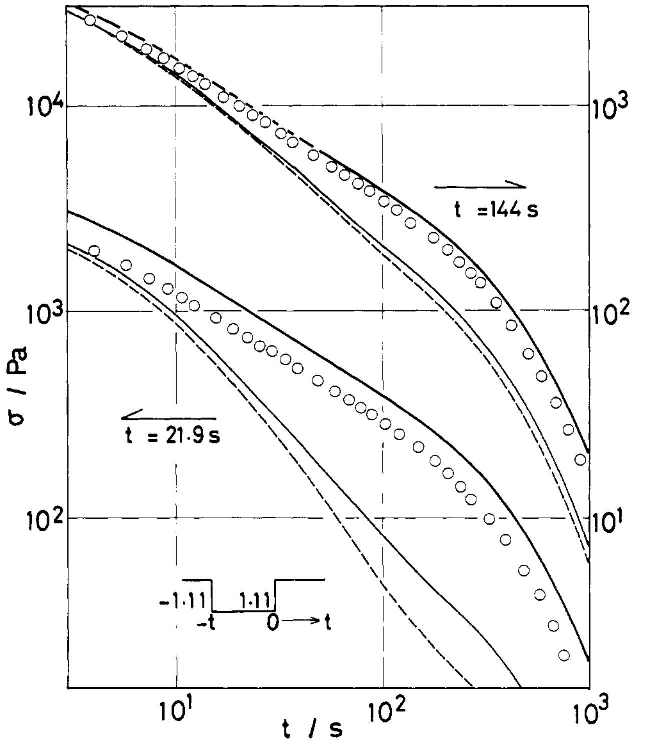

Figure 7. Shear stresses for double-step shear deformation of γ = 1.11 for polystyrene solution in diethyl phthalate;[15] M = 5.53 × 10^6 and c = 0.221 g/cm^3. The heavy lines represent stresses in single-step deformation. The light solid lines represent predictions of the DE theory and the light broken lines those of the BKZ theory.

strains in the opposite senses,[13] i.e., when $-\gamma_1 = \gamma_2 \equiv \gamma$. As reported earlier, the predicted values of the BKZ theory are too low compared with the observed values.[15] We examine the validity of eq 7 derived from the DE theory in this case. Figure 6 represents the result for a 0.221-g/cm^3 solution in diethyl phthalate of a polystyrene of M = 3.10 × 10^6 and Figure 7 that for the sample of 0.221 g/cm^3 and M = 5.53 × 10^6. Note that these two samples are classified as types I and II, respectively. The curves calculated by means of the DE theory are in excellent agreement with the experimental results in Figure 6 irrespective of the time interval t_1. Thus the DE theory is capable of predicting the shear stress for double-step shear strains as well as the strain dependence of the relaxation modulus for the type I sample.

On the other hand, the agreement is not good in Figure 7. Here the DE curves are indeed closer to the experimental results than are the BKZ curves, but they are not sufficiently close to be regarded as a good approximation. The effect of the factor $A(\beta)$ in eq 7 is not large enough to improve the agreement to a significant extent. For the sample of Figure 7 the nonlinear behavior is quite marked even at relatively small strains (see Figure 5). The shear stress $\sigma(t,t_1,-\gamma,\gamma)$ for γ = 0.444 was not in agreement with the prediction of the BKZ equation,[15] i.e., eq 7 with $A(\beta)$ = 1. At this value of γ, the factor $A(\beta)$ is 0.98 and the difference between eq 7 for the DE theory and the BKZ equation is within experimental error. Thus neither theory is able to predict the shear stress in this case. At γ = 0.222, the nonlinear effect is so small that either of the theories, DE and BKZ, or even the linear viscoelasticity theory gives a reasonable estimate of the stress.[15] It may be concluded that for this sample the DE theory is not capable of describing even the slightest nonlinear behavior of the stress in double-step shear strains in the opposite senses. For this sample, the theory consistently fails to predict the stresses in single- and double-step shear strains.

Other Flow Histories. In previous publications,[12,21] we have revealed that the stresses in steady shear flow and on the start and cessation of steady shear flow can be predicted with a BKZ strain-dependent phenomenological model[7] with the memory function derived from the strain-dependent relaxation modulus. The DEIA theory gives a strain-dependent constitutive equation with a particular form of the memory function.[3,4] The theory asserts that the memory function should be separable into two functions, one of time and the other of strain, and that the strain-dependent part is a certain function of strain invariants independent of the material. As shown in the preceding section, these statements are approximately realized for the type I sample in shear deformation over a wide range of long times. In other words, the theoretical memory function is approximately equal to that obtained from measured values of the relaxation modulus at long times. Since the contribution of long time modes is predominant to the stresses in relatively slow flow, the predicted results of the DEIA theory should not be too far from that of the phenomenological model. The latter results are in fair, if not perfect, agreement with the observed results.

For the type II samples, the observed strain-dependent function $h_1(\gamma)$ is entirely different from the theoretical function. Therefore, the theory is not capable of describing the flow behavior of the type II samples in spite of the fact that it gives a constitutive equation formally identical with the phenomenological model suitable also for the type II samples.[21] For example, the solution of Figures 2 and 7 does not exhibit the overshoot of shear stress at a rate of shear $\dot{\gamma} = 15/\tau_1{}^0$, at which the DEIA theory predicts a marked stress overshoot.[21]

Discussion

As seen above, the type I and type II samples exhibit rheological features different from each other in many respects. For the type I samples, the strain-dependent relaxation modulus is separable as eq 1 at times longer than a certain critical time τ_k. The quantity $\tau_1{}^0/\tau_k$ representing the width of the range where $G(t,\gamma)$ is separable is approximately equal to M/M_e, the number of entanglements per a molecule in the customary sense. The quantity $h_1(\gamma)$ to represent the strain dependence of the relaxation modulus is independent of the material and is approximately equal to the strain-dependent function $h(\gamma)$ of the Doi–Edwards theory. The shear stresses in double-step shear strains are described with eq 6 and 7. All these results are in accord with those of the DE theory. On the other hand, the stresses at the start and on the cessation of steady shear flow are described fairly well with the DEIA theory, which is apparently inconsistent with the DE theory in double-step strains in the opposite senses. Therefore if the independent alignment assumption required to derive the DEIA theory is a good one for flow histories in which the sense of flow does not change, as the theoreticians hope,[3,13] the Doi–Edwards theory constitutes an excellent molecular theory for the type I samples.

For the type II samples, on the contrary, most of the flow behavior is inconsistent with the theoretical prediction. The discrepancy between the observed and theoretical results is not likely to be due to any inappropriate property of the material, such as the broadness of the molecular weight distribution or incomplete dissolution. The former possibility has been disproved in the preceding section. The latter possibility is also unlikely because the linear viscoelasticity behavior of the solutions is not abnormal for ordinary entangled polymeric systems.[18] For example, the maximum relaxation time of the type II samples is proportional to $M^{3.5}$, and the relaxation spectrum exhibits a sharp cut-off at the long time end. Any microphase structures such as that in block copolymer systems[26] or any undissolved particles[31] will most probably affect the relaxation time measured at small strains and give rise to a broad tail at the long time region of the relaxation spectrum. Therefore we believe that the type II samples of high molecular weights or high concentrations belong to the entangled polymeric system to which the Doi–Edwards theory is supposed to be applicable. The result may suggest a possibility that another type of relaxation mechanism for highly entangled materials, in addition to or in the place of the snapping-back process and the reptation process of the Doi–Edwards theory, is still to be found.

In spite of the fact that the rheological properties are inconsistent with the theory for the type II samples, the empirical time constant τ_b representing the short time relaxation of the relaxation modulus might be related to the snapping-back process of the Doi-Edwards theory. The ratios $\tau_1{}^0/\tau_k$ and $\tau_1{}^0/\tau_b$ give the measure of the width of the time range of slow relaxation process, and the observed result, $\tau_1{}^0/\tau_k$ and $\tau_1{}^0/\tau_b \simeq M/M_e$, is in accord with the Doi-Edwards theory.[25] On the other hand, the molecular weight dependence of T_{eq} as given by the hypothesis of eq 15 is not in agreement with the theory, which says[1,4]

$$T_{eq} \propto M^2 \tag{16}$$

Equation 16 leads to

$$T_{eq} \propto (\tau_k \text{ and } \tau_b) \propto M^{2.5} \tag{17}$$

The discrepancy is similar to the discrepancy between T_d of the theory and the longest relaxation time $\tau_1{}^0$ observed, see eq 2 and 4. The latter discrepancy is probably due to some defect of the theory. As for the former, data are still too scanty for any definite conclusion. Measurements are in progress to obtain τ_k and $h(\gamma)$ over wide ranges of molecular weight and concentration for polystyrene solutions. It will be valuable if the same type of measurements are performed on other polymers, especially polybutadiene for which the entanglement spacing M_e is considerably smaller than that for polystyrene.

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