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Material Time Constant Characterizing the Nonlinear Viscoelasticity of Entangled Polymeric Systems

Kunihiro Osaki, Koji Nishizawa, and Michio Kurata*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan.

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ABSTRACT: For concentrated polystyrene solutions, the effect of varying strain on the relaxation modulus can be described with the tube-model theory of Doi and Edwards at times longer than a certain characteristic time τ_k determined for each sample. The characteristic time is proportional to the second power of the number of entanglements per molecule and has been conjectured to define the complete equilibration of the fluctuation of the primitive path length. Here, we see that τ_k is about 4.5 times as large as the configurational relaxation time of an isolated (unentangled) polymer molecule in a hypothetical viscous medium that exerts the same frictional force to polymer segments as the polymer solution does. We also see that the same holds true for polystyrene solutions of relatively low concentrations if the entanglement molecular weight M_e is assumed to be proportional to the −1.4 power of the concentration in this case.

Introduction

In 1978 Doi and Edwards proposed a novel molecular theory on the viscoelastic properties of entangled polymeric systems.[1] The theory has been proved to be well in accord with many experimental observations, especially on the nonlinear viscoelasticity.[2–4] The theory is based on the tube model of de Gennes.[5] In this model each polymer chain is allowed to move in a tubelike region that is bounded by surrounding polymer chains. This constraint on the motion of the polymer does not affect the rate of change of the primitive path length. The equilibration time of the contour length of the primitive path or chain T_{eq} is proportional to the second power of the number of entanglement points per chain N_e. The quantity T_{eq} is the same as the equilibration time of the large-scale configuration of a polymer molecule dissolved in a hypothetical unentangled viscous medium in which the viscous force exerted to polymer segments is the same as that exerted in the tubelike region. We call this time constant the configurational relaxation time for short and assign a notation τ_c for it. On the other hand, the large-scale orientation of the chain in the tube model changes very slowly as the chain creeps out of the tubelike region through reptating motion. Thus the time constant characterizing the change of orientation of the chain is that characterizing the disengagement of the chain from the tubelike region T_d. This is proportional to N_e^3 and is usually much larger than T_{eq} when N_e is large. According to a recent theory by Doi, T_d should be proportional to $N_e^{3.5}$ over a wide range of N_e of practical importance.[6] The Doi–Edwards theory leads to a rather simple expression for stresses at times sufficiently longer than T_{eq} in the stress relaxation process or for those in any flow histories of rates of strain much smaller than T_{eq}^{-1}.

On the other hand, the shear relaxation modulus at large deformations had extensively been studied for concentrated solutions of polystyrenes with narrow molecular weight distributions.[7,8] It was observed that the relaxation modulus $G(t,\gamma)$ could be factored into two functions, one of time t and the other of magnitude of shear γ, as

$$G(t,\gamma) = G(t)h(\gamma) \qquad t > \tau_k \tag{1}$$

at times longer than a certain critical value τ_k determined for each material. The strain-dependent function $h(\gamma)$ was common to many systems of various molecular weights and concentrations.[8] It turned out to have the same strain dependence as derived by Doi and Edwards.[1,2] Then the empirical quantity τ_k was suspected to represent a time "sufficiently longer than T_{eq}".[2] The idea is supported by some observations[9] that the viscoelastic behavior is in conflict with the prediction of the theory when the rate of shear is higher than τ_k^{-1}. In addition, the quantity τ_k has been proved to be proportional to N_e^2 in the range of high concentrations,[10] where the critical molecular weight corresponding to the entanglement spacing is inversely proportional to concentration.

Table I

$\tau_1^{\,0}$ and τ_k for Moderately Concentrated Polystyrene Solutions

$M_w/10^4$	$c/(10^{-2}$ g cm$^{-3})$	τ_k/s	$\tau_1^{\,0}$/s
448	5	20[a]	20
	6	22	54
	7	25	83
	8	30	122
842	2	6.5[a]	6.5
	3	30	42
	4	40	99
	5	40	160
	6	45	380

[a] $G(t,\gamma)$ is factorizable only at $t \geq \tau_1^{\,0}$.

The purpose of the present study is to examine the nature of τ_k in more detail and to see if it is really related to the theoretical quantity T_{eq}. For this purpose, we measure the concentration dependence of τ_k in moderately concentrated solutions, in which the critical molecular weight is affected more strongly by the concentration than in highly concentrated solutions. We also evaluate the configuration relaxation time τ_c in a hypothetical viscous medium and compare it with the value of τ_k.

Materials and Apparatus

Measurements were performed on polystyrene solutions in chlorinated biphenyl, Aroclor 1248. Two polystyrene samples were supplied from Toyo Soda Manufacturing Co. According to the data given by the supplier, the weight-average molecular weights M_w were 4.48×10^6 and 8.42×10^6, respectively, and the ratios of M_w to the number-average molecular weight M_n were 1.14 and 1.17, respectively. The concentration ranged from 0.02 to 0.08 g cm^{-3} at 30 °C as shown in Table I.

The shear relaxation modulus $G(t,\gamma)$ was measured with a cone-and-plate relaxometer.[11] The sample was held in the gap between the cone and the plate, and the plate was rotated instantaneously through a certain angle. The magnitude of shear γ was evaluated from the rotation angle. The shear stress was evaluated from the torque exerted on the cone. The quantity $G(t,\gamma)$ was obtained as the ratio of the shear stress to γ. For most of the samples, the measurements were performed over the range of γ from 0.5 to 6. For the remaining samples, measurements

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were performed up to the γ value of 20. All the measurements were performed at 30 °C.

Relevant Quantities and Equations

The maximum relaxation time $\tau_1{}^0$ for linear relaxation modulus $G(t)$ was evaluated from the slope of the asymptotic straight line at long times on a graph of log $G(t)$ plotted against t.[12] The characteristic time τ_k was defined as the time at which the relaxation modulus $G(t,\gamma)$ begins to be factored as shown in eq 1. The actual procedure of estimating τ_k and $h(\gamma)$ from $G(t,\gamma)$ will be shown later (see Figure 2).

For highly concentrated polystyrene solutions, we have seen that

$$\tau_1{}^0/\tau_k \propto (M/M_e)^{1.5} \qquad (2)$$

where M_e is the molecular weight of the chain between entanglement points.[10] This result implies that τ_k is proportional to $(M/M_e)^2$ (apart from an extra factor of concentration included in the segmental friction coefficient) since $\tau_1{}^0$ is proportional to $(M/M_e)^{3.5}$. For evaluation of M_e in eq 2, the following relation for concentrated solutions[13] is employed:

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

The values of M_e from various literature sources may be within 20% of the value from eq 3. A different choice for the value on the right-hand side will not much affect the results shown later. For moderately concentrated solutions, the quantity M_e is believed to vary as

$$c^{\alpha}M_e = \text{constant} \qquad \alpha > 1 \qquad (4)$$

Onogi et al. showed that α varies from 1.4 to 2.0, depending on the combination of polymer and solvent.[14] Doi asserts that α ranges from 2 to 1 as the concentration increases.[15] The recent blob theory gives $\alpha = 1.25$ when the excluded volume effect is large.[16] If eq 2 is to hold good in the range of concentration of the present measurements, the ratio $\tau_1{}^0/\tau_k$ should be proportional to $c^{1.5\alpha}$ instead of $c^{1.5}$.

In evaluating the configurational relaxation time τ_c in a hypothetical viscous medium, we assume that the frictional resistance of the polymer segments in the tubelike region is equal to that in a solution of a polymer with a molecular weight lower than the entanglement molecular weight at that concentration. We employ the spring-bead model, or the Rouse model,[17] for evaluation of τ_c and assign a notation τ_{cR} to indicate the model. For an unentangled polymer molecule in a viscous medium, the configurational (or vector mode) relaxation time τ_{cR} is twice as large as the maximum viscoelastic (or tensor mode) relaxation time τ_R.[18] The Rouse theory gives

$$\tau_R = \frac{6M\eta^0}{\pi^2 cRT} \qquad \text{(not entangled)} \qquad (5)$$

where η^0 is the viscosity of the polymer solution, R is the gas constant, and T is the absolute temperature. Equation 5 is in accord with experimental results for concentrated polymer solutions of low molecular weights, for which the viscosity is proportional to the molecular weight.[18] When the molecular weight is higher than about $2M_e$, the viscosity is proportional to $M^{3.5}$. We assume then that the viscosity is enhanced by a factor $(M/2M_e)^{2.5}$ due to the effect of entanglement[19] and obtain the expression

$$\eta_H = \eta^0(2M_e/M)^{2.5} \qquad (6)$$

for the viscosity of the hypothetical viscous medium that exerts the same frictional force to polymer segments as the entangled polymeric system does. The configurational relaxation time of an isolated polymer molecule in the hypothetical medium is given by

$$\tau_{cR} = \frac{12M\eta_H}{\pi^2 cRT} \qquad (7)$$

This can be evaluated from the data of η^0. The viscosity is evaluated from the linear relaxation modulus $G(t)$ through the relation[20]

$$\eta^0 = \int_0^{\infty} G(t)\,\mathrm{d}t \qquad (8)$$

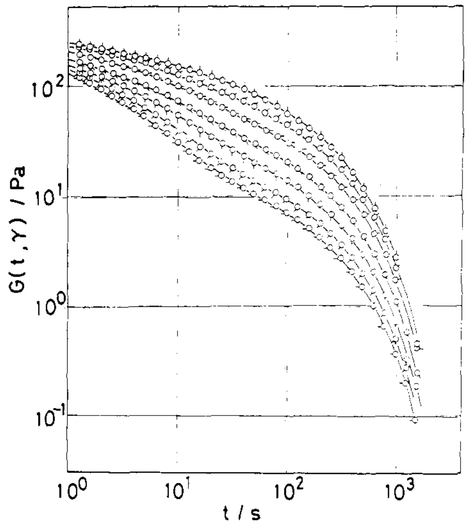

Figure 1. Relaxation modulus $G(t,\gamma)$ for polystyrene solution of chlorinated biphenyl at 30 °C. The molecular weight of the polymer is 8.42×10^6 and the concentration is 0.06 g cm^{-3}. Magnitudes of shear γ are <0.57, 1.25, 2.06, 3.04, 4.0, 5.3, and 6.1 from top to bottom.

Results and Discussion

Relaxation Modulus for Moderately Concentrated Solutions. The relaxation modulus $G(t,\gamma)$ for a 0.06 g cm^{-3} solution of the polystyrene of $M_w = 8.42 \times 10^6$ is shown in Figure 1 as an example. The curve at the top represents the results obtained for $\gamma \leq 0.57$ and so the linear relaxation modulus $G(t)$. As γ increases, the relaxation modulus $G(t,\gamma)$ decreases and the shape of the curve changes; $G(t,\gamma)$ for large γ markedly decreases in two different ranges of times, indicating the existence of two mechanisms of stress relaxation.

Each curve corresponding to $\gamma \geq 1.25$ in Figure 1 is shifted vertically so that it is superposed on the curve for $G(t)$ at $t \simeq \tau_1{}^0$. The result is shown in Figure 2. The amount of shift here is denoted by $-\log h(\gamma)$. Obviously, the quantity $G(t,\gamma)$ can be factored into two functions $G(t)$ and $h(\gamma)$ as in eq 1 at times longer than a certain time τ_k, 40 s in this case. Results similar to those shown in Figures 1 and 2 are obtained also for other solutions. The results for $\tau_1{}^0$ and τ_k are shown in Table I and the results for $h(\gamma)$ are shown in Figure 3.

The circles in Figure 3 represent the values of $h(\gamma)$ obtained experimentally. Filled circles are for $M_w = 8.42 \times 10^6$ and open circles for $M_w = 4.48 \times 10^6$, and various directions of the pips represent concentrations. At the lowest concentration studied for each molecular weight, the stress for $\gamma < 1$ was too small to be measured and so the function $h(\gamma)$ was not determined. One sees that the quantity $h(\gamma)$ scarcely varies with molecular weight or concentration. The theoretical value of $h(\gamma)$ due to the Doi–Edwards theory, represented by the solid curve, is in good agreement with the observed values over a wide range

Table II
Conformational Relaxation Time τ_{cR} and Related Quantities for Polystyrene Solutions

$M_w/10^4$	$c/(10^{-2}$ g cm$^{-3})$	η^0/(kPa s)	τ_{cR}/s	τ_k/s	$\tau_1{}^0$/s	τ_k/τ_{cR}	ref
67	40	4940	34	165	1100	4.9	ref 10
95	20	28.8	1.3	6.0	18.4	4.6	ref 10
	30	925	10	40	285	4.0	ref 10
	40	27800	110	380	4200	3.5	ref 10
448	6	2.60	3.6	22	54	6.1	this work
	8	22.0	5.7	30	122	5.3	this work
842	4	2.98	9.3	40	99	4.3	this work
	6	23.6	12	45	380	3.8	this work

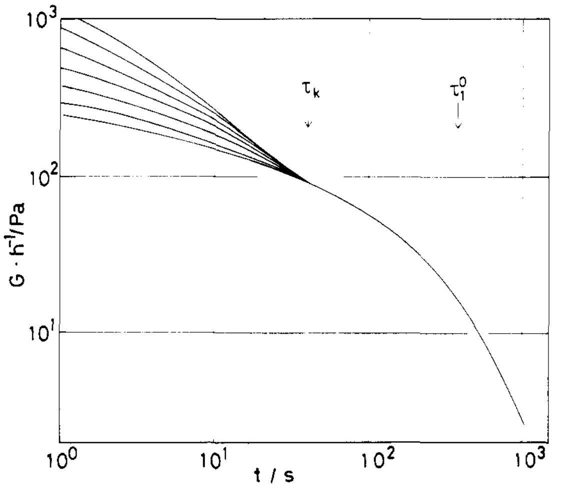

Figure 2. Reduced relaxation modulus $G(t,\gamma)/h(\gamma)$ derived from Figure 1. Each curve for $\gamma \geq 1.25$ in Figure 1 is shifted vertically by an amount $-\log h(\gamma)$ so that it superposes on the top curve at $t \simeq \tau_1{}^0$. Magnitudes of shear γ are 6.1, 5.3, 4.0, 3.04, 2.06, 1.25, and <0.57 from top to bottom.

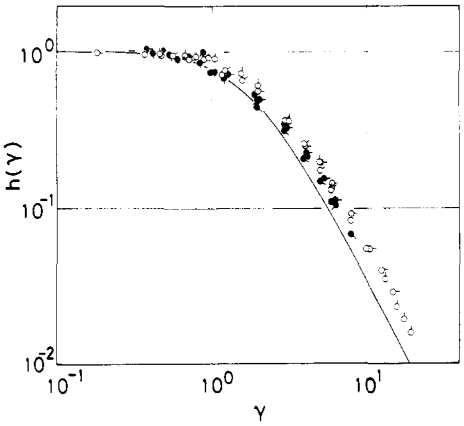

Figure 3. $h(\gamma)$ determined from the relaxation modulus. Filled circles represent polystyrene of molecular weight 8.42×10^6 and unfilled circles of 4.48×10^6. Directions of pips indicate concentrations as explained in the caption of Figure 4. The solid curve represents the theoretical value due to the Doi–Edwards theory.

of γ. (The curve is obtained without using the independent alignment assumption.[1]) Thus we may conclude that the strain dependence of the relaxation modulus at long times is well described with the Doi–Edwards theory even for solutions of relatively low concentrations.

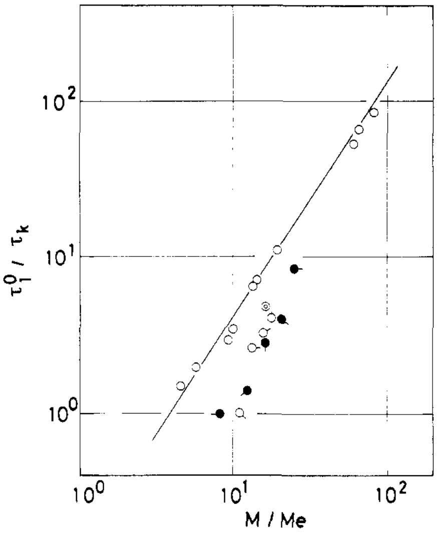

Figure 4. $\tau_1{}^0/\tau_k$ for polystyrene solutions of various molecular weights M and concentrations c. The abscissa is the number of entanglements per molecule evaluated with the use of eq 3. Unfilled circles without pips represent results for $c \geq 0.20$ g cm^{-3}; the double circle represents $M = 3.0 \times 10^6$ and $c = 0.112$ g cm^{-3}; filled circles represent $M = 8.42 \times 10^6$ and unfilled circles with pips, $M = 4.48 \times 10^6$. Directions of pips indicate concentrations: pip up, 0.08 g cm^{-3}; successive 45° rotations clockwise correspond to 0.07, 0.06, 0.05, 0.04, 0.03, and 0.02 g cm^{-3}. The solid line is drawn with slope 1.5.

Concentration Dependence of τ_k. The ratio $\tau_1{}^0/\tau_k$ is plotted against M/M_e in Figure 4. Here, the quantity M_e is evaluated with eq 3. The unfilled circles without pips represent the results for $c \geq 0.2$ g cm^{-3} reported earlier.[10] The double circle represents the result[21] for $c = 0.112$ g cm^{-3} and $M_w = 3.0 \times 10^6$. The circles with pips represent the present results. Evidently the values for $c \geq 0.20$ g cm^{-3} can be approximated by a straight line drawn with the slope 1.5. On the other hand, the values for $c \leq 0.112$ g cm^{-3} are much lower than those evaluated from the line.

In view of eq 4, we may suppose that the deviation is due to the illegitimate use of eq 3 at relatively low concentrations. If this is the case, we may evaluate the correct values of M_e for moderate concentrations by assuming that all the points should lie on the solid line. The quantity M_e thus determined is approximately a function of concentration alone as seen in Figure 5: The points obtained for samples of various molecular weights support a single line when plotted against concentration. The straight line drawn through the data points has a slope −1.4 and crosses the line representing eq 3 at $c = 0.3$ g cm^{-3}. Thus we obtain

$$cM_e = 2 \times 10^4 \text{ g cm}^{-3} \qquad c \geq 0.3 \text{ g cm}^{-3} \tag{9a}$$

$$c^{1.4}M_e = 1.23 \times 10^4 \text{ (g cm}^{-3})^{1.4} \qquad c < 0.3 \text{ g cm}^{-3} \tag{9b}$$

This result seems to be consistent with the experimental or theoretical results in the literature.[14-16] Thus the result for relatively dilute solutions may not be inconsistent with eq 2.

Configurational Relaxation Time τ_{cR}. The viscosity η^0 evaluated with eq 8 and the configurational relaxation time τ_{cR} evaluated with eq 6 and 7 are shown for a few samples in Table II. The values of M_e used in eq 6 are obtained from eq 9. The ratio τ_k/τ_{cR}, through scattering over the range from 3.5 to 6.1, does not seem to vary

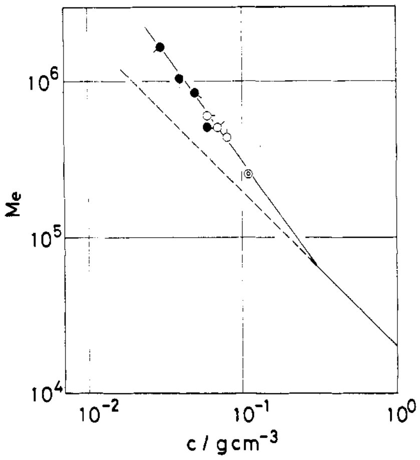

Figure 5. Concentration dependence of the entanglement molecular weight M_e determined from Figure 4 with the procedure given in text.

systematically with varying concentration or molecular weight. Therefore we may conclude that

$$\tau_k \simeq 4.5\tau_{cR} \tag{10}$$

This result may be in good accord with the view that τ_{cR} is equal to the equilibration time of the chain contour length T_{eq} and that τ_k represents a measure of a time sufficiently longer than T_{eq}. Suppose that a certain considerable portion of the stress is associated with a relaxation time τ_{cR} and the rest of the stress with a broad distribution of relaxation time over a wide range of time. The strength of the former portion of stress becomes about 1% of its full strength at $t = 4.5\tau_{cR}$. This is just the right magnitude for that portion to cease to be detectable from the rest of the stress.

The present evaluation of the configuration relaxation time is based on the assumption that the frictional force exerted on the polymer segment in the tubelike region is equal to that in an unentangled solution with the same concentration. The result obtained above may indicate that the frictional force in the tubelike region may be estimated fairly well with the present assumption.

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300-MHz ^{1}H NMR and 25-MHz ^{13}C NMR Investigations of Sequence Distributions in Vinyl Alcohol–Vinyl Acetate Copolymers

Geert van der Velden* and Jo Beulen

Central Laboratory, DSM, Geleen, The Netherlands. *Received November 24, 1981*

ABSTRACT: The microstructure of vinyl alcohol–vinyl acetate (VOH–VA) copolymers was studied by ^{13}C and ^{1}H NMR techniques. Sequence distributions could be obtained from the methine triads (VOH, VOH, VOH), (VOH, VOH, VA), (VA, VOH, VA), (VA, VA, VA), (VA, VA, VOH), and (VOH, VA, VOH) observed in the 300-MHz proton spectra of the copolymers. These sequence distributions were found to be in agreement with analogous sequence distributions calculated from methylene dyads and carbonyl triads in the ^{13}C NMR spectra of these copolymers. Combination of the two NMR techniques provides a powerful method for gaining information on the microstructure of this important class of copolymers.

1. Introduction

Previous papers have demonstrated that high-resolution ^{1}H NMR methods are extremely useful for microstructural analysis of ethylene–vinyl alcohol (E–VOH) and ethylene–vinyl acetate (E–VA) copolymers.[1,2] From 220-MHz ^{1}H NMR spectra of E–VOH and E–VA copolymers, the compositional and configurational distributions of the comonomers could be readily determined. As an alternative, ^{13}C NMR has been used for a detailed analysis of E–VA and E–VOH copolymers.[3,4] Moritani and Fujiwara[5] have combined ^{1}H and ^{13}C NMR to study the compositional distributions of vinyl acetate–vinyl alcohol (VA–VOH) copolymers. Through studies of the three ^{13}C NMR compositional methylene dyads, quantitative determination of sequence distributions in the copolymers has become possible. On the other hand, van Raaijen and van der Velden et al.[6] have mainly concentrated on the mixed configurational–compositional carbonyl triad, and quan-