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Viscoelastic Properties of Semidilute Polystyrene Solutions

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ABSTRACT: The complex modulus and the loss modulus were measured for semidilute solutions of polystyrene with high molecular weight in chlorinated biphenyl, a good solvent. The range of concentration c was 0.02–0.1 g cm^{-3}. The viscoelastic functions were qualitatively similar to those of concentrated solutions and melts. The entanglement molecular weight M_e, evaluated from the rubbery plateau modulus G_N, varied as $c^{-1.4}$. The relaxation time τ_s for the entanglement strand, evaluated from the complex modulus in the high-frequency transition region, was equal to the relaxation time of an unentangled polymer of molecular weight equal to M_e at the same concentration. The ratio of the longest relaxation time to τ_s was a unique function of M/M_e over the concentration range from semidilute solution to melt and was proportional to $(M/M_e)^{3.4}$, where M is the molecular weight.

Introduction

For characterizing the viscoelastic properties of polymer melts and concentrated solutions, two parameters, one representing the elastic property of the entanglement network and the other the local friction of the polymer chain, play essential roles.[1] Given these two rheological parameters in addition to quantities such as the molecular weight, concentration, and temperature, the principal features of viscoelasticity can be predicted. This observation is well recognized in recent molecular theories.[1,2] Now one of the major problems in polymer rheology is to understand the origin of the rheological parameters in terms of the structure and dynamics of polymeric systems.

The same concepts of entanglement and local friction are believed to be applicable to semidilute polymer solutions, in which the monomer concentration is low but the polymer coils well overlap one another due to the large coil volume for high molecular weight. In this concentration regime, the concepts of blob and scaling seem to be achieving some success in studies of viscosity and diffusion coefficient.[3-5] One may hope that some clue to the molecular origin of the rheological parameters may be obtained from studies of semidilute solutions.

On the other hand, viscoelastic studies of semidilute solutions are rather scarce. The few measurements of stress relaxation are limited to the time range of the longest relaxation time τ_1.[5-7] As a result the method of study has been only to examine the variation with molecular weight and concentration of the viscosity, the longest relaxation time, and the corresponding relaxation strength G_1. For concentrated solutions and melts, the elastic property is usually represented by the rubbery plateau modulus G_N, and the local friction is derived from the viscoelastic functions in the glass-to-rubber transition region. For semidilute solutions the viscoelasticity in such short-time regions has not been studied.

The purpose of the the present study is to extend the viscoelastic measurements to short-time ranges and examine if the traditional method of study can be applied to semidilute polymer solutions. The basic parameters are separately evaluated from the short-time data and compared with those reported in other concentration regimes.

Materials and Method

Materials. The polystyrene samples were products of Toyo Soda Manufacturing Co. The molecular weights given by the supplier are shown in Table I. The solvent was Aroclor 1248 (Monsanto Chemical Co.), a mixture of polychlorinated biphenyl of various degrees of chlorination. This was used as the solvent after removal of the volatile component under vacuum at 50 °C for 5 h. After this treatment, the evaporation of solvent was estimated as less than 0.2% in the process of measurements. The viscosity η_s and the density ρ_s of the solvent were expressed by

Table I
Polystyrene Samples

code	$M_w/10^6$	M_w/M_n
F850	8.42	1.17
F450	4.48	1.14
TS4	2.89	1.09

$$\eta_s = 0.3 \exp[341/(T - 246)] \text{ mPa s} \tag{1}$$

$$\rho_s = 1.467 - 0.0009(T - 273) \text{ g cm}^{-3} \tag{2}$$

where T is the absolute temperature.

The intrinsic viscosity $[\eta]$ of polystyrene in Aroclor was reported by Brueggeman et al.[8] for $2.0 \times 10^4 \leq M \leq 2.67 \times 10^5$. From their result and the additional fact $[\eta] = 218$ cm^3 g^{-1} for $M = 9.5 \times 10^5$ at 30 °C, one obtains

$$[\eta] = 1.49 \times 10^{-2} M^{0.70} \text{ cm}^3 \text{ g}^{-1} \tag{3}$$

The ranges of concentration were $0.02 \leq c/(\text{g cm}^{-3}) \leq 0.06$ for F850, $0.04 \leq c/(\text{g cm}^{-3}) \leq 0.08$ for F450, and $c = 0.1$ g cm^{-3} for TS4, at 30 °C.

Measurements. The stress relaxation was measured with a cone-and-plate relaxometer reported previously.[9] The shear relaxation modulus $G(t)$ was evaluated from the data with the magnitude of shear γ less than 0.8. The ratio of stress to γ was independent of γ in this range. Measurements were performed at 30 °C.

The dynamic complex modulus $G^* = G'(\omega) + iG''(\omega)$ was measured with a cone-and-plate rheometer (Rheopexy Analyzer, Iwamoto Seisakusho Co., Kyoto). The magnitude of shear was 0.8 and the range of angular frequence ω was $6.28 \times 10^{-2} \leq \omega/\text{s}^{-1} \leq 6.28$. Measurements were performed over the temperature range 10–50 °C and the results were reduced to 30 °C with the time–temperature reduction method.[10] The shift factor a_T varied with the temperature in the same manner as the solvent viscosity did.

Results and Discussion

Viscoelastic Functions. The real part G' and the imaginary part G'' of the complex modulus for solutions of F850 are shown in Figures 1 and 2, respectively. For concentrations 0.05 and 0.04 g cm^{-3}, one sees typical features of the plateau region, characterized by the slow change of G' and a maximum and a minimum of G''. One also sees a region similar to the glass-to-rubber transition region observed for melts and concentrated solutions, characterized by the $^1/_2$ slope of the log G'' curve. In this paper we call this region simply the transition region since we are not sure if the "glass-to-rubber transition" is a good name for the region of relatively low modulus.

The plateau region becomes less clear as the concentration decreases. The maximum and the minimum of G'' are not detected at $c = 0.03$ g cm^{-3}. At $c = 0.02$ g cm^{-3} the curves increase gradually up to the transition region

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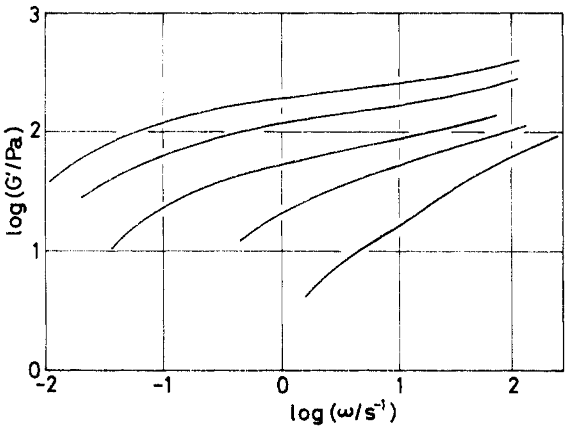

Figure 1. Real part G' of complex modulus for solutions of F850 in A1248 reduced to 30 °C. Concentrations in g cm^{-3} are 0.05, 0.04, 0.03, 0.025, and 0.02, from top to bottom.

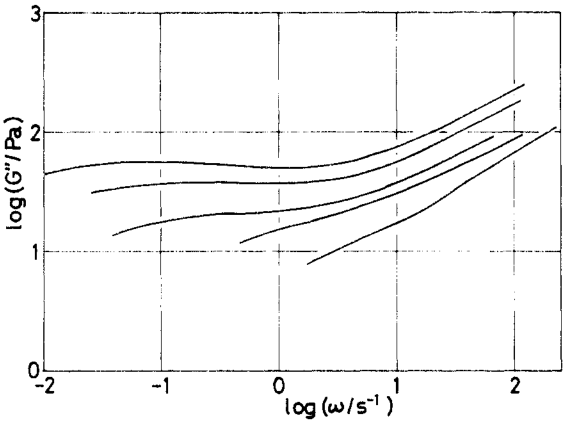

Figure 2. Imaginary part G'' of complex modulus for solutions of F850 in A1248 reduced to 30 °C. Concentrations in g cm^{-3} are 0.05, 0.04, 0.03, 0.025, and 0.02, from top to bottom.

without showing any sign of the plateau region.

Qualitatively the same results were obtained for other solutions. For F450 the G'' curve exhibited a maximum and a minimum at c = 0.06 and 0.08 g cm^{-3}. The curve for c = 0.04 g cm^{-3} had the diffuse symptom of the plateau region. At c = 0.025 g cm^{-3}, no sign of the plateau region was detected. The G'' curve exhibited a maximum and a minimum in the case of TS4 at c = 0.1 g cm^{-3}. The maximum values G''_m are given in Table II. In some cases, G'' remained constant over a wide range of ω without passing extrema. The plateau values of G'' are also included (in parentheses).

The relaxation modulus $G(t)$ was a decreasing function of t, c, and M. Due to the limited range of time and temperature, the relaxation curves did not exhibit marked characteristic features as seen for the dynamic data. An example of the relaxation curve may be found in a previous paper.[6] An approximation formula[11]

$$G(t) = G'(\omega) - 0.4G''(0.4\omega) + 0.014G''(10\omega)|_{\omega=1/t} \quad (4)$$

was used to derive $G(t)$ from the dynamic data. The approximate values were in good agreement with the directly measured values in the range where the time scales of the two sets of data overlapped.

At very long times, the relaxation modulus can be fitted with an exponential function

$$G(t) = G_1 \exp(-t/\tau_1) \quad (5)$$

Here τ_1 is the longest relaxation time and G_1 is the complementary relaxation strength. These parameters are listed in Table II.

Table II
Viscoelastic Parameters for Semidilute Polystyrene Solutions

$10^{-4}M$	10^2c/(g cm^{-3})	τ_1/s	G_1/Pa	G''_m/Pa	$10^3\tau_s$/s	G_N/Pa
289	10			340		
448	4			*a*	19	110
	5	21	34			
	6	58	58	112	6.9	430
	8	122	132	165	5.3	730
842	2.5			*a*	32	45
	3	42	13	(22.5)[b]	18.5	76
	4	92	24.5	36	9.5	170
	5	212	42	57	8.0	250
	6	380	52			

[a] Not detectable. [b] Plateau value.

Viscoelastic Parameters from Complex Moduli. The viscoelastic functions for the semidilute solutions exhibited the same features as those for concentrated solutions and melts. It may be reasonable to evaluate the before-mentioned parameters therefrom. For concentrated solutions and melts, the entanglement molecular weight M_e is usually employed as a basic parameter in the place of the rubbery plateau modulus G_N. These two quantities are connected through the relation[1]

$$G_N = cRT/M_e \quad (6)$$

where R is the gas constant and T is the absolute temperature. The local friction coefficient is determined from the viscoelastic functions in the transition region with the use of the Rouse theory.

In order to employ eq 6, one has to extract the G_N value from data in the plateau region. Graessley et al. have shown[12] that the plateau and the transition regions can be separated from each other with almost no assumption only when M/M_e is larger than about 100. Otherwise one has to make some assumption with respect to the shape of the viscoelastic functions. In the present paper, we assume after Doi[2] that the viscoelastic function is composed of the contribution from the entanglement network and that from the relaxation of entanglement strand described by the Rouse theory;[13] i.e.

$$G(t) = G_N(t) + G_R(t) \quad (7)$$

Here $G_N(t)$ is the contribution from the entanglement network and its detail is unknown except that it becomes a constant G_N (yet to be determined) in the transition region. As the Rouse component $G_R(t)$, we employ the relaxation modulus calculated for the polymer with the most probable molecular weight distribution and with the number-average molecular weight M_e (yet to be determined). The complex modulus $G'_R + iG''_R$ corresponding to $G_R(t)$ thus defined is tabulated in Ferry's book.[14] One expects that the following relations hold good in the frequency range where the contribution from the entanglement network is negligible.

$$G'(\omega) \cong G_N + G'_R(\omega)$$
$$G''(\omega) \cong G''_R(\omega)$$

By comparing these functions with the experimental results at high frequencies, it is easy to evaluate G'_N and G''_N from G' and G'' and thus to determine G_N.

An example of the separation is shown in Figure 3. The cross represents the point (τ_s^{-1}, G_N) where τ_s is the maximum relaxation time of the Rouse model. It may be obvious that the present data cannot be uniquely separated into two components without the assumption given above

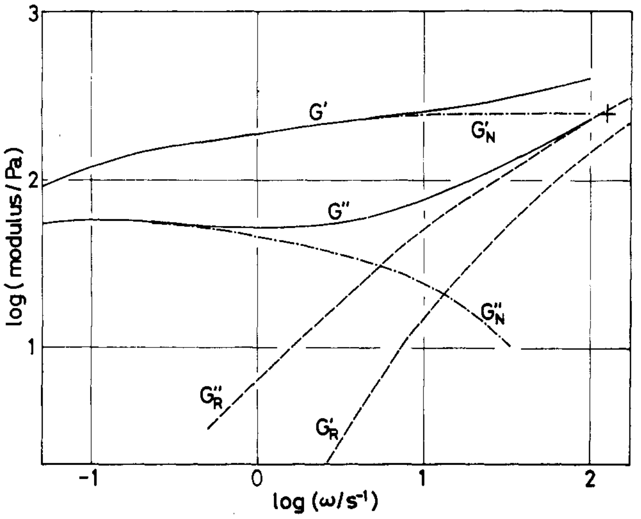

Figure 3. Separation of dynamic data into entanglement component (dash-dotted line) and Rouse component (dashed line) for 0.05 g cm^{-3} solution of F850. Cross indicates coordinate (τ_s^{-1}, G_N).

or the like. With this assumption, the quantities τ_s and G_N can be determined to within ±5%. The values of G_N and τ_s are listed in Table II.

The same procedure was applied to a published $G(t)$ for the 0.4 g cm^{-3} solution of polystyrene ($M = 6.70 \times 10^5$) in Aroclor. The G_N value obtained was in good agreement with the reported value which was determined from the inflection point of the log–log relaxation curve.[15] Thus the present method will give G_N values consistent with those obtained with other methods for concentrated systems. In order to examine the effect of the arbitrary assumption, we tried to fit the data with eq 7 except that we used $2M_e$ as the number-average molecular weight for $G(t)$ in place of M_e. The new procedure gave a G_N value 10% lower than before. Thus the result does not depend on the assumption too strongly.

Characteristic Moduli and Entanglement Molecular Weight. The characteristic moduli G_N, G''_m, and G_1 are plotted against concentration in Figure 4. The data points at high concentrations ($c > 0.1$ g cm^{-3}) were obtained by Kimura.[16] At any concentration the ratio among these moduli is approximately constant:

$$G_N{:}G''_m{:}G_1 \cong 6.0{:}1.55{:}1 \qquad (8)$$

The ratio $G_N/G''_m = 3.87$ is comparable to the value 3.56 reported by Graessley et al.[12] as the average for various polymeric systems. According to the tube model theory,[17] one expects

$$G_N{:}G''_m{:}G_1 \cong (\pi^2/8){:}(1/2){:}1 \qquad (9)$$

apart from a small change in G_N which depends on the mathematical approximation in the theory; thus $G_N/G''_m \cong 2.47$. Compared with this value, the observed results for various systems are larger and as long as the molecular weight distribution is fairly sharp, the values are always close to 3.6. This result may imply that the deviation from the theory is not due to the molecular weight distribution but to the existence of some relaxation process at relatively short times which is missing in the tube model theory.

In the concentration range studied ($c \le 0.1$ g cm^{-3}), the characteristic moduli vary with the concentration more rapidly than c^2. By fitting the data points with a straight line in Figure 4, one obtains a slope 2.4. An approximate expression for G_N is

$$G_N = 3.44 \times 10^5 c^{2.4} \text{ Pa} \qquad (c \le 0.1 \text{ g cm}^{-3}) \qquad (10)$$

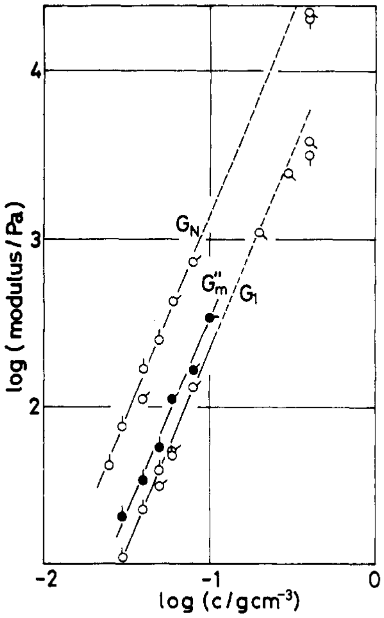

Figure 4. Characteristic moduli G_N, G''_m, and G_1 for polystyrene solutions in A1248 at 30 °C. Various directions of pips represent molecular weights: pip up, $10^{-4} M = 842$; successive 45° rotations clockwise correspond to $10^{-4}M = 448$, 289, 95, and 67.

The data at $c = 0.4$ g cm^{-3} are apparently smaller than the value extrapolated with eq 10. It is not impossible to draw one straight line with a lower slope to cover a wider concentration range. The choice is delicate and we have no definite reason to choose one. However, we believe that the present data are better fit by eq 10, which is not good at higher concentrations.

It may be noted that the concentration dependence observed here is consistent with the result of the blob-scaling hypothesis.[3] This states that

$$G_N \propto \xi^{-3} \qquad (11)$$

where ξ is the correlation length and varies with the concentration as $\xi \propto c^{\nu/(1-3\nu)}$. Here ν, the scaling power index (theoretical value $\cong {}^3/_5$), may be evaluated from the intrinsic viscosity through

$$[\eta] \propto M^{3\nu-1} \qquad (12)$$

With the use of eq 3, one obtains

$$\nu = 0.567 \qquad (13)$$

and so $G_N \propto c^{2.43}$, which is in agreement with the experimental result.

The entanglement molecular weight M_e evaluated from eq 6 and 10 is expressed by

$$M_e = 7.3 \times 10^3 c^{-1.4} \qquad (c \le 0.1 \text{ g cm}^{-3}) \qquad (14)$$

If one takes

$$M_e = 1.8 \times 10^4 c^{-1} \qquad (15)$$

for higher concentrations,[1] one obtains the same value for M_e at $c = 0.1$ g cm^{-3} from the two equations. The M_e value for $c = 0.4$ g cm^{-3} in Figure 4 fits eq 15 well.

Properties of Characteristic Times. According to the current concept of entangled systems,[1,2] the quantity τ_s characterizes the motion of the segment and τ_1 the motion of the whole chain. The motion of the whole chain is slowed down due to entanglement coupling and the ratio τ_1/τ_s should be a unique function of the number of entanglements per molecule, M/M_e. The ratio τ_1/τ_s is plotted against M/M_e for semidilute polystyrene solutions

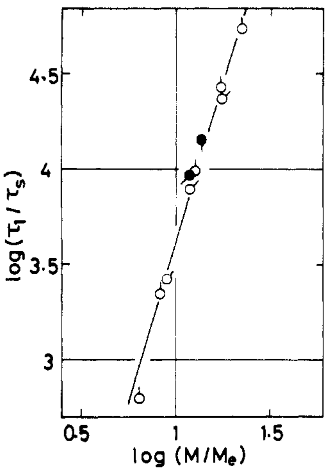

Figure 5. Ratio τ_1/τ_s plotted against M/M_e for semidilute polystyrene solutions in A1248 (unfilled circles). Directions of pips are as defined in Figure 4. Filled circles are for higher concentrations: pip down, $M = 6.7 \times 10^5$ and $c = 0.4$ g cm^{-3}; 45° rotation clockwise, $M = 2.15 \times 10^5$ and undiluted.

in Figure 5. Equation 14 was used to evaluate M_e. It is seen that the data for F850 and F450 lie on the same line. All the data points can be expressed well by the equation

$$\tau_1/\tau_s = 1.6(M/M_e)^{3.4} \qquad (16)$$

In the same figure, the data for $c = 0.4$ g cm^{-3} ($M = 6.7 \times 10^5$, 30 °C) and for a melt ($M = 2.15 \times 10^5$, 160 °C) are added. These were taken from published results[15,18] and the values of τ_s and τ_1 were evaluated with the same procedure as employed for the semidilute solutions. Equation 15 was employed to evaluate M_e. One sees that the points for higher concentrations agree with those for the semidilute solutions. This result may be noticeable since for approximately the same value of M/M_e, the melt has $M_e = 1.8 \times 10^4$ and the 0.04 g cm^{-3} solution of F850 has $M_e = 6.6 \times 10^5$. The values of M_e are different by a factor of 37 and the characteristic moduli for these systems are different by a factor of 1000. Thus the slowing down of the chain motion due to the entanglement is determined solely by the number of entanglements per molecule over a very wide range of concentration. It may be remarked that proper choice of eq 14 and 15 is indispensable for obtaining the unified result of Figure 5 over a wide range of concentration.

Now we examine the content of the parameter τ_s. According to the Rouse theory, the maximum relaxation time τ_R of a polymer with molecular weight M is given by

$$\tau_R = \frac{\zeta b^2}{6\pi^2 kT}\left(\frac{M}{M_0}\right)^2 \qquad (17)$$

where ζ is the friction coefficient, b^2 is the mean-square end-to-end distance and M_0 is the molecular weight, respectively, of the Rouse segment, and k is the Boltzmann constant. The quantities ζ, b^2, and M_0 may depend on the concentration. We expect that the local motion of the polymer chain is not affected by the entanglement; the quantity τ_s should be obtained from eq 17 with M replaced by M_e. Thus the ratio τ_R/M^2 for the unentangled solution should be the same function of c as the ratio τ_s/M_e^2 for the entangled system is.

These quantities are plotted against the concentration in Figure 6. The values of τ_R were taken from the paper of Schrag et al.[8] The viscoelastic functions shown in this paper do not show the plateau region; the molecular weights are much smaller than M_e values obtained from eq 14. The data of τ_R in the Schrag paper obtained with the solvent viscosity 7 Pa s were multiplied by 0.119/7 to be compared with the present data obtained with $\eta_s = 0.119$ Pa s. One sees in Figure 6 that τ_s/M_e^2 for entangled systems and τ_R/M^2 for unentangled systems compose a common function of the concentration. Thus one can state that the chain motion within each entanglement stand is the same as the motion in an unentangled chain and the size and friction of the Rouse segment are not affected by the existence of the entanglement.

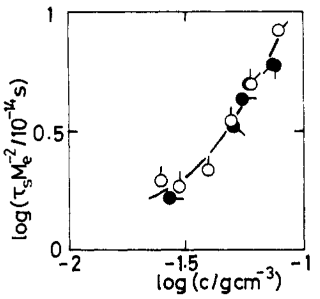

Figure 6. Quantities τ_s/M_e^2 for entangled systems (unfilled circles) and τ_R/M^2 for unentangled systems (filled circles) plotted against concentration c. Various directions of pips represent molecular weights: pip up, $10^{-4}M = 842$; successive 45° rotations clockwise correspond to $10^{-4}M = 448$, 26.7, 8.2, 5.1, and 1.98.

The result of Figure 6 may be restated as follows. In the frequency range of the transition region, the viscoelastic function is not affected by lowering the molecular weight, even much below the entanglement molecular weight. This has been confirmed by a few experiments for melts and highly concentrated solutions, after reducing the data to an iso-free volume state in some cases.[1] Figure 6 is probably the first case to confirm the above statement for semidilute solutions.

In Figure 6 the quantity τ_s/M_e^2 varies rather rapidly with concentration: τ_s/M_e^2 is roughly proportional to c^2 at $c > 0.04$ g cm^{-3}. If one assumes that the Rouse segment is equivalent to a blob of radius $r \propto \xi$ and that the friction coefficient of the blob is equal to that of a sphere of its size, then $\zeta = 6\pi\eta_s r$ and so

$$\frac{\tau_s}{M_e^2} \propto \frac{r^3}{M_0^2} \propto c^{(3\nu-2)/(1-3\nu)} \qquad (18)$$

since $r \propto c^{\nu/(1-3\nu)}$ and $M_0 \propto c^{1/(1-3\nu)}$. With the use of eq 13, $\nu = 0.567$, one obtains $\tau_s/M_e^2 \propto c^{0.43}$. This concentration dependence is far too weak as compared with the observed result. Thus the concentration dependence of τ_s can not be determined by the assumption given above. The assignment of the blob to the Rouse segment may be wrong or else the simple nondraining assumption for the friction coefficient may be inadequate.

Summary and Further Comment

One can conclude that the viscoelastic behavior of semidilute polystyrene solutions is essentially the same as that of melt and highly concentrated solutions. The basic parameters to determine the viscoelastic properties are G_N, τ_s, and M/M_e, where M_e is determined from G_N with eq 6. When the value of M/M_e is the same, the viscoelastic functions for a melt and a semidilute solution are identical in appropriately reduced scales.

Now we are left with two parameters M_e (or G_N) and τ_s to be determined with the rheological method. The concentration dependence of M_e is consistent with the result of the blob-scaling theory in the semidilute regime. On the other hand, the concentration dependence of τ_s cannot be described with the blob-scaling concept at least without some additional assumption. One possibility is that the friction coefficient increases more rapidly with concentration than is expected from the nondraining sphere of the blob for some still unclarified reason, such as the decrease of the free volume.[10] If this is the case, the blob-scaling result, eq 18, may hold valid at still lower concentrations or in some other (less viscous) solvent. An experiment at lower concentrations with a polymer of $M = 2.5 \times 10^7$ failed due to the degradation of the polymer. Measurements in less viscous solvents and higher frequencies will be valuable in elucidating the content of the parameter τ_s. Measurements at higher frequencies and lower concentrations may be valuable also for detecting the onset of entanglement in the semidilute solutions.

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Viscoelasticity of Randomly Cross-Linked Polymer Networks. Relaxation of Dangling Chains†

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ABSTRACT: A model based on the diffusion of dangling chains (in the presence of topological constraints) is used to predict the long-time, viscoelastic relaxation of randomly cross-linked polymer networks. In this calculation, the Pearson–Helfand theory for polymer stars is modified to account for the random distribution of chain lengths present in networks. An exact, numerical result is obtained which is found to agree with the previous Curro–Pincus theory at long times. In this limit, the theoretical relaxation modulus can be approximated by a power-law time dependence as in the phenomenological Thirion–Chasset equation. The cross-link density dependence of the exponent is in agreement with experimental data on natural rubber.

Introduction

Polymer networks typically exhibit exceedingly long viscoelastic relaxation times.[1] For example, it can take hundreds of hours for lightly cross-linked natural rubber to equilibrate in a stress relaxation or creep experiment.[2,3] Recently Curro and Pincus[4] developed a theory for this long-time viscoelastic behavior of networks which is in agreement with experimental observations. The Curro–Pincus theory is based on the ideas of de Gennes[5] regarding the reptation of branched polymer molecules in the presence of topological constraints. The purpose of the present investigation is to develop a more quantitative theory by extending the recent results of Pearson and Helfand[6] on star molecules to randomly cross-linked polymer networks.

A polymer network randomly cross-linked from polymer chains of finite molecular weight invariably contains network imperfections consisting of dangling chains ends.[7] Ferry[1] has postulated that the relaxation of these dangling ends, in the presence of entanglements, is responsible for the observed long relaxation times. The Curro–Pincus theory, as well as the present theory, employs a model based on the diffusion of dangling chains in the presence of topological constraints.

The diffusion of a linear polymer chain is strongly suppressed in a melt because of the presence of entanglements which act as topological constraints. The diffusion mechanism in this case is thought to consist of a reptation or "snakelike" motion of the chain.[8] The topological nature of a dangling chain or polymer star molecule, however, prevents the ordinary reptation process from occurring. De Gennes[5] has postulated that such a branched molecule relaxes to its equilibrium state by the branched chain retracing or retracting along its primitive path.

In the recent Pearson–Helfand theory[6] for polymer stars, the path retraction process is modeled by considering the chain end to be undergoing Brownian motion in a suitable

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† This paper is dedicated to Dr. Pierre Thirion on the occasion of his retirement.