

Viscoelastic Properties of Polymer Solutions in High-Viscosity Solvents and Limiting High-Frequency Behavior. I. Polystyrene and Poly(α -methylstyrene)

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ABSTRACT: Storage (G') and loss (G'') moduli were measured for dilute solutions of polystyrene (PS) and poly(α -methylstyrene) (PMS) in Aroclor (chlorinated diphenyl) with the modified Birnboim transducer. The molecular weights (M) were 5.1×10^4 , 8.2×10^4 , and 2.67×10^5 for PS and 3.55×10^5 and 8.7×10^5 for PMS, and the ranges of concentration (c) were 1.5×10^{-2} to 7.6×10^{-2} g/ml for PS and 1.5×10^{-2} to 4.6×10^{-2} for PMS, respectively. The solvent viscosity η_s varied from 5000 to 9.3 poise over the temperature range of 10 to 35°C employed. The frequency range was 0.02 to 630 Hz. The limiting value of the dynamic viscosity at high frequency η_{∞}' is described by an equation $\ln(\eta_{\infty}'/\eta_s) = [\eta']_{\infty} c$ over the whole range of concentration, where $[\eta']_{\infty}$ is a constant independent of M and is 14.3 and 22.2 ml/g for PS and PMS, respectively. The limiting value of G' at high frequency is approximately proportional to c . The time-temperature reduction rule was successfully applied to G' and $G'' - \omega\eta_s$ and the shapes of frequency dependence curves of the reduced moduli were described well by the theory of Peterlin.

KEY WORDS Viscoelasticity / Dilute Solution / Storage Modulus / Complex Dynamic Viscosity / Polystyrene / Poly(α -methylstyrene) / Peterlin Theory /

It has been observed for several dilute polymer solutions that the dynamic viscosity approaches a finite limiting value at high frequencies, higher than that of the solvent.¹⁻⁴ This fact is not in agreement with the Rouse-Zimm spring-bead model theories, according to which the dynamic viscosity approaches the solvent viscosity at high frequencies.⁵ Thus it is believed that some additional mechanism for dissipation of energy remains to be explained by molecular theories. However, very few data have been available thus far.

Recently, the application of the modified Birnboim transducer apparatus with a computerized data acquisition system has made it possible to measure limiting high-frequency behavior of the dynamic mechanical properties of polymer solutions in viscous solvents, with high precision.^{4,6,7} Some of these results have

been published.¹ We now give more extensive results obtained for solutions of polystyrene and poly(α -methylstyrene) in chlorinated diphenyl, with various combinations of concentration and molecular weight.

MATERIALS AND METHOD

The polymer solutions measured were polystyrene and poly(α -methylstyrene) in Aroclor 1254. Standard polystyrene 7a was obtained from the Pressure Chemical Company; the molecular weight was given as 5.1×10^4 . Other samples of polystyrenes, S108 and S102, were obtained from Dr. H. W. McCormick of Dow Chemical Company, with molecular weights 2.67×10^5 and 8.2×10^4 , respectively. The poly(α -methylstyrene) samples were prepared by Dr. K. Sakato and collaborators of Kyoto University.⁸ One of the samples (BB5) has a molecular weight of 3.55×10^5 with a very narrow distribution as determined from ultracentrifugation

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($M_w/M_n < 1.01$). The molecular weight of the other sample (A1) was originally reported as 9.7×10^5 but the viscosity-average molecular weight in toluene was determined as 8.7×10^5 at the time of the present study, suggesting some degradation; the molecular weight distribution of this sample is not expected to be so narrow. The viscosities of the Aroclor 1254 solvent, lot D-612, at several temperatures were determined to be 5000, 1100, 250, 70, 22, and 9.3 poise at 10, 15, 20, 25, 30, and 35°C, respectively.

The polystyrene solutions were prepared at 60°C with occasional stirring. About three weeks were necessary to get homogeneous solu-

tions. In the case of poly(α -methylstyrene), the polymer was freeze-dried and then added to the solvent, requiring a few days at room temperature. To assure dissolution, the solution was warmed several times at 60°C for brief periods before use. It might be worth noting that it is almost impossible to dissolve poly(α -methylstyrene) in a liquid of high viscosity without danger of degradation unless it is freeze-dried. The concentrations of the samples are given in Tables I and II.

Storage and loss moduli were measured with the modified Birnboim Transducer equipped with a computerized on-line data acquisition system

Table I. Parameters at low and high frequencies reduced to 25.0°C for polystyrene solutions in Aroclor 1254 ($\eta_s = 70$ poise)

Sample	2a ^a	7a	S102 ^a	S102	S108	S108 ^a	S108	S108	6a ^{a,b}
$M_w \times 10^{-3}$	19.8	51	82	82	267	267	267	267	860
$c \times 10^2$, g/ml	7.57	7.56	5.09	7.57	1.53	2.74	3.83	5.54	1.52
η , poise	358	660	455	980	270	440	700	1410	19.8
$\log J_e^0$	-5.96	-5.19	-4.87	-4.62	-3.97	-4.15	-4.06	-4.11	-3.19
η_{∞}' , poise	200	218	146	218	88.6	102	120	163.5	3.28
$\log G_{\infty}'$	5.52	5.46	5.32	5.51	4.78	5.05	5.20	5.32	4.74
$\log G_{\infty}'/\nu_2$	6.66	6.60	6.63	6.65	6.62	6.63	6.64	6.60	6.68
P_i/N	10.6	11.6	11.6	11.6	11.6	11.6	11.6	11.6	11.6
h^*	0.40	0.30	0.30	0.19	0.30	0.20	0.14	0.10	0.09
ϕ/f	2.5	1.8	1.5	1.6	1.6	1.55	1.6	1.6	2.0
$\log \tau_1$	-3.15	-2.10	-1.90	-1.59	-1.28	-1.13	-0.85	-0.65	-0.54
$\log M_{ve}/M_w$	-0.36	-0.03	0.03	0.09	0.05	0.09	0.20	0.21	0.18

^a Data of Massa, *et al.*⁴

^b Results in Aroclor 1248 ($\eta_s = 2.57$ poise).

Table II. Parameters at low and high frequencies reduced to 25°C for poly(α -methylstyrene) solutions in Aroclor 1254 ($\eta_s = 70$ poise)

Sample	BB9	BB9	BB9	BB9	A1
$M_w \times 10^{-3}$	355	355	355	355	870
$c \times 10^2$, g/ml	1.51	2.38	3.21	4.62	1.39
η , poise	270	554	941	2470	482
$\log J_e^0$	-3.80	-3.70	-3.88	-3.89	-3.00
η_{∞}' , poise	97.5	117	133	187	98.8
$\log G_{\infty}'$	4.48	4.74	4.93	5.12	4.40
$\log G_{\infty}'/\nu_2$	6.32	6.39	6.45	6.48	6.28
P_i/N	15.8	15.8	15.8	15.8	17.5
h^*	0.28	0.17	0.11	0.06	0.16
ϕ/f	1.6	1.6	1.6	1.6	1.6
$\log \tau_1$	-0.92	-0.67	-0.55	-0.24	0.0
$\log M_{ve}/M_w$	0.12	0.18	0.18	0.27	0.30

as described elsewhere.^{6,7} Measurements were performed at 5°C intervals from 10°C to 35°C for most of the samples.

EXPERIMENTAL RESULTS

Complex Modulus

Some of the results for the storage and loss moduli measurements are shown in Figures 1-3. In these figures are plotted the reduced storage modulus $G_p' = (\rho_0 T_0 / \rho T) G'$ and the reduced loss modulus $(G'' - \omega \eta_s)_p = (\rho_0 T_0 / \rho T) (G'' - \omega \eta_s)$ against the reduced angular frequency ωa_T with double logarithmic scales. Here ρ and T are the density and the absolute temperature, respectively, the subscript zero refers to the standard temperature, 25°C in this case, and η_s is the viscosity of the

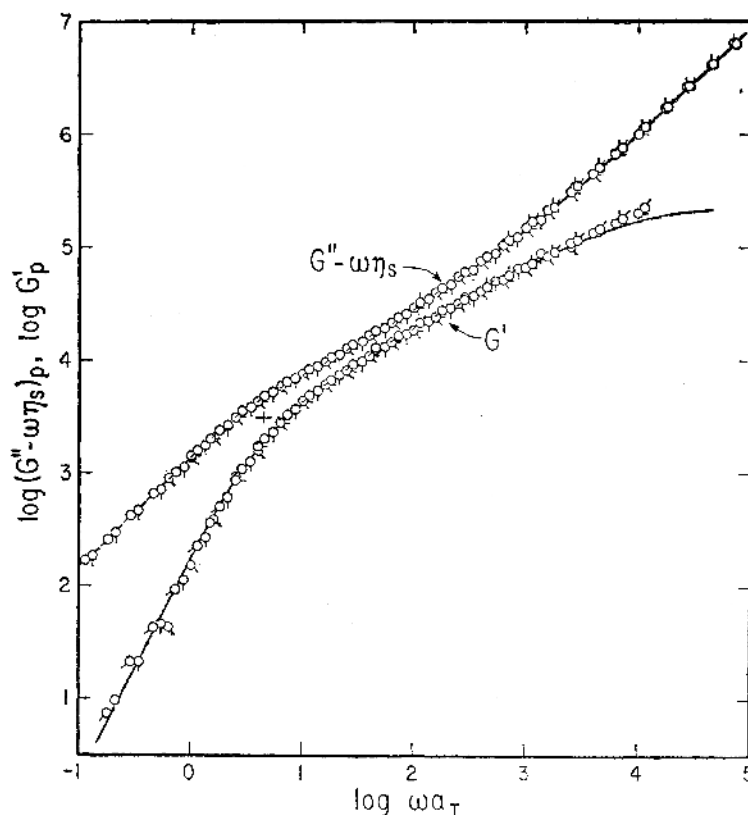


Figure 1. The storage (G_p') and the loss ($(G'' - \omega\eta_s)_p$) moduli reduced to 25°C for a polystyrene solution in Aroclor 1254. $M = 2.67 \times 10^6$ and $c = 5.54 \times 10^{-2}$ g/ml. Various directions of pips show the temperatures of measurement; pip up, 9.9°C, and 45° clockwise rotations correspond to 14.9, 19.8, 24.8, 29.7, and 34.9°C, respectively. The curves are drawn after the Peterlin theory with $N = 222$, $h^* = 0.10$, and $\phi/f = 1.6$.

solvent. The shift factor a_T was obtained from the viscosity η at the limit of small ω as $\rho T(\eta - \eta_s)_0 / \rho_0 T_0(\eta - \eta_s)$ if η was available, but otherwise from the parallel shift of $\log G_p'$ and $\log (G'' - \omega\eta_s)_p$ along the $\log \omega$ axis to get the superposition of $\log G'$ and $\log (G'' - \omega\eta_s)$ at 25°C, respectively. Successful application of the method of temperature—time reduction has already been reported for polystyrene solutions in Aroclor.⁴ This was confirmed in the present work with some additional data for polystyrene solutions as well as for poly(α -methylstyrene) solutions.

Figure 1 shows the results for a 3.62-% solution of polystyrene of $M = 2.67 \times 10^6$; they are typical of solutions of relatively high concentra-

tion and high molecular weight. The frequency dependence of the complex modulus may be conveniently described if one divides the measured frequency range into three parts. In the range of very low frequency, $\log G_p'$ and $\log (G'' - \omega\eta_s)_p$ change linearly with $\log \omega a_T$ with slopes of 2 and 1, respectively. This result is in agreement with the general theory of viscoelastic fluids. The viscosity η , the storage modulus coefficient A_G (low-frequency limit of G_p'/ω^2), and the steady shear compliance J_e^0 , two of which are independent, can be obtained from this region. At intermediate frequencies, both $\log G_p'$ and $\log (G'' - \omega\eta_s)_p$ are roughly linear functions of $\log \omega a_T$ with similar slopes (the "power-law region"). At high frequencies, the

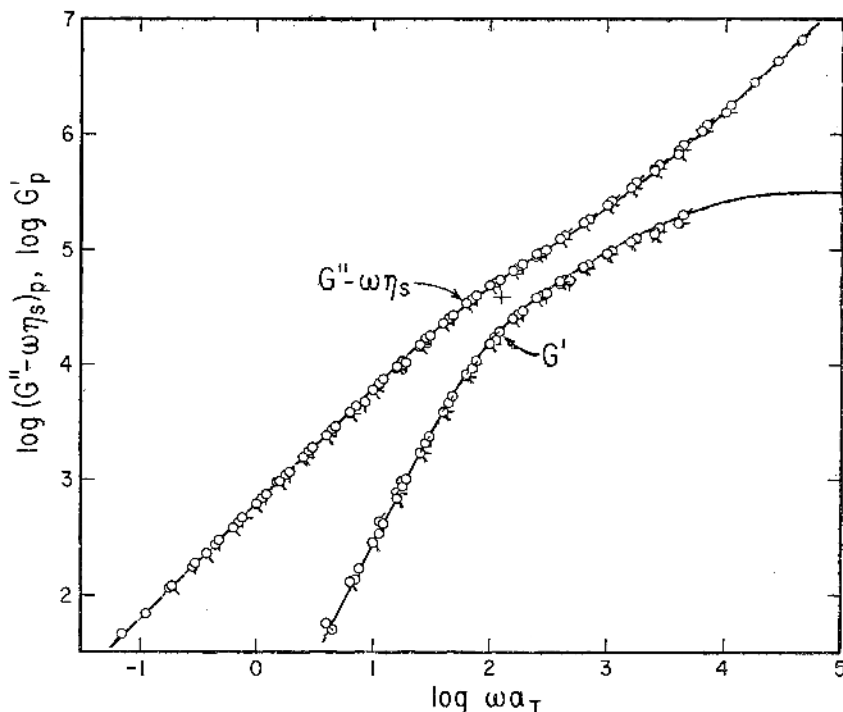


Figure 2. The storage (G_p') and the loss ($(G'' - \omega\eta_s)_p$) moduli reduced to 25°C for a polystyrene solution in Aroclor 1254. $M = 5.1 \times 10^4$ and $c = 7.56 \times 10^{-2}$ g/ml. Pip upper right indicates 15.0°C, and 45° clockwise rotations correspond to 19.9, 25.0, 30.0, and 34.9°C, respectively. The curves are drawn after the Peterlin theory with $N' = 42$, $h^* = 0.30$, and $\phi/f = 1.8$.

slope of $\log(G'' - \omega\eta_s)_p$ becomes unity again, indicating $\eta_{\infty}' \neq \eta_s$ where η_{∞}' is the limiting value of the real part of the complex dynamic viscosity at high frequency. The storage modulus measurements do not extend to such high frequencies because the precision is less satisfactory.⁶ The curves shown are calculated from the Peterlin theory, as explained below.

Figure 2 gives the results for a 5-% polystyrene solution of $M = 5.1 \times 10^4$, which are typical of low molecular weights. There is no "power-law region"; $(G'' - \omega\eta_s)_p$ goes through a slight inflection between two segments of unit slope. The ratio $(G'' - \omega\eta_s)_p/G_p'$ is larger in this region than in Figure 1. Thus the main qualitative difference between Figure 1 and Figure 2 is in the power-law region.

Figure 3 shows one of the results for poly(α -methylstyrene) of 3.55×10^5 molecular weight. No special difference from Figure 1 is found in

this figure as far as the qualitative features are concerned. The frequency dependences of the complex modulus for other samples are also similar to those shown in Figures 1—3 or are of intermediate nature, so the original graphs are not shown. The quantities η_s , η_{∞}' , and J_e^0 are given in Tables I and II for all the systems examined.

Viscosity at High Frequencies

We will examine here the molecular weight and concentration dependence of the limiting value η_{∞}' at high frequency. The data given by Massa⁴ will be included in the discussion.

Among possible methods of expressing the concentration dependence, the plot of $\log(\eta_{\infty}'/\eta_s)$ vs. c is useful as shown in Figure 4, where c is the concentration in g/ml. Figure 4 includes the data of Massa⁴ and the present work as well as the results of Moore obtained for solutions of polystyrene S108 in dibutyl phthalate at very

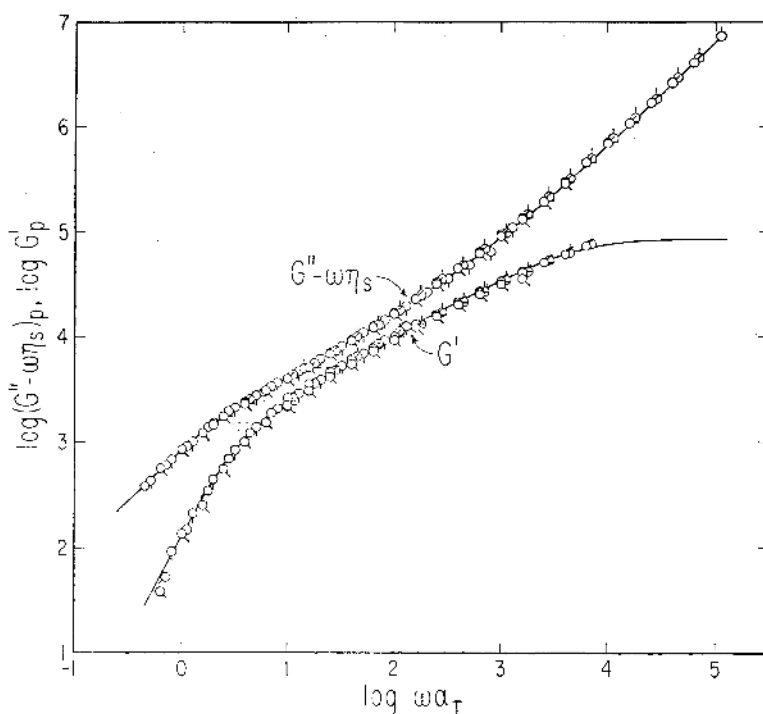


Figure 3. The storage (G') and the loss ($(G'' - \omega\eta_s)_p$) moduli reduced to 24°C for a poly(α -methylstyrene) solution in Aroclor 1254. $M = 3.55 \times 10^6$ and $c = 3.21 \times 10^{-2}$ g/ml. Pip up indicates 10.0°C, and 45° clockwise rotations correspond to 14.9, 19.8, 24.9, 29.7, and 34.9°C. The curves are after the Peterlin theory with $N=190$, $h^*=0.11$, and $\phi/f=1.6$.

high frequency.³ Moore's results were obtained at such high frequencies that the significance of a comparison with the other values is uncertain but they are included for the convenience of readers. The following points are obvious from Figure 4.

(i) η_{∞}' does not depend on the molecular weight of the polymer unless the molecular weight is extremely low (below 5×10^4).

(ii) $\log(\eta_{\infty}'/\eta_s)$ is approximately a linear function of c up to the highest concentration investigated in this study, *i.e.*, 7.6×10^{-2} g/ml.

(iii) For different species of polymers, η_{∞}' is different. The intrinsic viscosities at high frequency, $[\eta']_{\infty}$, as obtained from the slope of the lines in Figure 4, are 14.3 and 22.2 ml/g for polystyrene and poly(α -methylstyrene), respectively. The former value agrees with very recent measurements of Cooke and Matheson⁹ on polystyrene in di-(2-ethyl hexyl) phthalate in the frequency

range from 35 to 100 kHz, from which $(\eta_{\infty}' - \eta_s)/\eta_s c$ appears to be near 14 ml/g for molecular weights from 1 to 4×10^5 and a concentration of about 0.01 g/ml. From Moore's data³ for polystyrene in dibutyl phthalate in the frequency range 23 to 100 MHz, however, this value is distinctly lower, 6.8 ml/g. Possibly at these much higher frequencies the phenyl groups do not contribute to the energy dissipation (see Discussion).

(iv) The relative viscosity at high frequency, η_{∞}'/η_s , does not seem to depend on the solvent viscosity in the Aroclor solvents. This is suggested by the results for a polystyrene solution in Aroclor 1248 (viscosity 2.57 poise at 25°C) shown in Figure 4 and also by the fact that the time-temperature superposition is successfully applied to those systems and the shift factors are not different from those of the solvent itself (for these low concentrations).

Another more familiar type of plot of η_{∞}' is

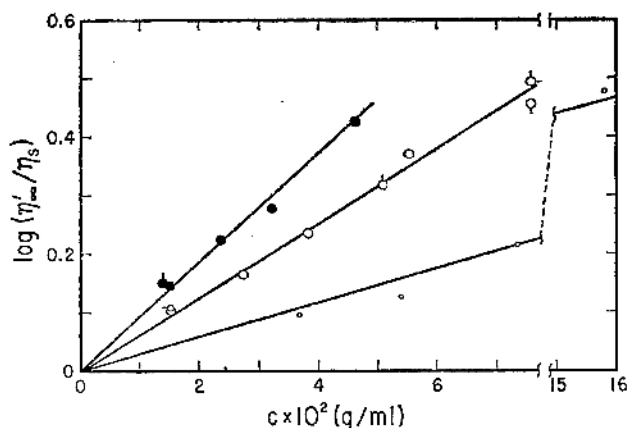


Figure 4. The plot of $\log(\eta'_{\infty}/\eta_s)$ vs. c . Open circles are for polystyrene and various directions of pips indicate molecular weights: no pip, 2.67×10^5 ; up, 8.2×10^4 ; right, 5.1×10^4 ; down, 1.98×10^4 and left, 8.6×10^5 . Various sizes of the circles represent various solvents; large circles, Aroclor 1254 ($\eta_s=70$ poise); medium, Aroclor 1248 ($\eta_s=2.57$) and small, dibutyl phthalate (0.164).³ Filled circles are for poly(α -methylstyrene) in Aroclor 1254. No pip, $M=3.55 \times 10^6$ and pip up, $M=8.7 \times 10^6$.

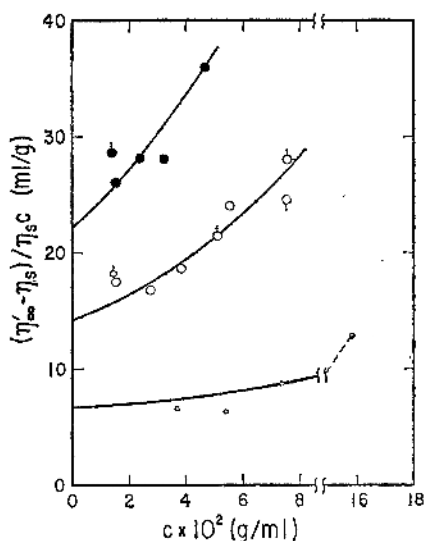


Figure 5. The plot of $(\eta'_{\infty} - \eta_s)/\eta_s c$ vs. c . The meaning of the circles is the same as in Figure 4.

shown in Figure 5. In this figure, the high-frequency specific viscosity divided by c , $(\eta'_{\infty} - \eta_s)/\eta_s c$, is plotted against c . It is qualitatively not much different from the graphs in which $(\eta - \eta_s)/\eta_s c$ is plotted against c except that the extrapolated values at $c \rightarrow 0$ as well as the slopes are small and are independent of molecular weight. The Huggins constant k' at high fre-

quency is about 0.5, as expected from the linearity of the plot of Figure 4.¹⁰ So the features of Figure 5 may be described as follows: the relation between $(\eta'_{\infty} - \eta_s)/\eta_s c$ and c for any molecular weight is very similar to that of $(\eta - \eta_s)/\eta_s c$ for a low molecular weight (about 15000 for polystyrene). The weak dependence of η'_{∞} on c is a consequence of the low value of $[\eta']_{\infty}$, not a low value of k' .

DISCUSSION

Viscosity at High Frequencies

Here the possible origin of the finite value of $\eta'_{\infty} - \eta_s$ for dilute polymer solutions will be discussed. First, it may be pointed out that a simple relation $\ln(\eta'_{\infty}/\eta_s) = [\eta']_{\infty} c$ applies over the rather wide range of concentration investigated. Expressed in differential form, $d\eta'_{\infty}/dc = [\eta']_{\infty} \eta'_{\infty}$. This type of concentration dependence is theoretically expected if the viscosity increment due to one element corresponds to a constant relative increment of the viscosity independent of the concentration.^{9,11}

Now, from a phenomenological aspect, finite $\eta'_{\infty} - \eta_s$ must be due to either (i) a purely dissipative mechanism, or (ii) relaxation mechanisms with such short relaxation times that they are essentially separated from the shortest relaxa-

tion time of the fairly continuous relaxation spectrum observed in this study. The latter conjecture follows from the fact that the dynamic viscosity changes little over an appreciable range of high frequencies. If the finite value of $\eta_{\infty}' - \eta_s$ is caused by the motion of the polymer molecule itself, the latter must be highly localized, since there is no dependence on molecular weight. Examples could be the rotational vibration of a certain portion of the main chain around the main chain axis or the motion of side groups.¹² There is an indication of high-frequency relaxation mechanism, with a relaxation time corresponding to frequencies slightly higher than those observed in this study, for polystyrene solutions in Aroclor 1248 in the study of oscillatory flow birefringence, which appears to be related to local motions of the phenyl groups.¹³ Such a phenomenon might also account for the difference between our values (and those of Cooke and Matheson's) and those of Moore.

Another possibility is that the nature of the solvent is changed by addition of the polymer, resulting in an altered effective η_s . If the latter is increased, $\eta_{\infty}' - \eta_s$ may be finite and positive even if the motion of the polymer chain itself is of purely relaxational nature. The effect on the viscosity could be interpreted in terms of a decrease in average free volume.¹⁴ Alternatively, one might assume some particular structure insensitive to the temperature and specific for the configuration of Aroclor and polystyrene or poly(α -methylstyrene); for example, a sheath of solvent interacting with the polymer chain which could restrict motions of the chain independent of the flow field in the remainder of the solvent.⁴ This model is consistent with the result of flow birefringence studies indicating that some solvent molecules are oriented in the neighborhood of each polymer chain.¹⁵

Frequency Dependence of G' and G'' ; Limiting High-Frequency Value of G'

The data of Figures 1 and 3 were fitted to the Thurston—Peterlin formulation¹⁶ of the Peterlin theory,¹⁷ which is a modification of the Rouse—Zimm bead-spring theories⁵ to account for an intramolecular energy loss accompanying configurational changes. The parameters here are the finite number of submolecules N , the

reduced hydrodynamic interaction parameter $h^*(=h/N^{1/2}$, where h is the hydrodynamic interaction parameter of the Zimm theory), and the ratio ϕ/f which is a measure of the ratio of the inner friction to the environmental friction opposing configurational changes. For polystyrene, N was chosen primarily on the basis of earlier analysis of birefringence data,¹⁸ as in ref 4. For poly(α -methylstyrene), no birefringence data are available and the assignment of parameters is somewhat less certain. The parameters are included in Tables I and II, and the curves drawn from the theory with these parameters fit the data extremely well as is seen in Figures 1 and 3, even though the theory applies strictly only at infinite dilution whereas these polymer concentrations are appreciable. (However, this agreement is concerned with the shape of the frequency dependence only; the calculated magnitudes of G' and G'' have been adjusted slightly as indicated by the position of the cross in each figure, whose ordinate corresponds to $G_{\pm} = cRT/M$ in the theory. The experimental value of G_{\pm} gives a molecular weight M_{app} which is usually higher than the true molecular weight but approaches it as the concentration decreases, as shown by the ratio M_{app}/M in the tables.)

The Peterlin theory predicts limiting high-frequency values for G' , as is apparent in Figures 1—3. These values of G_{∞}' are listed in Tables I and II, as well as the ratio G_{∞}'/v_2 , where v_2 is the volume fraction of polymer. Although in principle confirmation can be obtained from a direct experimental value of G_{∞}' evaluated from integration of G'' data,⁴ the present data are not sufficiently extensive for this purpose. However, the process of obtaining G_{∞}' from the Peterlin theory may be regarded as a phenomenological extrapolation of the data independent of the assumptions of the theory itself.

The ratio G_{∞}'/v_2 , given in the Tables, is approximately a constant for polystyrene over the whole range of c and M employed. It seems to increase slightly with increasing concentration for poly(α -methylstyrene), but this is not certain. It may be safely stated that G_{∞}'/v_2 does not change much with M or c and its value for polystyrene solutions is larger than that for

poly(α -methylstyrene) solutions by a factor of about 1.5 to 2.

Significance of the Peterlin Parameters

The Peterlin parameter N is determined almost uniquely. It is interesting to note that P/N , where P is the degree of polymerization, is approximately a constant for one polymer species and is about 50-% higher for poly(α -methylstyrene) than for polystyrene. So, in the sense of Peterlin theory, a segment is composed of about 11 and 16 monomer units for polystyrene and poly(α -methylstyrene), respectively. This might be reasonable if one considers the difference in stiffness of these polymers. The other parameters h^* and ϕ/f have some arbitrariness in curve fitting. The value of 1.6 for ϕ/f was used for most of the calculations for convenience, but approximately the same result could have been obtained if 1.8 were used and h^* changed to compensate. It is not sensitive to the change of molecular weight, concentration or polymer species. The parameter h^* is regarded as describing the degree of hydrodynamic interaction between segments. Apparently it decreases with increasing molecular weight and concentration. This result implies that concentration dependence has to be included in the theory if one wants to discuss the significance of h^* for finite concentrations.

Now let us turn the attention to the frequency dependence. It is remarkable how well the Peterlin theory can reproduce the data of the complex modulus up to the highest frequencies measured, where leveling off of the storage modulus starts to appear (see Figure 2). Additional, even better examples of curve fitting have been reported elsewhere.⁴

One interesting point is that one can never obtain such good curve fitting by adding a constant viscosity term to the theories of Rouse, Zimm or any of their modifications not including additional energy dissipation. The main defects of such a constant viscosity addition are:

(i) The change of G' at the high frequency end of the lower region is too sharp; the power law region persists up to too high frequency and then G' suddenly becomes constant so that the observed gradual change of G' in this range cannot be described.

(ii) The number of modes N' calculated from

G_{∞}'/v_2 for this method as $N' = MG_{\infty}'/v_2RT$ are smaller than N given by the Peterlin theory by a factor of about 5 for both of the polymers: P/N' is about 60 and 90 for polystyrene and poly(α -methylstyrene), respectively as compared to 11 and 16 for the value of P/N . These values of N' are too small to explain the wide span of the relaxation spectrum observed.

This failure of adding a purely dissipative mechanism to the simple spring-bead contributions eliminates the suggested mechanism (i) of the preceding section as the origin of finite $\eta_{\infty}' - \eta_s$. On the other hand, this failure should be expected because the simple spring-bead theories probably should not be applied at such high frequencies. A model for the worm-like chain was proposed by Hearst and Harris to describe the high-frequency behavior,¹⁹ but the hydrodynamic properties of the model have not been investigated yet.

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