Creep Behavior of Polymer Solutions. IV. Polystyrene in Chlorinated Diphenyl below M_c

Yoshiyuki Einaga,[1a] Kunihiro Osaki,[1a] Michio Kurata,*[1a] Tsutomu Sugie,[1b,c] and Mikio Tamura[1b]

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan, and Department of Industrial Chemistry, Kyoto University, Sakyo, Kyoto 606, Japan. *Received February 27, 1973*

ABSTRACT: The creep compliance was measured for concentrated solutions of polystyrenes of low molecular weights ($M = 1.98 \times 10^4$ and 5.1×10^4) in chlorinated diphenyl. The ranges of concentration and temperature studied were $0.5 < c < 0.7$ g/ml and $0 < T < 70°$, respectively. The time-concentration reduction method was applied to the relaxation moduli which were calculated from the creep compliances at various concentrations. The reduction was applicable over the whole range of time scale except for the range of very long time for $M = 5.1 \times 10^4$. The shift factor a_c at high concentrations depended on the molecular weight, reflecting the molecular weight dependence of the segmental friction coefficient ζ in the polymer solutions. The free volume theory was applied to a_c to examine the properties of ζ. It was revealed that the free volume theory may be applicable over a wide range of concentration for polystyrene in chlorinated diphenyl. The viscosity divided by ζ was proportional to $(cM)^{1.0}$ if the molecular weight dependence of ζ was taken into account. The rubbery plateau region was absent in the relaxation moduli. The shape of the relaxation moduli was reproduced by the Rouse theory if the molecular weights were modified: M for calculation of theoretical values had to be about 60% higher than real M. The steady-shear compliance was approximately proportional to c^{-2} and was higher than the value predicted by the Rouse theory. These results were compared with dynamic properties of moderately concentrated solutions of high molecular weight polystyrenes. The shape of the relaxation spectra kept on varying gradually down to low concentrations for the latter solutions and the rubbery plateau region was observed even at low concentrations.

A number of studies have been devoted to the viscoelastic properties of polymer solutions.[2a] It is believed now that a type of intermolecular interaction called the entanglement coupling is responsible for the typical mechanical properties at long time scale of polymer concentrates of high molecular weight. Examples of such mechanical properties are the very strong dependence of the viscosity on molecular weight and the existence of a wide range of time scale where the relaxation modulus varies very little with varying time. These properties are observed only for systems whose molecular weight M is higher than a critical molecular weight M_c. The critical molecular weight M_c depends on the concentration for each combination of the polymer and solvent and it is believed to be related to the entanglement spacing or the "molecular weight" of the fraction of polymer chain between neighboring entanglement points. The critical molecular weight may be evaluated most conveniently from the molecular weight dependence of the viscosity η.[2a,b] It is well known that η is proportional to a very high power (typically 3.4) of M if M is higher than M_c and otherwise to M after a small correction for the molecular weight dependence of the segmental friction coefficient (in fact, this is the definition of M_c)

$$\begin{aligned} \eta &= KM^{3.4} \qquad M>M_c \\ &= K'M^{1.0} \qquad M<M_c \end{aligned} \tag{1}$$

where K and K' are constants independent of M. The critical molecular weight M_c is inversely proportional to the volume fraction v_2 of polymer for many systems.[2a,b]

$$v_2 M_c = M_{c0} \tag{2}$$

where M_{c0} is the critical molecular weight for the undiluted polymer and is about 4×10^4 for polystyrene.

In the preceding papers of this series,[3-5] we have reported creep behavior of polystyrene in chlorinated diphenyl in the range of molecular weight higher than the critical molecular weight. Dependences on M, concentration c and temperature T of the creep compliance $J(t)$ were discussed in three regions of time scale, namely, transition region, plateau region, and flow region. The strength of creep compliance in the plateau region is characterized by its value J_{inf} corresponding to the inflection point in the plot of log J *vs.* log t. J_{inf} was independent of M and inversely proportional to the second power of c. The mechanical behavior in the long time scale is characterized by the viscosity η and the steady-state compliance J_e^0. It was revealed that a relation analogous to that of Berry and Fox[6] holds for polystyrene in chlorinated diphenyl

$$\eta/a_c \propto (cM)^{3.4} \tag{3}$$

where a_c is the shift factor of the time-concentration reduction in the transition region. The steady-state compliance J_e^0 was independent of M and inversely proportional to the third power of c when M and c were sufficiently high. However, J_e^0 became to be dependent on M and varied in a complicated manner with varying c when the product cM approached 4×10^4, the reported value of M_{c0} in eq 2 for polystyrene. Here c is the concentration in g/ml and its value is close to that of v_2. It was suggested that the strengths of relaxation modes of very long relaxation times are proportional to the third or higher power of c while those corresponding to the plateau region to the second power of c. Such a variation of strength of relaxation modes with varying relaxation time is not explained on the molecular basis with the use of current theories for entangled systems.[2a]

In this paper, we will give the experimental results on

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(1) (a) Institute for Chemical Research, Kyoto University, Uji; (b) Department of Industrial Chemistry, Kyoto University, Kyoto; (c) UNITIKA Co. Ltd., Tonouchi, Uji, Japan.

(2) (a) See, for example, J. D. Ferry, "Viscoelastic Properties of Polymers," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1970. (b) See, for example, R. S. Porter and J. F. Johnson, *Chem. Rev.*, **66**, 1 (1966).

(3) K. Osaki, Y. Einaga, M. Kurata, and M. Tamura, *Macromolecules*, **4**, 82 (1971).

(4) Y. Einaga, K. Osaki, M. Kurata, and M. Tamura, *Macromolecules*, **4**, 87 (1971).

(5) Y. Einaga, K. Osaki, M. Kurata, and M. Tamura, *Macromolecules*, **5**, 635 (1972).

(6) G. C. Berry and T. G Fox, *Advan. Polym. Sci.*, **5**, 261 (1968).

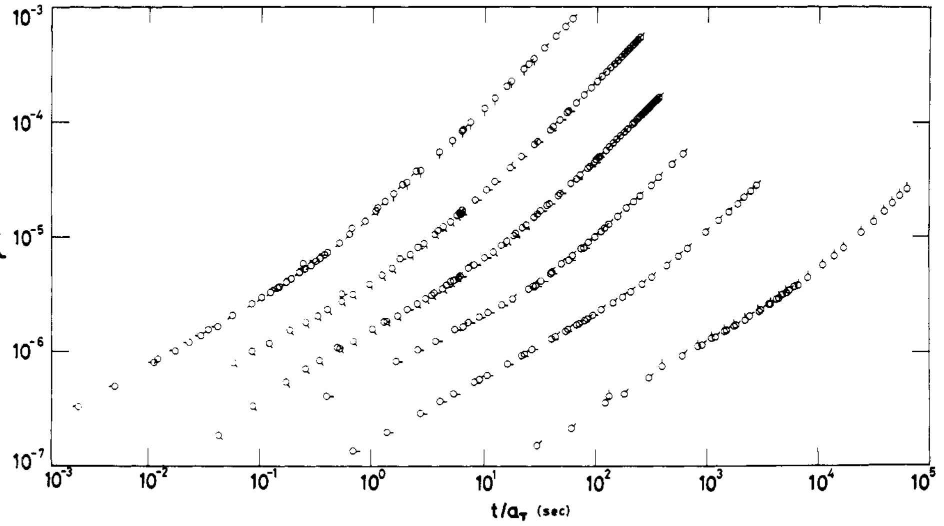

Figure 1. Plots of creep compliance $J_p(t)$ reduced to 30° against reduced time t/a_T for solutions of polystyrene **7a** in Aroclor 1248. Concentrations in g/dl are 45.71, 51.80, 56.96, 61.94, 67.33, and 71.14, respectively, from top to bottom. Various directions of pips represent temperatures; pip up, 40° and successive 45° rotations clockwise correspond to 30, 20, 10, 15, 7.5, and 0°, respectively.

dynamic properties of solutions of polystyrene in chlorinated diphenyl corresponding to the molecular weight near or below the critical value. The properties observed are expected to be those for systems in which the entanglement coupling is not fully developed or absent. There are two ways to approach the critical molecular weight in the case of polymer solutions; one is to decrease M while keeping c constant and the other to decrease c while keeping M constant. Since the systems of high M and low c have relatively low viscosities, they are not suitable for creep measurements. Measurements of dynamic complex modulus are employed instead for these systems.

Experimental Section

Materials. The polymer solutions studied are concentrated solutions of standard polystyrenes **2a** and **7a** and moderately concentrated solutions of **1b′**, **3a**, **6a**, and **14a** supplied from the Pressure Chemical Co., in chlorinated diphenyl (Aroclor 1248). The weight-average molecular weights M_w are 1.98×10^4, 5.1×10^4, 2.00×10^5, 4.11×10^5, 8.6×10^5, and 1.80×10^6, respectively, and the ratios of M_w to the number-average molecular weight M_n are 1.06, 1.06, 1.06, 1.06, 1.15, and 1.25, respectively. The solvent, Aroclor 1248 supplied from Monsanto Chemical Co., is a mixture of partially chlorinated diphenyl. Its viscosity and density at various temperatures were given in a previous publication.[4] Preparation of the polymer solutions has also been described before.[4]

Measurements. Measurements of the creep compliance and the creep recovery for concentrated solutions of **2a** and **7a** were performed with the creep apparatus reported in the previous paper.[3] The maximum shear strain applied was approximately 1 shear unit. The stress dependence of creep compliance was not observed under this condition. Dynamic moduli were measured for moderately concentrated solutions of the samples **1b′**, **3a**, **6a**, and **14a** with a rheometer of a coaxial cylinder type. Details of the apparatus and measurements can be found elsewhere.[7,8] Measurements for each solution were performed at various temperatures in the range of 0-70°.

Results and Discussion

Creep Compliance. The creep compliance $J(t)$ was measured for high c-low M systems; solutions of **2a** ($0.57 < c < 0.71$ g/ml) and of **7a** ($0.46 < c < 0.71$). The creep compliance at various temperatures were reduced to a reference temperature for each solution by the method of reduced variables;[2a] that is, log $J_p(t)$ obtained at various temperatures was plotted against log t/a_T to attain a single composite curve, where $J_p(t) = J(t)\rho T/\rho_0 T_0$ is the reduced creep compliance, ρ is the density of the solution, a_T is a function of T and the subscript 0 implies the reference temperature. The shift factor a_T was empirically determined so as to obtain the best superposition of the data. The composite curve for the solutions of the sample **7a** of various concentrations are shown in Figure 1. A reference temperature of 30° was chosen. It is seen that $J_p(t)$ increases monotonically with increasing time. In the range of very short time, $J_p(t)$ is of the order of 10^{-7} cm^2/dyn and there is a wide range of time scale where the slope of the curve is a little higher than ½ and approximately the

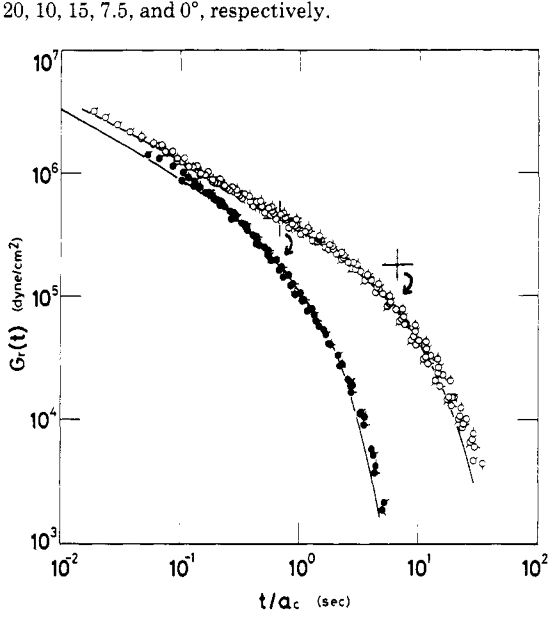

Figure 2. Reduced relaxation modulus $G_r(t)$ plotted against reduced time t/a_c for solutions of polystyrenes **7a** (open circles) and **2a** (closed circles). Various directions of pips represent concentrations; for open circles, pip up 71.14 g/dl and successive 45° rotations clockwise correspond to 67.33, 61.94, 56.96, 51.80, and 45.71, respectively; for closed circles, pip up, 70.98 g/dl and successive 45° rotations clockwise correspond to 67.79, 61.82, and 56.94, respectively. Reference concentrations c_r are 56.96 for **7a** and 56.94 g/dl for **2a**. Solid lines represent theoretical curves by Rouse theory with modification given in text. Crosses indicate the longest relaxation time τ_1 on abscissa and cRT/M on ordinate for each theoretical curve.

(7) T. Kotaka and K. Osaki, *Bull. Inst. Chem. Res. Kyoto Univ.*, **39**, 331 (1961).

(8) K. Osaki, M. Tamura, M. Kurata, and T. Kotaka, *J. Phys. Chem.*, **69**, 4183 (1965).

Table I
Shift Factor a_c, Viscosity η, and Steady-State Compliance J_e^0 for Polystyrene in Aroclor 1248 at 30°[a]

Code	M_w	c (g/dl)	a_c	η (P)	J_e^0 (cm^2/dyne)	
14a	1.80×10^6	14.00		1.1×10^5	1.5×10^{-4}	(62°)
		10.51		3.0×10^4	3.2×10^{-4}	(40°)
		6.98		2.8×10^3	4.85×10^{-4}	(40°)
		4.22		3.2×10^2	1.07×10^{-3}	
6a	8.60×10^5	14.03		1.3×10^4	9.0×10^{-5}	
		10.53		3.1×10^3	2.1×10^{-4}	
		6.98		4.2×10^2	3.7×10^{-4}	
		4.20		8.0×10^1	5.2×10^{-4}	
3a	4.11×10^5	16.83		3.2×10^3	8.8×10^{-5}	
		14.03		1.18×10^3	7.6×10^{-5}	
		10.51		3.3×10^2	7.0×10^{-5}	
		7.06		8.0×10^1	1.3×10^{-4}	
		4.24		2.3×10^1	1.8×10^{-4}	
lb′	2.00×10^5	21.02		1.8×10^3	3.6×10^{-5}	
		16.81		5.5×10^2	2.2×10^{-5}	
		14.05		2.5×10^2	3.2×10^{-5}	
		10.51		9.5×10^1	3.3×10^{-5}	
		7.02		2.7×10^1	3.4×10^{-5}	
7a	5.10×10^4	71.14	8.70×10^2	2.4×10^9	1.31×10^{-6}	(40°)
		67.33	4.35×10^1	1.07×10^8	1.42×10^{-6}	
		61.94	5.26×10^0	1.22×10^7	1.80×10^{-6}	
		56.94	1	2.26×10^6	2.10×10^{-6}	(20°)
		51.80	2.22×10^{-1}	4.63×10^5	2.90×10^{-6}	(20°)
		45.71	4.55×10^{-2}	7.9×10^4	2.90×10^{-6}	(16.5°)
2a	1.98×10^4	70.98	1.79×10^2	1.55×10^8	4.0×10^{-7}	
		67.79	3.85×10^1	2.76×10^7	5.4×10^{-7}	
		61.82	4.55×10^0	2.79×10^6	6.4×10^{-7}	(20°)
		56.94	1	5.05×10^5		
		51.15		7.14×10^4		

[a] Some of the data for J_e^0 were obtained at temperatures different from 30° as indicated.

same for all the solutions studied. The slope begins to increase with increasing time in the intermediate time scale and rapidly approaches 1 in the long time region. The inflection point, clearly observed[5] in the plot of log J_p *vs.* log t/a_T for solutions satisfying $cM \gg 4 \times 10^4$, is not seen here. It is deduced that the rubbery plateau region of the relaxation spectrum does not exist for these solutions of low molecular weight. The creep compliance for these systems is characterized by two regions, the transition region with the slope of about ½ and the flow region of about 1. This result is in sharp contrast with that for samples of high molecular weights. The creep compliance shifts to the longer time scale with increasing concentration. Similar results were obtained for the solutions of the sample **2a**.

Time-Concentration Reduction. Creep compliances $J_p(t)$ (reduced to 30°) for the samples **2a** and **7a** were transformed into relaxation moduli $G_p(t)$ by an approximation method.[9] The values of $G_p(t)$ smaller than 10^4 dyn/cm^2 may include large error because d log $J_p(t)$/d log t was larger than 0.9 in these cases. Relaxation moduli for various concentrations were combined by the time-concentration reduction method to give the reduced relaxation modulus for each molecular weight with the use of the reduced variables[10a]

$$G_r(t) = f(c)G_p(t) \text{ and } t/a_c \qquad (4)$$

with $f(c) = c_r/c$, where the subscript r implies the quantity at the reference concentration. The time-concentration reduction with $f(c) = c_r/c$ is supposed to be applicable in the transition region. On the other hand, the reduction in the flow region requires that $f(c) = J_e^0/J_{er}^0$.[10b] It has been revealed that this function is much different from c_r/c for highly entangled systems.[2a,5]

The results of reduced plots with $f(c) = c_r/c$ are shown in Figure 2 where 0.570 g/ml is chosen as c_r and the shift factors a_c, given in Table I, were empirically determined to attain the best superposition of the data for various concentrations in the range of relatively short time scale. It is seen that relaxation moduli of the polymer of the lower molecular weight (**2a**) can be reduced to a single composite curve except at very short time scale where the data are rather scanty. On the other hand, relaxation moduli for the sample **7a** are not reduced so well in the range of long time scale, *i.e.*, $G_r(t)$ for higher concentrations is higher (or lies in the longer time scale). This deviation in the flow region reflects the difference between c_r/c and J_e^0/J_{er}^0 for this sample in the range of concentration studied. It may be concluded that $f(c)$ may be chosen as c_r/c over the whole range of time scale if the molecular weight is very low (the product cM is 1.4×10^4 for the highest concentration of the solutions of **2a**). As the molecular weight is increased, a small deviation appears in the flow region even if cM is smaller than 4×10^4, the value of M_{c0} for polystyrene in eq 2. The deviation may correspond to the initial stage of the entanglement coupling.

Another point to be made concerning this figure is that the reduced relaxation moduli for samples of different molecular weights are different in the transition region. G_r for the sample **7a** is about 20% higher or lies in the longer time scale by a factor of about 1.7 than that for **2a**. This result is in contrast with that for high molecular weight systems for which the reduced relaxation moduli do not depend on M in the transition region.[2a,5] We will discuss this point later.

Shift Factor a_c and Segmental Friction Coefficient. Figure 3 shows the concentration dependence of the shift factor a_c obtained above in the time-concentration reduction. Circles represent the results for low M samples. The solid line represents the shift factor for high M samples, given in the previous paper,[5] reduced to the same refer-

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(9) H. Leaderman in "Rheology," F. R. Eirich, Ed., Vol. 2, Academic Press, New York, N. Y., 1958. See also chapter 4 of ref 1.

(10) (a) Reduced variables may be chosen as $J_r(t) = [J_p(t) - t/\eta]/f(c)$ and t/a_c instead of eq 4. Variables of eq 4 were chosen because the errors in subtracting t/η from $J_p(t)$ and in transforming $J_p(t)$ into $G_p(t)$ are about the same and because $G_p(t)$ is more familiar in the treatment of liquids. (b) H. Markovitz, *J. Phys. Chem.*, 69, 671 (1965).

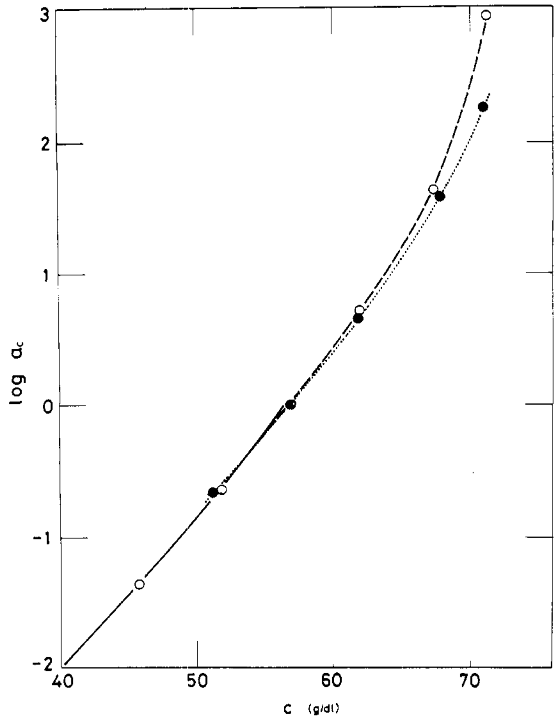

Figure 3. Concentration dependence of shift factor a_c for polystyrenes **7a** (open circles) and **2a** (closed circles) in Aroclor 1248 at 30°. Solid line indicates a_c for polystyrenes of high molecular weights reported before.[5] Reference concentration c_r is 56.96 g/dl.

ence concentration that is used for low M samples of the present study. It is obvious that a_c for low M systems are in agreement with that for high M systems in the range of relatively low concentration ($c < 0.57$ g/ml) where measurements are performed for both systems. It is also observed that there is no difference in a_c for samples **2a** and **7a** in this range of concentration. However, a_c for the sample **7a** begins to increase more rapidly at the concentration of about 0.60 g/ml and the difference increases with increasing concentration. The molecular weight dependence of a_c has not been observed so far. Since a_c represents the concentration dependence of the segmental friction coefficient ζ, this result probably implies the existence of the molecular weight dependence of ζ for the polymer solution of very low molecular weight (The molecular weight dependence of ζ has been observed for undiluted polymers.[2a]), and may be responsible for the difference in $G_r(t)$ in the transition region for two samples in Figure 2.

The concentration dependence of a_c may be interpreted in terms of the concept of the free volume. If one assumes that the fractional free volume f is linearly dependent on concentration, one obtains[11,12]

$$f(v_1) = f(v_{1r}) + \beta(v_1 - v_{1r}) \quad (5)$$

$$-1/2.303 \log a_c = f(v_{1r}) + [f(v_{1r})]^2/\beta(v_1 - v_{1r}) \quad (6)$$

where β is a constant and v_1 the volume fraction of the solvent. Equation 6 indicates that a straight line should be obtained when $-1/\log a_c$ is plotted against $1/(v_1 - v_{1r})$. The plot is shown in Figure 4 for solutions of **2a** and **7a**. Straight lines are obtained for each sample over the whole range of concentration studied. The constants $f(v_{1r})$ and β were evaluated as 0.035 and 0.037, respectively, for **7a** and 0.038 and 0.042, respectively, for **2a**. The observed

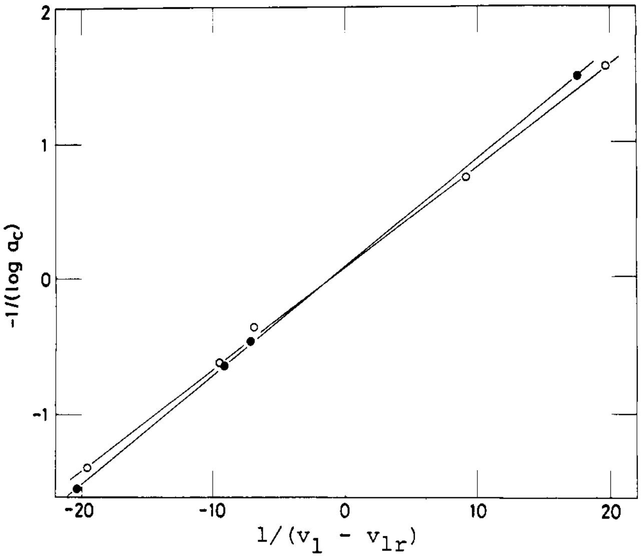

Figure 4. $-1/\log a_c$ plotted against $1/(v_1 - v_{1r})$ for polystyrenes **7a** (open circles) and **2a** (closed circles) in Aroclor 1248 at 30°.

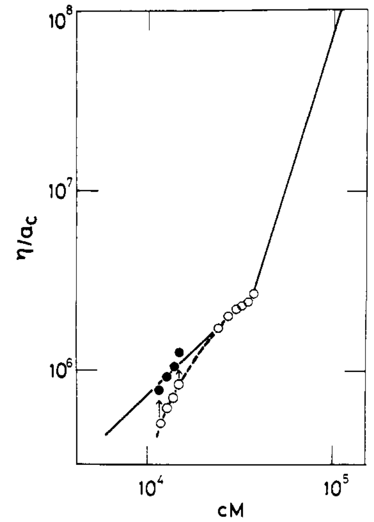

Figure 5. Ratio of viscosity η to shift factor a_c plotted against cM in double logarithmic scale (open circles) for polystyrenes **7a** (upper five points) and **2a** (lower four) in Aroclor 1248 at 30°. Closed circles represent η/a_c after correction for molecular weight dependence of a_c for **2a**. Straight line to the right indicates η/a_c reported before.[5] Straight line to the left is drawn with slope 1.

difference in $f(v_{1r})$ corresponds to about 10 for the ratio of the segmental friction coefficients at the reference concentration for these two samples if the relation $\zeta \propto e^{1/f}$ is assumed. This ratio is too large to explain the difference in $G_r(t)$ in the transition region for these samples. However, the evaluated value of the ratio may not be very significant since a slight error in $f(v_{1r})$ can cause a large deviation in the friction coefficient. The fraction of free volume for the undiluted polymer at 30° is estimated by extrapolation with the use of eq 5 as about 0.02 for both samples, which is of a reasonable magnitude as compared with 0.025 evaluated with the use of the universal constants in the WLF equation at the glass transition temperature.[2a] This last result implies that eq 5 and 6 may hold well up to higher concentrations (including undiluted polymers) with the same set of parameters that are obtained in the concentration range of this study.

Viscosity and Steady-State Compliance. The viscosity η at 30° was evaluated from the reduced creep compliance as shown in Figure 1 and given in Table I. It depends very

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(11) H. Fujita and A. Kishimoto, *J. Chem. Phys.*, **34**, 393 (1961).

(12) A. Teramoto, R. Okada, and H. Fujita, *J. Phys. Chem.*, **67**, 1228 (1963).

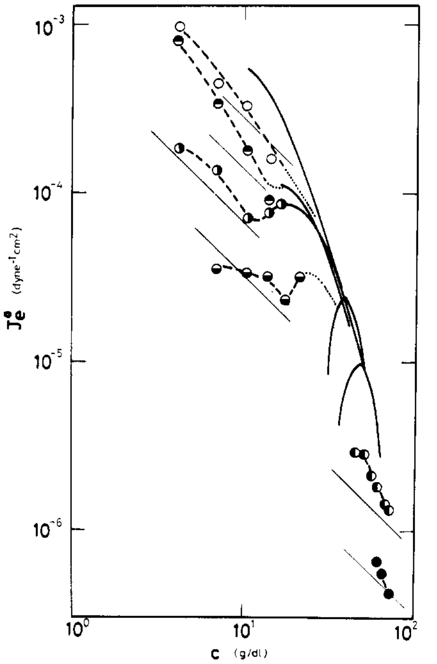

Figure 6. Steady-state compliance J_e^0 plotted against concentration c for polystyrene in Aroclor 1248. Various types of circles represent molecular weights; open circles, 1.80×10^6; up-half black, 8.6×10^5; right-half black, 4.11×10^5; down-half black, 2.00×10^5; left-half black, 5.1×10^4; closed circles, 1.98×10^4. Thick solid lines represent J_e^0 reported before[4], and thin solid lines prediction of Rouse theory.

strongly on the concentration. It has been pointed out that the very strong dependence of η on c for polystyrene in chlorinated diphenyl is due to the concentration dependence of the segmental friction coefficient ζ.[5,6] Since the shift factor a_c represents the concentration dependence of ζ, the part of the concentration dependence of η due to that of ζ may be eliminated by dividing η by a_c. The ratio η/a_c is plotted against the product cM for solutions of **2a** and **7a** in Figure 5. Here the open circles are the results for **2a** and **7a** and the solid line with the higher slope is the result for high M samples given in the previous paper[5] (with a_c reduced to the same reference concentration that is used in the present study). The data for the sample **7a** are approximately on a straight line of slope 1 which meets the other straight line of the slope 3.4 at $cM = 3.6 \times 10^4$. This value is well compared with the reported values of M_{c0} of eq 2 for polystyrene. The data for **2a** are below the straight line of slope 1 but may be regarded to lie on a convex curve (dashed line) together with those for **7a**. This result is in parallel with that observed in the plot of log η *vs.* log M for undiluted polymers,[6,13] and seems to indicate that the data for **2a** lie below the straight line due to the smaller friction coefficient at the reference concentration as compared with that for **7a**. This conjecture is supported by the fact that the data for **2a** may be reduced (filled circles) so that they lie on the straight line by multiplying a factor 1.7, which is the difference in $G_r(t)$ in the short time region of Figure 2 due to the molecular weight dependence of the friction coefficient and that η/a_c is proportional to the product cM when $cM < M_{c0}$ in low M-high c systems if the molecular weight dependence of ζ is taken into account.

The steady-state compliance J_e^0 for solutions of **2a** and **7a** as given in Table I was evaluated from the creep recovery and is plotted against c in Figure 6 (two groups of points in the range of very high concentration). Obviously J_e^0 increases and is inversely proportional to about the second power of c. The straight lines represent the prediction of the Rouse theory.[14] The experimental values are of the same order of magnitude as of predicted but their concentration dependence is much stronger than predicted.

Comparison with Rouse Theory. For systems in which the entanglement coupling is not the main reason of relaxation processes, the Rouse theory[14] may be applied to predict the dynamic behavior even if the friction coefficient ζ for a segment does not consist of the friction due to the solvent drag force alone.[2a,15] The content of ζ is not very important when one compares the shape of the relaxation spectrum since it is a kind of adjustable parameter at the present stage of the theories even for dilute polymer solutions for which ζ may be due to the solvent viscosity.[2a]

Comparisons of the Rouse theory with the experimental results are shown in Figure 2 where the solid lines represent the theoretical values of $G_r(t)$. As a matter of fact, the theory does not reproduce the data very well unless the molecular weight used for calculations of $G_r(t)$ is modified. The values of molecular weights in calculating theoretical curves are larger than those given in the Experimental Section by factors 1.55 and 1.71 for the samples **2a** and **7a**, respectively. These correction factors correspond to the differences between the experimental values of J_e^0 and those predicted from the Rouse theory at the reference concentration in Figure 6. When this modification of the molecular weight is performed, the theoretical curves become in good agreement with the experimental except in the range of very long time scale where the error in transforming J_p into G_p may be significant. Thus the shape of relaxation curves are similar to that predicted by the theory but application of the theory needs a modification of M for low M-high c systems. It may be noted that the theory we are concerned with is not the modified Rouse theory which assumes the enhancement of ζ due to the entanglement coupling.[16] It has been shown[5] that the shape of relaxation curves is very different from that predicted from the modified Rouse theory in the case of $cM \gg M_{c0}$.

Dynamic Mechanical Properties for High M-Low c Systems. Complex moduli were measured for solutions of samples **1b′**, **3a**, **6a**, and **14a** in Aroclor 1248 at concentrations as indicated in Table I. The concentrations for **14a** are a little higher than is given by eq 2 and those for **1b′** lower. The results of dynamic measurements in the same concentration ranges were published by Holmes *et al.*[17] while the present study was in progress. We will not show the raw data of complex moduli since they are in good agreement with those of Holmes *et al.* We will only point out the characteristic variation of the relaxation spectrum with varying molecular weight and concentration. The relaxation spectrum $H(\tau)$ as calculated from the loss modulus by the Tschoegl approximation[18] is shown in Figures 7 and 8. Figure 7 shows the effect of varying molecular weight on $H(\tau)$ at the concentration 0.105 g/ml. For each sample except **1b′**, $H(\tau)$ is characterized by three regions; transition region in the short time range and plateau region and flow region in the long time end. In the transition region, $H(\tau)$ varies approximately proportional to $\tau^{-1/2}$ and is

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(13) See, for example, T. G Fox, S. Gratch, and S. Loshaek in "Rheology," Vol. 1, F. R. Eirich, Ed., Academic Press, New York, N. Y., 1956.

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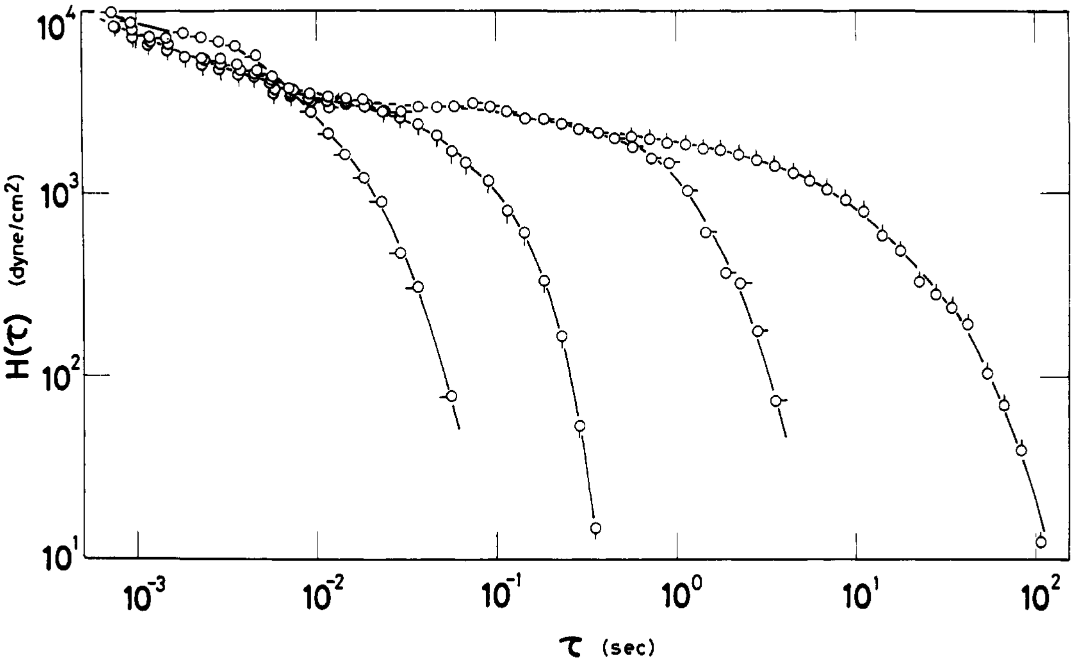

Figure 7. Relaxation spectrum $H(\tau)$ plotted against relaxation time τ for 7.5 wt % solutions of polystyrene in Aroclor 1248 at 30°. Various directions of pips represent molecular weights; pip up, 1.80×10^6; pip right, 8.6×10^5; pip down, 4.11×10^5; pip left, 2.0×10^5.

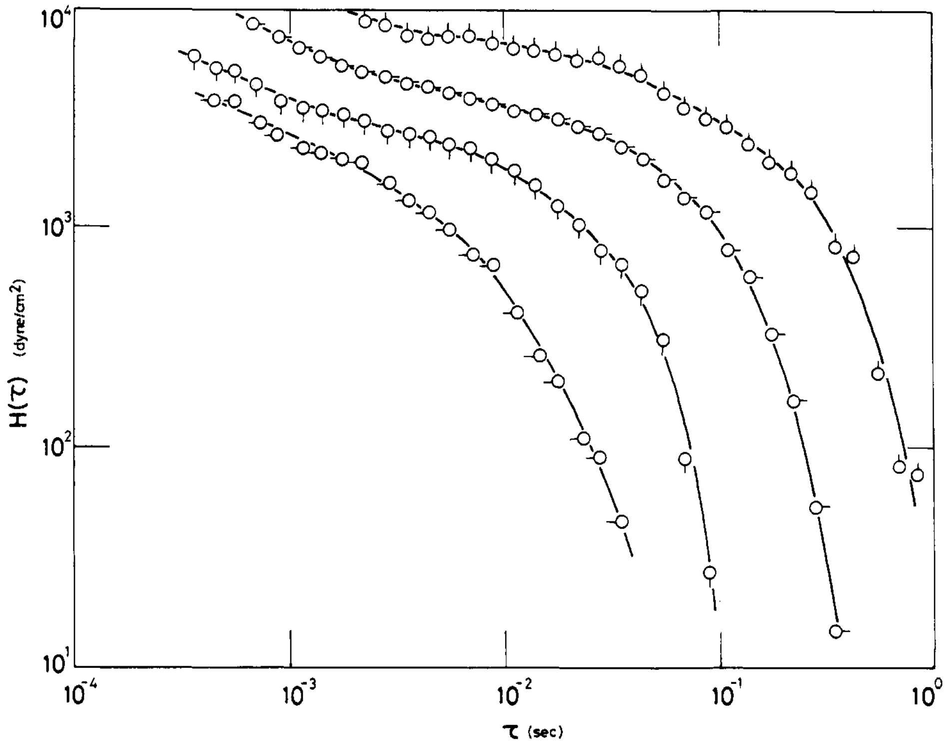

Figure 8. Relaxation spectrum $H(\tau)$ plotted against relaxation time τ for solutions of polystyrene with $M = 4.11 \times 10^5$ in Aroclor 1248 at 30°. Various directions of pips represent concentrations; pip up, 14.03; pip right, 10.51; pip down, 7.06; pip left, 4.24 g/dl.

independent of M. In the plateau region, it does not vary appreciably with τ and is independent of M. The width of this region increases as M is increased. The flow region is the region where $H(\tau)$ decreases very rapidly with increasing τ and its location is at the longer time scale for higher M. The plateau region is not observed for the sample **1b′**. For this sample $H(\tau)$ is higher compared with others in the transition region. This trend may be similar to that observed for undiluted polystyrene of low molecular weight at the long time end of the transition region.[19]

Figure 8 represents the effect of varying concentration on $H(\tau)$ for solutions of the sample **4a** in Aroclor 1248. In contrast with the effect of increasing M, the relaxation spectrum increases with increasing c in the whole range of time scale. The plateau region is not seen for the lowest concentration. The symptom of the plateau appears at 0.07 g/ml and becomes more marked at higher concentrations. It may be noted here that the concentration where the plateau region first appears is much lower than that

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corresponding to eq 2 for this polymer (c = 0.07 g/ml gives 2.8×10^4 for the product cM). This result is in contrast with that for low M-high c systems for which no sign of the plateau region was seen even at the highest concentration for the sample **7a** ($cM = 3.6 \times 10^4$). Thus the shape of the relaxation spectrum seems to change very gradually with varying c in the case of high M-low c systems. The viscosity, given in Table I, varies gradually with varying M and the power dependences as shown in eq 1 do not apply for these systems. Accordingly the critical molecular weight, even if defined in some way, will not have such a definite significance as in the case of low M-high c systems.

The steady-state compliance J_e^0 for high M-low c systems as given in Table I is plotted against c in Figure 6 to improve the figure shown in the previous paper.[4] Thick solid lines represent the results given before.[4] The present results seem to confirm the existence of minima in the relation of log J_e^0 and log c for two samples, **1b′** and **4a.** It is seen that J_e^0 for these samples below the concentration corresponding to the minima are approximately equal to the predicted values of the Rouse theory shown by thin solid lines.[14] For higher M, no minimum is observed and the slope decreases gradually as c decreases. J_e^0 for the sample of the highest M, **14a,** of the present study is lower than that reported before (solid line at the top). It was revealed from the gel permeation chromatogram that the sample **14a** used before had a wide distribution of molecular weight probably due to thermal degradation at the last stage of the study.

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Ion Clustering and Viscoelastic Relaxation in Styrene-Based Ionomers. II. Effect of Ion Concentration

A. Eisenberg* and M. Navratil

Department of Chemistry, McGill University, Montreal, Canada. *Received November 13, 1973*

ABSTRACT: A study of the viscoelastic properties of styrene ionomers containing up to 10 mol % of sodium methacrylate was undertaken. It was found that in the region of low ion concentration (up to 6 mol % of salt) time–temperature superposition is obeyed and equations of the WLF type are applicable. For the material for which time–temperature superposition is valid, the glass transition temperature (T_g) increases approximately linearly with concentration of ions, with $\mathrm{d}T_g/\mathrm{d}C \approx 2°/\mathrm{mol}$ % up to 6 mol % salt. For the samples above that value, the increase in T_g is faster. With increasing ion concentration there is an increase in both WLF parameters C_1 and C_2 and also a broadening of the distribution of relaxation times. In all samples of high molecular weight and an ion concentration above 1% two inflection points are visible on the stress relaxation master curve. The upper inflection point increases with increasing ion concentration. Water uptake experiments for samples which are subject to time–temperature superposition reveal that only one water molecule is absorbed per ion pair at equilibrium. With increasing ion concentration the primary (*i.e.,* diffusional) relaxation mechanism is observed to slow down. This slowing down is a function of both the ion concentration and the length of the polymer chain which has to cooperate to reach a specific modulus. Above 6 mol % of salt time–temperature superposition is no longer applicable. Water uptake experiments for these samples do not seem to lead to equilibrium values; the rate of water uptake increases with increasing ion concentration and after 6 months the number of water molecules per ion pair ranges from 3 to 6 per sodium ion. Failure of time–temperature superposition above 6 mol % of ionic groups, results of water uptake, and the glass transition studies are consistent with the hypothesis that clustering occurs above 6 mol % of our system. The failure of time–temperature superposition in these materials seems to result from the introduction of an additional relaxational mechanism due to the presence of microphase separation. For polymers of low molecular weight containing more than 6% of ions, time–temperature superposition is found to be applicable again above *ca.* 180°. Clustering is confirmed by preliminary X-ray studies.

The unusual physical properties of ion-containing polymers have been the subject of considerable attention during the past decade as evidenced by two recent review articles.[1,2] Two main problems complicating the interpretation of viscoelastic results have emerged. The first of these is the fact in the ion-containing polymers, time–temperature superposition has, by and large, been found inapplicable.[3-5] The second concerns the supermolecular structure of these polymers. While some workers found experimental[6-10] and theoretical[11] evidence for microphase separation, results of other studies fail to show these phenomena.[12-14] If microphase separation occurs and the lifetime of the aggregates thus formed is finite, time–temperature superposition would not be expected to hold since it is most probable that the clusters contribute to the relaxation behavior and since the activation energies of the two resulting processes are probably not the same. Thus it is of interest to investigate both microphase separation and

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