obliging us to use more than two parameters for the description of this type of branched polymers. However, as already pointed out by Casassa,[21] considerable caution should be involved in the choice of models meant to give account of experimental results. All we can say is that the assumption we have made in this paper concerning multiple contacts between segments in the region of high segment density leads to very plausible and self-consistent results.

Appendix

Equation 8 may also be written

$$A_2 = \left(\frac{2^4}{3^{3/2}}\right)\pi N_{\mathrm{A}}\left(\frac{b^2}{6m}\right)^{3/2}\frac{g^{3/2}\alpha^3}{M^{1/2}} \times \int_0^\infty [1 - \exp(-K'e^{-4/3y^2})\exp(-Ke^{-y^2})]y^2\mathrm{d}y \quad \text{(A1)}$$

If K is small enough, we may obtain by limiting the development of $\exp(-Ke^{-y^2})$ to the first two terms

$$A_2 = \left(\frac{2^4}{3^{3/2}}\right)\pi N_{\mathrm{A}}\left(\frac{b^2}{6m}\right)^{3/2}\frac{g^{3/2}\alpha^3}{M^{1/2}}\left\{\int_0^\infty [1 - \exp(-K'e^{-4/3y^2})]y^2\mathrm{d}y + K\int_0^\infty \exp(-y^2) \times \exp(-K'e^{-4/3y^2})y^2\mathrm{d}y\right\} \quad \text{(A2)}$$

The first term on the right-hand side of this expression stands for the A_2 value when K is equal to zero, *i.e.*, the A_2 value at Flory's Θ temperature, namely $A_{2\Theta}$.

By introducing y' as new variable, $y' = (2/\sqrt{3})y$, it is possible to write $A_{2\Theta}$ in terms of the function $J(X)$ which has been calculated by Flory

$$J(X) = 4\pi^{-1/2}(X^{-1})\int_0^\infty [1 - \exp(-Xe^{-y^2})]y^2\mathrm{d}y$$

then

$$A_{2\Theta} = \frac{N_{\mathrm{A}}}{2}\pi^{3/2}\left(\frac{b^2}{6m}\right)^{3/2}\frac{g^{3/2}\alpha^3}{M^{1/2}}K'J(K')$$

The integral which appears in the second term of the right-hand side of eq A2 can be expanded in the following way

$$\int_0^\infty [\exp(-y^2)\exp(-K'e^{-4/3y^2})]y^2\mathrm{d}y = \int_0^\infty \exp(-y^2)y^2\mathrm{d}y + \sum_{p=1}^{\infty}\frac{(-1)^p}{p!}K'^p \times \int_0^\infty \exp\left[-y^2\left(1 + \frac{4p}{3}\right)\right]y^2\mathrm{d}y$$

Then, after integration, we get the final expression for A_2

$$A_2 = \pi^{3/2}N_{\mathrm{A}}\left(\frac{b^2}{6m}\right)^{3/2}\left[\frac{C'_{M,l}}{\alpha^3 g^{3/2}}\frac{J(K')}{M^{1/2}} + \left(\frac{2^4}{3^{3/2}}\right)C_{M,l}\psi\left(1 - \frac{\Theta}{T}\right)G(K')\right]$$

whereby the function $G(K')$ has been computed and is given by the following expression

$$G'(K') = \sum_{p=0}^{\infty}\frac{(-1)^p}{p!}\frac{K'^p}{\left(1 + \frac{4p}{3}\right)^{3/2}}$$

Creep Behavior of Polymer Solutions. III. Creep Compliance of Concentrated Polystyrene Solutions

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ABSTRACT: The creep compliance $J(t)$ of polystyrene solutions in chlorinated diphenyl was measured at various temperatures (−20 to 30°). The ranges of molecular weight M and concentration c were 9.7×10^4–1.8×10^6 and 10–60 g/dl, respectively. The temperature coefficient of the fractional free volume as evaluated from a_T, the shift factor obtained from the time–temperature reduction method, was approximately equal to that for undiluted polystyrene over the whole range of concentration investigated. The time–concentration reduction method was applied to the creep compliance in the transition region, giving the shift factor a_c which is proportional to the segmental friction coefficient. The viscosity divided by the segmental friction coefficient was proportional to the 3.4th power of the product cM. The time–concentration reduction method was not applicable to the relaxation modulus calculated from $J(t)$ in the flow and the plateau regions. This result indicates that the strength of one or a few relaxation mechanisms at the longest time end are proportional to the third or a higher power of c, in contrast to that in the plateau region which was found to be proportional to c^2.

In previous papers of this series, we reported an apparatus for measurements of creep and creep recovery and the experimental results of the viscosity η and steady-state compliance J_e^0 obtained for polystyrene solutions in chlorinated diphenyl.[2] It has been found that J_e^0 is independent of the molecular weight M and inversely proportional to the third power of the concentration c at large values of M and c. This behavior is in contrast to the so-called Rouse–Zimm behavior, $J_e^0 \propto M/c$, which is found to be valid up to a certain concentration depending on M. The inverse N-shaped transition from the c^{-1} dependence of J_e^0 to the c^{-3} dependence occurs in a limited range of concentration adjacent to the critical concentration.

The study of J_e^0 and η as functions of M and c is essential

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(1) (a) Institute for Chemical Research; (b) Department of Industrial Chemistry.

(2) (a) K. Osaki, Y. Einaga, M. Kurata, and M. Tamura, *Macromolecules*, 4, 82 (1971); (b) Y. Einaga, K. Osaki, M. Kurata, and M. Tamura, *ibid.*, 4, 87 (1971).

TABLE I

THE PARAMETERS T_0, α, AND a_c FOR POLYSTYRENE SOLUTIONS IN AROCLOR 1248

Code	M_w	c, g/dl	T_0, °K	$\alpha \times 10^4$	a_c
14a	1.80×10^6	34.05			3.40×10^{-1}
		30.75			9.83×10^{-2}
		27.48			4.49×10^{-2}
		24.43			3.50×10^{-2}
		20.75			1.12×10^{-2}
		17.69			1.06×10^{-2}
		14.34			8.84×10^{-3}
		10.81			3.24×10^{-3}
6a	8.60×10^5	40.04	130	1.46	7.20×10^{-1}
		36.30	150	2.10	4.64×10^{-1}
		32.10	148	2.13	2.33×10^{-1}
		30.68	154	2.24	1.52×10^{-1}
		27.59			4.44×10^{-2}
		23.83	111	1.36	3.05×10^{-2}
		18.96			1.55×10^{-2}
		17.93	171	3.16	1.02×10^{-2}
		14.12	176	3.59	5.34×10^{-3}
3a	4.11×10^5	49.02			5.29
		41.50			1.00
		36.79	166	2.53	3.23×10^{-1}
		33.23	162	2.32	1.56×10^{-1}
		30.22	179	3.32	9.35×10^{-2}
		24.90	202	5.61	2.90×10^{-2}
		22.02	181	3.72	1.79×10^{-2}
		17.73	194	5.44	1.22×10^{-2}
		14.12	202	6.52	7.30×10^{-3}
1a	1.60×10^5	60.98	202	4.14	6.15×10^2
		55.48			6.66×10^1
		51.31			1.24×10^1
		45.96	157	2.08	2.74
		42.46			1.65
		39.40	169	2.59	8.00×10^{-1}
		36.98	173	2.87	4.65×10^{-1}
		33.94			2.10×10^{-1}
		30.80			1.93×10^{-1}
4a	9.72×10^4	61.26	190	3.06	6.78×10^2
		55.75			6.96×10^1
		51.00	185	3.20	1.38×10^1
		45.60	175	2.85	3.22
		42.44	178	2.99	1.90
		39.35			8.00×10^{-1}
		36.94			6.55×10^{-1}

for an understanding of the nature of entanglement. The information obtainable is, however, rather restricted, because these two parameters are mainly determined by the relaxation modes distributed near the maximum relaxation time. It is therefore desirable to study the behavior of the creep compliance $J(t)$ over a wide range of the time scale, and to clarify the effect of such variables as M, c, and temperature T on the distribution of the relaxation modes. Such a study is carried out in this paper for polystyrene solutions in chlorinated diphenyl.

Experimental Section

The polymer samples used were the "standard" polystyrenes, 14a, 6a, 3a, 1a, and 4a, supplied by Pressure Chemicals Co. (Pittsburgh, Pa.). Their weight-average molecular weights M_w were 1.80×10^6, 8.60×10^5, 4.11×10^5, 1.60×10^5, and 9.72×10^4, respectively, and the ratios of M_w to the number-average molecular weight M_n were less than 1.25, 1.15, 1.06, 1.06, and 1.06, respectively, according to the data sheet from the company. The solvent was Aroclor 1248, a mixture of partially chlorinated diphenyl, supplied by the Monsanto Chemical Co. The preparation of polymer solutions was described in part II of this series.[2b]

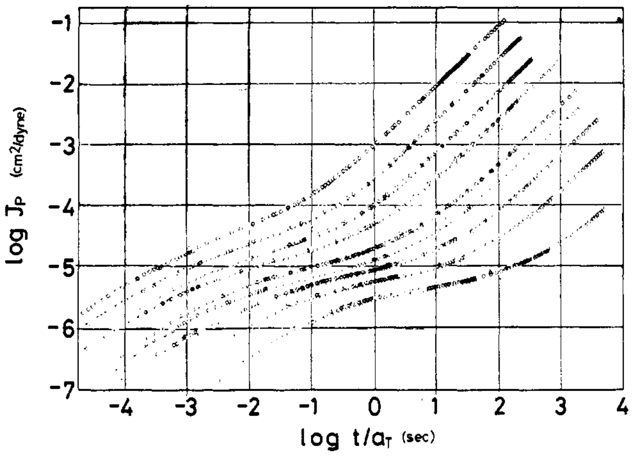

Figure 1. Reduced creep compliances for solutions of polystyrene 3a at various concentrations reduced to 30°. Concentrations are 49.02, 41.50, 36.79, 33.23, 30.22, 24.90, 22.02, 17.73, and 14.12 g/dl from bottom to top, respectively.

Creep measurements were made on each polymer sample at various temperatures between −20 and 30° in a wide variety of concentrations as indicated in Table I. The details of the apparatus were described in part I.[2a]

Results

The creep compliances $J(t)$ obtained at various temperatures were reduced to a single composite curve for each solution by the method of reduced variables.[3] Figure 1 shows the composite curves obtained for the solutions of sample 3a at various concentrations. Here $J_p(t)$ represents the reduced creep compliance, $J(t)T\rho/T_r\rho_r$, T and ρ represent the temperature and solution density, respectively, and the suffix r denotes the reference state which is arbitrarily chosen at 30°. The shift factor a_T was determined empirically so as to obtain the best superposition among the $J(t)$ curves of different temperatures. Composite curves similar to those given in Figure 1 are obtained for all the polymer samples studied. Raw data are available on request. These curves generally consist of three regions, the transition, plateau, and terminal regions. The slope of the curves in the transition region is about two-thirds for all the solutions studied. Although the observed region is limited to a rather small part of the total transition region, it is notable that the slope exceeds one-half predicted by the Rouse theory or its modified version. The slope of most creep curves in the terminal region approaches unity, indicating that the state of viscous flow is achieved in the observed range of time scale. Between the transition and terminal regions there exists a plateau region where $J(t)$ does not appreciably depend on t. The creep compliance in the plateau region increases with decreasing concentration, and the width of the region decreases: The plateau region is fairly wide and flat at high concentrations, while it is only an inflection at low concentrations as seen in Figure 1.

Discussion

Temperature Dependence. The effect of temperature on the creep compliance is represented by the shift factor a_T. As is well known, this quantity represents the temperature

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(3) J. D. Ferry, "Viscoelastic Properties of Polymers," 2nd ed, Wiley, New York, N. Y., 1970.

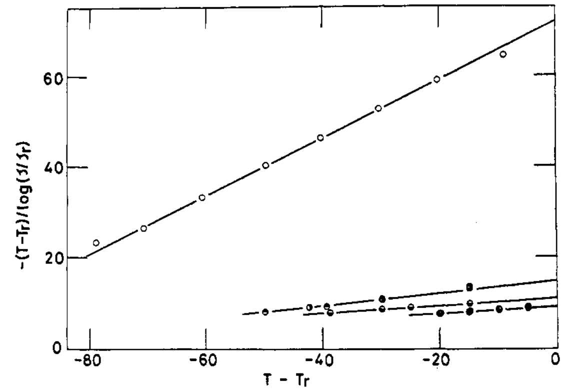

Figure 2. $-(T - T_r)/\log a_T$ plotted against $T - T_r$ for polystyrene solutions in Aroclor 1248 at various concentrations. T_r is 30°. Concentrations are 0, 14.12, 36.96, and 61.00 g/dl from top to bottom, respectively. (○) Solvent Aroclor 1248; and other types of circles represent polymer samples: (◓) 6a, (◑) 3a, (◒) 1a, (◐) 4a.

dependence of the friction coefficient ζ for a flow unit responsible for the chain motion: $a_T = \zeta/\zeta_r$, where ζ_r is the friction coefficient at the reference temperature. The temperature dependence of a_T is usually described by the so-called WLF equation[4] which may be interpreted on the basis of the free volume theory. However, this equation requires three parameters to express the ratio of the friction coefficients at two temperatures and is not very useful unless the glass-transition temperature T_g or the expansion coefficient of the fractional free volume α_f is known.

Berry and Fox have recently utilized the Vogel equation, which may be written in the form[5]

$$\ln \zeta = \ln \zeta_0 + 1/\alpha(T - T_0) \tag{1}$$

Here ζ_0 is the inherent segmental friction coefficient and α and T_0 are constants. One can visualize the physical meanings of α and T_0 by comparing the Vogel equation with an analogous equation suggested by the free volume concept[6,7]

$$\ln \zeta = \ln \zeta_0 + B/f \tag{2a}$$

$$f = f_g + \alpha_f(T - T_g) \tag{2b}$$

where f and f_g are the fractional free volume at T and T_g, respectively, and B is a constant not far from unity. From eq 1 and 2, the following relations are obtained

$$\alpha = \alpha_f/B \tag{3}$$

$$f = \alpha_f(T - T_0) \tag{4}$$

It is evident from eq 3 that α has practically the same meaning as α_f. Another parameter T_0 is interpreted as the temperature at which the fractional free volume f becomes zero and η becomes infinity.

If the temperature T_r is arbitrarily chosen as reference, eq 1 is written in the following form[5]

$$-(T - T_r)/2.303 \log (\zeta/\zeta_r) = i + m(T - T_r) \tag{5}$$

with

$$T_0 = T_r - i/m \tag{6}$$

$$\alpha = m^2/i \tag{7}$$

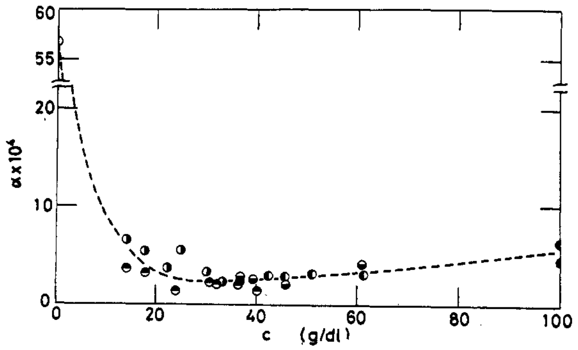

Figure 3. α plotted against c. Closed circles represent the published values for undiluted polystyrene due to Ferry (top) and Miller (bottom)).[7] Other marks have the same meaning as in Figure 2.

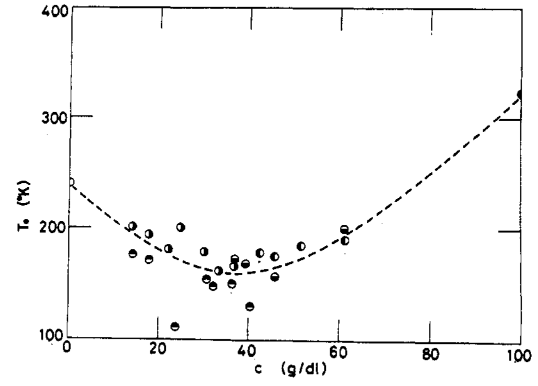

Figure 4. T_0 plotted against c. Each mark has the same meaning as in Figure 3.

A straight line can be obtained if the quantity $-(T - T_r)/\log a_T$ is plotted against $(T - T_r)$, and the parameters α and T_0 can be evaluated from the slope m and the intercept i of this line.

Examples of this plot are shown in Figure 2, where the open circles represent the data for the solvent, Aroclor 1248, and the half-filled circles of various types the data for the polymer solutions. Here the viscosity of Aroclor was measured with capillary viscometers. Equation 5 is found to be applicable to these polymer solutions and to yield reasonable values for α and f. The values of α thus obtained are summarized in Table I and plotted against the concentration c in Figure 3. They are practically independent of M. The parameter α as a function of c rapidly decreases with increasing c in the range of the lowest concentrations, and then it becomes nearly constant over the wide range of concentration from 15 to 60 g/dl, though it displays a shallow minimum. This constant value is nearly equal to the value currently reported for undiluted polystyrenes,[3,7] *i.e.*, 4.8×10^{-4} or 6.9×10^{-4} cm³/deg, though slightly lower. Thus, in the present combination of polymer and solvent, the expansion coefficient of the fractional free volume possibly reflects that of the polymer alone even at concentrations as low as 20 g/dl.

The values of another parameter T_0 are also summarized in Table I and plotted against c in Figure 4. The points are considerably scattered; but seem to be independent of the molecular weight. It is seen that T_0 decreases with increasing c in the range of low concentrations, passes a minimum at about 40 g/dl, and increases at higher concentrations. The same tendency was also observed for polystyrene solutions in dibenzyl ether by Berry, *et al.*, though the minimum reported by them was not so deep as shown in Figure 4. This

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[4] J. D. Ferry, R. L. Landel, and M. L. Williams, *J. Appl. Phys.*, 26, 359 (1955).

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

[6] M. L. Williams, *J. Appl. Phys.*, 29, 1395 (1958).

[7] A. A. Miller, *J. Polym. Sci., Part A*, 1, 1837 (1963); A. A. Miller, *ibid.*, 2, 1095 (1964).

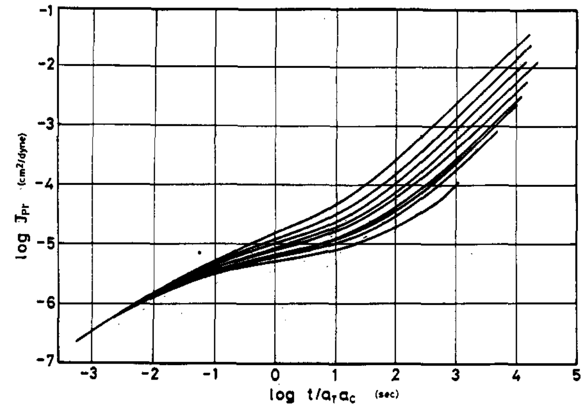

Figure 5. Result of time–concentration reduction for creep compliances of Figure 1. Concentration increases from top to bottom as shown in Figure 1.

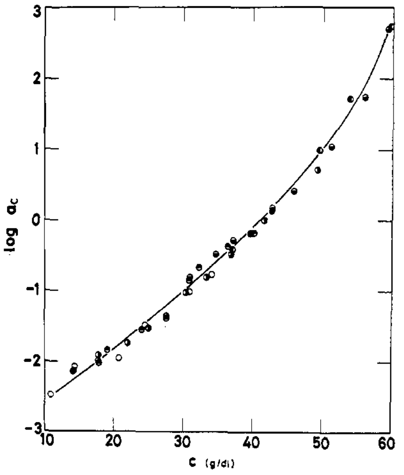

Figure 6. Log a_c plotted against c. c_r is 41.50 g/dl. Open circles represent the solutions of sample 14a and the meaning of other marks is the same as in Figure 2.

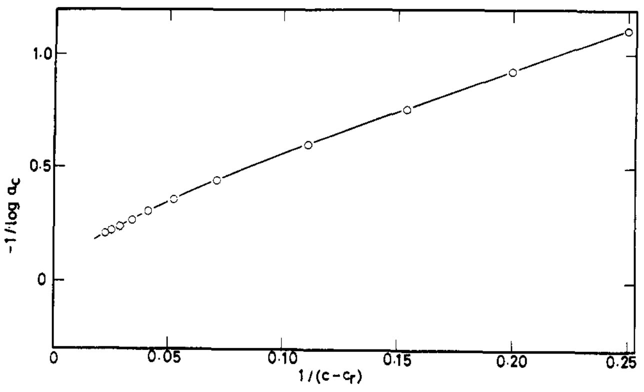

Figure 7. $-1/\log a_c$ plotted against $1/(v_1 - v_{1_r})$. v_{1_r} is 0.408 g/dl. Log a_c was evaluated from the solid line in Figure 5.

may be due to the low viscosity, and therefore to the low T_0, of their solvent. On the other hand, the solvent Aroclor 1248 used in this study has a very high viscosity. T_0 is found to be 242°K, which is extremely high compared with that of dibenzyl ether. The minimum value of T_0 in the polystyrene–Aroclor system is lower than that of Aroclor 1248 by about 80° and that of undiluted polystyrene[3,6,7] by about 160°.

The fractional free volume f may be calculated from the values of α and T_0 by using eq 3 and 4. Setting $B = 1$ as usual, we have

$$f = \alpha(T - T_0) \tag{8}$$

The value of f obtained at 30° was about 0.05 in the concentration range from 15 to 60 g/dl.

The results shown above may be summarized as follows. (1) The expansion coefficient α of the fractional free volume is almost independent of M and c over a wide range of variables and is approximately equal to the value for the undiluted polymer. (2) The temperature T_0 as a function of c has a minimum at about 40 g/dl. The minimum value of T_0 is considerably lower than the value for the undiluted polymer or even lower than the value for the solvent, Aroclor.

These results suggest that the additivity of the free volumes of polymer and solvent does not hold in the range of concentration studied; the free volume is much smaller than expected from the additivity This is in contrast to the fact that the total volume of the solution is well approximated by the sum of volumes of polymer and solvent. The concentration dependence of the free volume must be quite different from that of the total volume.

Transition Region. Viscoelastic properties in the transition region are supposed to be attributable to the motions of a rather short segment of the polymer chain between entanglement loci.[3] In this case, the creep compliance $J(t)$ is inversely proportional to the number of these movable polymer segments in a unit volume, and hence to the weight concentration c of the polymer. The position of the transition region on the time scale is determined only by the segmental friction coefficient ζ. Thus, the creep curves at various concentrations should be reduced to a single curve in the transition region, if $(c/\rho_2)J(t)$ is plotted against t/a_c'. Here ρ_2 is the density of pure polymer and a_c' is the shift factor on the time scale, which can be regarded as the ratio of the segmental friction coefficient in solution to the one in undiluted polymer.

The reduced variables given above may be rewritten in terms of a reference concentration c_r other than the undiluted polymer

$$J_r(t_r) = (c/c_r)J(t) \tag{9}$$

$$t_r = t/a_c \tag{10}$$

where a_c is defined as the ratio $a_c'(c)/a_c'(c_r)$. In this study, 41.50 g/dl was arbitrarily chosen as the reference c_r. The shift factor a_c was so chosen as to attain the best fit of the data at various concentrations at the shortest time range studied. As an example, a reduced plot is given in Figure 5 for creep compliances shown in Figure 1.

The values of a_c are given in Table I and are plotted against c in the semilogarithmic scale in Figure 6. In our measurements, only a narrow range of the transition region was observed. Therefore, the determination of a_c is subject to considerable error. Nevertheless, we may conclude that a_c is independent of M and very strongly dependent on c. The strong dependence of the viscosity η on concentration as observed in part II may be atrributed to this behavior of a_c.

The shift factor a_c can be formulated as a function of c with the use of the modified Doolittle equation, if the fractional free volume is assumed to be linearly dependent on concentration.[8,9]

$$f(v_1) = f(v_{1_r}) + \beta(v_1 - v_{1_r}) \tag{11}$$

$$-1/2.303 \log a_c = f(v_{1_r}) + [f(v_{1_r})]^2/\beta(v_1 - v_{1_r}) \tag{12}$$

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

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

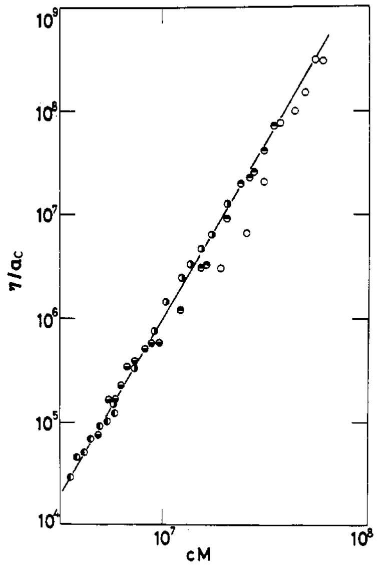

Figure 8. η/a_c plotted against cM on a double logarithmic scale. The meaning of each mark is the same as in Figure 5. Straight line corresponds to the relation $\eta/a_c \propto (cM)^{3.4}$.

Here β is a constant, v_1 is the volume fraction of the solvent, and the subscript r represents the reference state.

Equation 12 indicates that a straight line should be obtained when $-1/\log a_c$ is plotted against $1/(v_1 - v_{1_r})$. A test of this requirement is shown in Figure 7. The experimental points do not lie on a straight line but on a line with downward curvature, indicating that the assumption of the additivity of free volume does not strictly hold in the observed range of concentration. This result is in accord with that obtained from the analysis of a_T.

According to Berry and Fox[5] one can write

$$\eta = F(c, M)\zeta(c,T) \tag{13}$$

where ζ is the segmental friction coefficient and F is the structural factor. Since a_c represents the concentration dependence of ζ, the ratio η/a_c must be proportional to F with a coefficient independent of c. This ratio is plotted against cM in the double logarithmic scale in Figure 8. Obviously, the data points for various combinations of M and c can be expressed by the simple relation that

$$\eta/a_c \propto (cM)^{3.4} \tag{14}$$

This relation coincides with the semiempirical relation which was proposed by Fox, *et al.*[5,10] Our result obtained in the analysis of the creep compliance $J(t)$ offers additional support to this relationship. In this study, the concentration dependence of the segmental friction coefficient was directly evaluated from the shift factor a_c in the transition region, while it was calculated from the concentration dependence of the parameters, T_0 and α, in the Vogel equation for the viscosity, by Berry and Fox.[5]

Plateau Region. A comparatively flat segment in the curves of Figure 1 is currently interpreted as the pseudoequilibrium compliance of an entanglement network. The molecular weight of the network strand between entanglement loci is supposed to be estimated from the value of $J(t)$ in this region with the aid of the theory of rubberlike elasticity.[3] This value of $J(t)$ was evaluated in this study at the inflection point in Figure 1, and was designated as J_{inf}. Although the position of the inflection point along the abscissa is not easy to determine, the value of compliance itself is easily determined to within ±5%. The values of J_{inf} are shown in Figure 9 by circles. The upper solid line represents the steady-state compliance J_e^0 as a function of c, which was given in part II.[2b] It is clear in this figure that J_{inf} is inversely proportional to the second power of concentration and independent of molecular weight, while J_e^0 depends more strongly on concentration. The values of J_{inf} and J_e^0 extrapolated to the undiluted polymer are 9×10^{-7} and 1.5×10^{-6} cm^2/dyn, respectively. Thus, the ratio of J_e^0 to J_{inf} is about 1.67 in the pure polymer. This ratio increases with decreasing c and reaches a value as large as ten at lowest concentration studied. This result suggests the possibility that various modes of the relaxation mechanism show different dependence on concentration. In addition, it may be noted that J_{inf} is proportional to c^{-2} in the whole range of concentration studied, while J_e^0 depends on c in a rather complicated way, as mentioned in the introductory remarks.

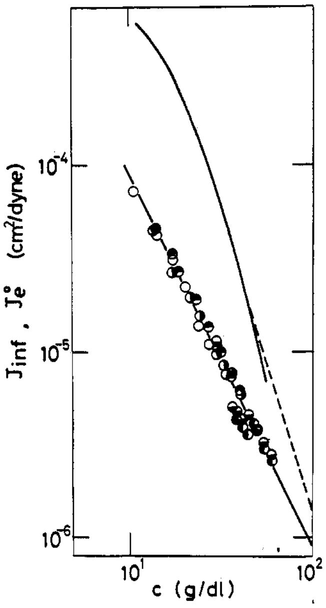

Figure 9. J_{inf} and J_e^0 plotted against c on a double logarithmic scale. Each circle mark has the same meaning as in Figure 5. Upper solid line represents J_e^0, lower solid line represents the relationship $J_{\mathrm{inf}} \propto c^{-2}$, and upper dashed line represents $J_e^0 \propto c^{-3}$.

The creep compliance at the inflection point, J_{inf}, may be regarded to be approximately equal to the so-called entanglement compliance J_{eN}^0 defined by Ferry.[3,11] This is related by the following equation to the average entanglement spacing M_e which is one of the most important parameters in the concept of molecular entanglement[3-12]

$$J_{eN}^0 = (1/g_N)M_e/cRT \tag{15}$$

where g_N is a front factor close to unity and RT has the usual meaning. Since the lower straight line in Figure 9 can be represented by $c^2 J_{\mathrm{inf}} = 9 \times 10^{-7}$, one can calculate M_e as

$$cM_e = 2.3 \times 10^4 \tag{16}$$

assuming that $J_{\mathrm{inf}} = J_{eN}^0$ and $g_N = 1$ in eq 15. The entanglement spacing M_e is thus inversely proportional to concentra-

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[10] V. R. Allen and T. G Fox, *J. Chem. Phys.*, **41**, 337 (1964).

[11] J. F. Sanders, J. D. Ferry, and R. H. Valentine, *J. Polym. Sci., Part A-2*, 6, 967 (1968).

[12] See, for example, R. S. Porter and J. F. Johnson, *Chem. Rev.*, **66**, 1 (1966).

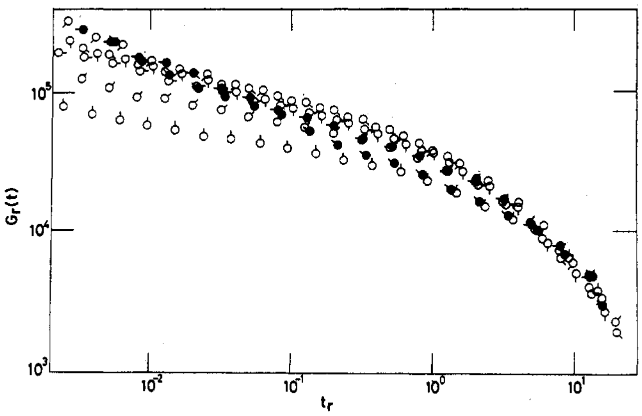

Figure 10. $G_r(t)$ plotted against t_r for solutions of sample 3a on a double logarithmic scale. c_r is 30.22 g/dl. Various directions of pips represent concentrations: pip up, 49.02 g/dl; successive 45° rotations clockwise correspond to 41.50, 36.79, 33.23, 30.22, 24.90, 22.02, 17.73, and 14.12 g/dl, respectively.

tion in accord with the published results.[3] The number on the right-hand side of eq 16 is approximately in agreement with that deduced from different origin.[3,12]

Terminal Region. The method of reduced variables will remain applicable in the terminal region when a considerable number of relaxation modes have the same concentration dependence.[3] However, the reduced variables to be used in this region have to be different from those used in the transition region. Using the undiluted polymer as the reference, one can generally define a set of reduced variables as

$$f(c)[J(t) - t/\eta] \text{ and } tf(c)\eta(c)/\eta_0$$

Here η_0 is the viscosity of the undiluted polymer and $f(c)$ is a function of concentration. A power law equation, $f(c) = c^n$, has often been assumed in application of the method.[3] In the transition region, the exponent n is equal to one, as mentioned before. In the flow region, $n = 2$ or 3 has been used as an appropriate choice.[13,14] A simple consideration reveals that $f(c)$ should be inversely proportional to J_e^0 if the method of reduced variables can be strictly applied to the flow region.[15] Thus, one may define the following set of reduced variables

$$J_r(t) = [J_e^0(c_r)/J_e^0(c)](J(t) - t/\eta) \qquad (17)$$

$$t_r = tJ_e^0(c_r)\eta(c_r)/J_e^0(c)\eta(c) \qquad (18)$$

where c_r is the reference concentration selected arbitrarily.

This method of reduced variables was examined by plotting $G_r(t) = [J_e^0(c)/J_e^0(c_r)]G(t)$, instead of $J_r(t)$, against t_r, where $G(t)$ represents the relaxation modulus calculated from $J(t)$ through the approximation of Smith.[16] $G_r(t)$ was employed because this quantity is more convenient than $J_r(t)$ to survey the feature of the distribution of various relaxation modes. An example of the plot is shown in Figure 10. The characteristic features of this figure may be summarized as follows. (1) The reduced relaxation moduli $G_r(t)$ at various concentrations give a single composite curve at the end of the longest time scale as it should be. The successful superposition is, however, restricted to within a narrow range of time scale. (2) In the range of short time scale, $G_r(t)$ monotonically increases with decreasing concentration. (3) At the shoulder part of the curves, $G_r(t)$ first increases with increasing concentration, passes a maximum at about 30.22 g/dl, and then decreases. This concentration corresponds to the concentration at which J_e^0 attains to a maximum in the J_e^0 *vs.* c plot.

The above features indicate that the method of reduced variables is not applicable to the present system in the long-time region. In terms of the discrete relaxation spectrum, this failure of the time–concentration reduction implies that either the relaxation time or the strength of each relaxation mode is affected by the concentration in a different way. We have already pointed out that J_e^0 and J_{inf} are proportional to c^{-3} and c^{-2}, respectively. As is well known, the former is mainly determined by the modes of longer relaxation times than the latter.[3] Thus, we may conclude that the strength of one or a few relaxation mechanisms near the longest time end is proportional to the third or higher power of c, in contrast to the strength in the plateau region proportional to c^2.

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(13) T. W. DeWitt, H. Markovitz, F. J. Padden, and L. J. Zapas, *J. Colloid Interfac. Sci.*, **10**, 174 (1955); H. Markovitz and D. Brown, *Trans. Soc. Rheol.*, **7**, 137 (1963).

(14) M. R. Hatfield and G. B. Rathmann, *J. Appl. Phys.*, **25**, 1082 (1954).

(15) H. Markovitz, *J. Phys. Chem.*, **69**, 671 (1965).

(16) T. L. Smith, *Trans. Soc. Rheol.*, **2**, 131 (1959).