mately constant. In Figure 5, the quantity $J(t) - t/\eta$ is shown by black circles, which should be equal to the creep recovery started at sufficiently long time, *i.e.*

$$\lim_{t_1 \to \infty} R(t,t_1)$$

In fact, the creep recovery at $t_1 = 2114.2$ sec was in good agreement with $J(t) - t/\eta$. These results show that the rigidity of the thread can be ignored and that the creep as well as creep recovery of moderately soft materials can be satisfactorily measured by this apparatus.

Estimation of η and J_e. It was shown in the preceding section that two parameters characteristic of slow deformation, η and J_e, can be obtained with good precision by measuring creep and creep recovery. The same parameters often have been evaluated from creep data alone by applying the principle of eq 2. Ninomiya's method[4] is now widely used for that purpose. It consists of plotting two quantities J/t and mJ/t against $1/t$. Here m is the slope in the plot of $\log J$ *vs.* $\log t$. The intercepts on the ordinate of these two plots, J/t *vs.* $1/t$ and mJ/t *vs.* $1/t$ should mutually coincide and give $1/\eta$. On the other hand the slope of the line for J/t at $1/t \to 0$ gives J_e. Usually the line for mJ/t is nearly parallel to the abscissa, and η is determined with reasonably good accuracy from the intercept of this line and the ordinate. The evaluation of J_e from the slope of the line for J/t is, however, subjected to a rather large error.

To illustrate the Ninomiya method, we replotted the data from the 12% solution of polystyrene in Figure 6, where open circles represent J/t and filled circles represent mJ/t plotted against $1/t$. The heavy straight line is drawn with the slope and intercept which are consistent with the values of J_e and η already established from the creep and creep recovery measurements. It is seen that all the data corresponding to $m > 0.9$ lie on this straight line. This indicates that reasonably correct estimates of η and J_e are obtainable from creep data alone if a sufficient number of the data $J(t)$ are available in the range of $m > 0.9$. On the contrary, if the data are restricted to the range $m \leqq 0.85$, a 20% error in J_e is unavoidable, and if $m \leqq 0.80$, a 10% error in η and a 50% error in J_e result.

In the paper of Ninomiya it is claimed that η and J_e can be estimated well from the data corresponding to $0.9 > m > 0.7$. Our data show that Ninomyiya's method is quite useful. However, it is to be stressed that the data with $m > 0.85$ are indispensible for accurate evaluation of J_e. Although the data are not reproduced here, we have some evidence that the shape of the curves in Ninomiya's plot depends on the kind of materials and thus the range of m necessary for a good estimation of J_e may depend on materials.

Acknowledgment. The authors wish to thank Professor John D. Ferry for his helpful discussions during his stay at Kyoto University in 1968. This work was supported by a grant for scientific research from the Ministry of Education of our government.

Creep Behavior of Polymer Solutions. II. Steady-Shear Compliance of Concentrated Polystyrene Solutions

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

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan, and Department of Industrial Chemistry, Kyoto University, Sakyo, Kyoto 606, Japan.
Received April 10, 1970

ABSTRACT: The steady-shear compliance J_e and the viscosity η were measured on concentrated solutions of narrow distribution polystyrene in chlorinated diphenyl with a new type of apparatus for measurement of creep and creep recovery. The range of molecular weight studied was $9.7 \times 10^4 \sim 1.8 \times 10^6$ and that of concentration was 0.1~0.6 g/ml. The steady-shear compliance first increased with increasing concentration c, reached a maximum, and then decreased in proportion to c^{-3}. J_e was independent of molecular weight in the range of high concentration where it was proportional to c^{-3}. The maximum in J_e was lower and appeared at higher concentration if the molecular weight was lower. The concentration above which J_e obeyed the c^{-3} dependence was higher for lower molecular weight. The viscosity η was proportional to $M^{3.4}$ in the whole range of concentration. Thus, the entangled system for which the viscosity is proportional to the 3.4th power of molecular weight is further divided into two classes according to the behavior of J_e. Only in the highly entangled state does J_e become proportional to c^{-3} and independent of M. The assumption of uniform excess friction in the modified Rouse theory is not applicable to this highly entangled state of polystyrene.

As was pointed out in the preceding paper,[2] two types of dependence of the steady-shear compliance J_e on molecular weight M and concentration c have been reported for concentrated solutions of polymers, often on the same polymer–solvent system. They are

$$J_e \propto M/c \tag{1}$$

and

(1) (a) Institute for Chemical Research, Kyoto University; (b) Foreign Research Fellow at the Department of Chemistry, University of Wisconsin, in 1970–1971; (c) Department of Industrial Chemistry, Kyoto University.

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

$$J_e \propto 1/c^2 \quad (2)$$

independent of M. The first relationship is compatible with the interpretation of entanglement due to Ferry, *et al.*,[3a] and others,[3b] in which the entanglement coupling between molecules is supposed to contribute an excess friction to all segments of polymer molecules. Thus, in this case, each molecule behaves, in a slow deformation process, as if it were immersed independently of other molecules in a medium with increased viscosity. The relaxation spectrum of the system is then shifted toward long time scale from the position for dilute solutions, but with the terminal shape unchanged. On the other hand, the second relationship, eq 2, shows that the elastic properties of the system are not affected by the molecular weight of an individual molecule. Thus, the situation is in a sense analogous to that of vulcanized rubber systems, and it suggests that a collective motion extending over a group of molecules would play an essential role in the slow deformation process of the entangled system. But no satisfactory theory has been presented yet for describing the latter behavior.

The conflict between eq 1 and 2 may arise from the difference in the system or the concentration range investigated, but it must be attributed, at least in part, to the inappropriateness of the methods used in evaluation of J_e. Indirect measurements of J_e are often subject to a large error which may lead to a wrong relationship between J_e, M, and c.

In view of the existing conflict of experimental results, we find it necessary to perform direct measurements of J_e on concentrated polymer solutions, especially in a wide range of M and c. This paper presents the results of such measurements which were performed on a series of concentrated solutions of polystyrenes with narrow molecular weight distribution.

Experimental Section

Materials. The polymer solutions studied were concentrated solutions of polystyrene in chlorinated diphenyl. The polymer samples were the standard polystyrenes, 14a, 6a, 3a, 1a, and 4a, supplied by Pressure Chemical Co. The weight-average molecular weight M_w of each sample was 1.80×10^6, 8.60×10^5, 4.11×10^5, 1.60×10^5, and 9.72×10^4, and the ratio of M_w to the number-average molecular weight M_n was 1.25, 1.15, 1.06, 1.06, and 1.06, respectively, according to the data sheet from the company.[4] The solvent, Aroclor 1248 supplied by Monsanto Chemical Co., was a mixture of chlorinated diphenyl with various degrees of chlorination. Its viscosity was 1.25 P at 30°.

In the range of concentration studied, polystyrene was dissolved in Aroclor without difficulty. Homogeneous solutions were obtained by stirring the solutions with an iron wire at an elevated temperature, 60°. Another method of dissolution was also attempted, in which methylene chloride was used as an accelerator. But no difference was observed between the properties of the solutions prepared by these two methods.

Measurements. Measurements of the steady-shear compliance J_e and viscosity η were performed with the creep apparatus described in the preceding paper.[2] The creep compliance $J(t)$ and the creep recovery $R(t,t_1)$ were measured. The latter started after a sufficiently long creep time, t_1. The steady-shear compliance J_e was calculated as the limiting value of $R(t,t_1)$ at a long creep recovery time, t. Then, the creep recovery $R(t,t_1)$ was subtracted from $J(t)$ and the difference was plotted against the time, t. If a straight line was obtained and it went through the origin of the coordinate, the viscosity η was calculated from its slope. If not, the data were discarded as a whole. The latter case occurred sometimes when the viscosity was lower than 10^4 P, and it determined the lower limit of concentration measurable by the present apparatus. The evaluation of J_e was performed at 30° unless the viscosity of the system was too low and hindered precise determination of J_e. In the case of low viscosities, the steady-shear compliance was evaluated at 20° or lower temperatures.

Results

Table I shows the data of η and J_e which were obtained for various combinations of molecular weight M and concentration c at 30°. Some data of J_e were obtained at lower temperatures as noted in parentheses.

Figure 1 illustrates the concentration dependence of J_e, from which the following deductions were made. (i) In the range of high concentration, the steady-shear compliance becomes independent of the molecular weight. It decreases with increasing concentration in inverse proportion to the third power of concentration.

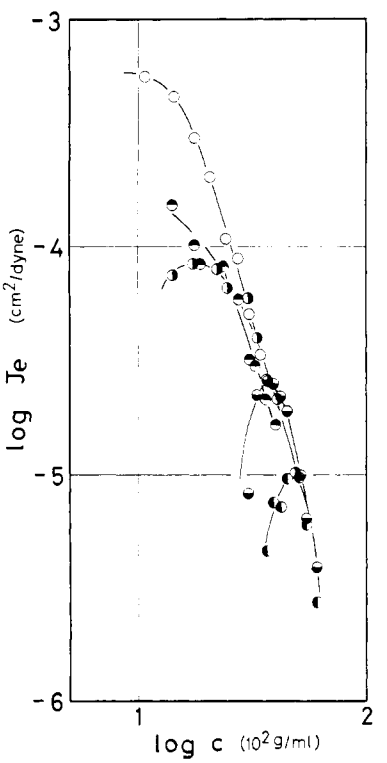

Figure 1. Steady-shear compliance J_e plotted against concentration c on a double logarithmic scale: open circles, solutions of polystyrene 14a; up-half black, 6a; right-half black, 3a; down-half black, 1a; and left-half black, 4a.

(3) (a) J. D. Ferry, R. F. Landel, and M. L. Williams, *J. Appl. Phys.*, **26**, 359 (1955); (b) A. J. Chompff and J. A. Duiser, *J. Chem. Phys.*, **45**, 1505 (1966).

(4) Actually, each polymer sample was dissolved in benzene and precipitated in methanol three times to eliminate degraded molecules which might be present in the sample. The sample was then freeze-dried from benzene solutions. The intrinsic viscosities of the treated samples 14a, 6a, and 3a were 4.13, 2.29, and 1.29 dl/g in benzene at 25°, respectively. These give almost the same values of M_w as the nominal ones, 1.80×10^6, 8.1×10^5, and 3.9×10^5, calculated by the intrinsic viscosity–molecular weight relationship due to Orofino and Wenger, *J. Phys. Chem.*, **67**, 566 (1963).

TABLE I
THE PARAMETERS OF SLOW DEFORMATIONS, η AND J_e, FOR POLYSTYRENE SOLUTIONS IN AROCLOR AT 30°

Code	M_w	c, 10^2 g/ml	η	J_e
14a	1.80×10^6	34.05	1.01×10^8	3.38×10^{-5}
		30.75	3.03×10^7	5.02×10^{-5}
		27.48	6.62×10^6	8.90×10^{-5}
		24.43	3.44×10^6	1.08×10^{-4}
		20.75	8.60×10^5	2.01×10^{-4}
		17.69	2.15×10^5	3.00×10^{-4}
		14.34	5.86×10^4	4.60×10^{-4}
		10.81	9.68×10^3	5.60×10^{-4} (15°)
6a	8.60×10^5	40.04	5.27×10^7	1.64×10^{-5}
		36.30	1.91×10^7	2.14×10^{-5}
		32.10	5.95×10^7	3.00×10^{-5}
		30.68	3.44×10^6	3.20×10^{-5}
		27.59	8.79×10^5	5.90×10^{-5}
		23.83	2.80×10^5	8.17×10^{-5} (20°)
		18.96	5.06×10^4	8.40×10^{-5} (15°)
		17.93	3.08×10^4	1.01×10^{-4} (15°)
		14.12	6.40×10^3	1.51×10^{-4} (10°)
3a	4.11×10^5	49.02	6.77×10^7	1.01×10^{-5}
		41.50	6.47×10^6	2.15×10^{-5}
		36.79	1.52×10^6	2.56×10^{-5}
		33.23	5.20×10^5	4.00×10^{-5}
		30.22	2.32×10^5	6.00×10^{-5}
		24.90	4.18×10^4	6.60×10^{-5} (10°)
		22.02	1.39×10^4	8.00×10^{-5} (20°)
		17.73	4.10×10^3	8.40×10^{-5} (0°)
		14.12	1.10×10^3	7.50×10^{-5} (0°)
1a	1.60×10^5	60.98	3.58×10^8	3.85×10^{-6}
		55.48	3.79×10^7	6.40×10^{-6}
		51.31	6.25×10^6	1.00×10^{-5}
		45.96	1.06×10^6	1.90×10^{-5}
		42.46	5.70×10^5	2.20×10^{-5}
		39.40	1.82×10^5	2.50×10^{-5}
		36.98	7.80×10^4	2.60×10^{-5}
		33.94	3.53×10^4	1.24×10^{-5} (15°)
		30.80	1.46×10^4	8.30×10^{-6} (15°)
4a	9.72×10^4	61.26	8.17×10^7	2.70×10^{-6}
		55.75	7.05×10^6	6.00×10^{-6}
		51.00	1.28×10^6	9.80×10^{-6}
		45.60	2.24×10^5	9.60×10^{-6} (20°)
		42.44	9.76×10^4	7.20×10^{-6} (15°)
		39.35	3.62×10^4	7.60×10^{-6} (15°)
		36.94	1.90×10^4	4.60×10^{-6} (0°)

(ii) As the concentration decreases, J_e gradually becomes insensitive to c, attains a maximum, then decreases. In this range of concentration J_e is dependent of M, *i.e.*, an increasing function of M. (iii) For sample 4a with the lowest molecular weight, J_e drops more rapidly at high concentrations than expected from (i).

The viscosity given in Table I is strongly dependent on concentration. As shown in Figure 2, the slope d log η/d log c becomes steeper with increasing concentration, attaining a value as high as 15 at the highest concentration studied. All curves shown in Figure 2 can be superimposed to give a single composite curve by shifting them vertically by a factor $(M/M_0)^{3.4}$. Here M_0 represents the molecular weight of sample 14a as a reference material. The composite curve thus obtained is shown in Figure 3, where k is chosen as $3.4 \log (M_0/M)$.

The molecular weight dependence of the viscosity is illustrated in Figure 4 at some selected concentrations. In this figure, the interpolated values of viscosity at each selected concentration are plotted against the molecular weight in a double logarithmic scale. The straight lines are drawn with the slope 3.4 and all the data lie on these lines to good approximation. Thus, it may be concluded that a single power law is sufficient for expressing the molecular weight dependence of the viscosity in the range of variables studied.

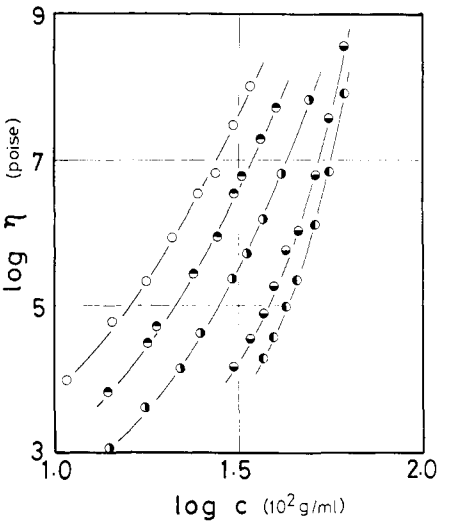

Figure 2. Viscosity η plotted against concentration c at various molecular weights on a double logarithmic scale. Designations are the same as in Figure 1.

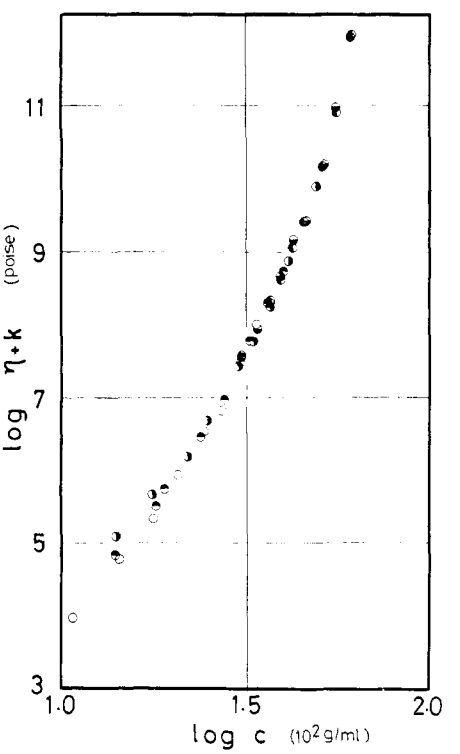

Figure 3. The curves of log η *vs.* c in Figure 2 are shifted vertically to give a single composite curve. The vertical shift factor k is a constant which is determined by M. Designations are the same as in Figure 1.

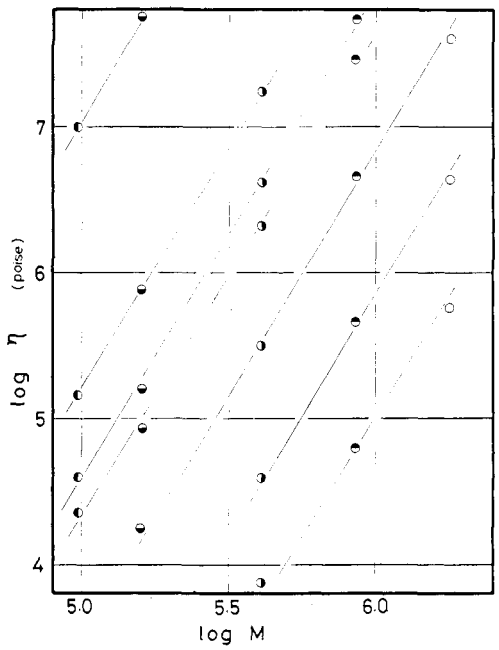

Figure 4. Viscosity η plotted against molecular weight M, at various concentrations on a double logarithmic scale. Concentrations are 56.30, 44.70, 39.80, 37.60, 31.60, 25.10, and 20.00 g/dl from top to bottom, respectively. Solid lines correspond to the relation $\eta \propto M^{3.4}$.

Discussion

Viscosity. As was mentioned above, the viscosity of the present system was strongly dependent on concentration, especially in the range of c higher than 0.5 g/ml. This is probably due to the fact that the system approaches the glass transition point in this range of concentration. When the concentration is low, the glass transition temperature T_g is much lower than the experimental temperature, 30°. However, T_g of the system increases with increasing concentration, and finally it must approach 100°, the value for undiluted polystyrene. Thus, at a concentration somewhere between 0.7 and 1.0 g/ml, the solution is expected to convert to the glassy state. Under the circumstances, the friction coefficient ζ may increase with an extremely high rate as the concentration increases, resulting in a strong dependence of η on c. This problem will be discussed again in a later communication.

The viscosity η of concentrated polymer solutions is often expressed in the form

$$\eta = F\zeta \tag{3}$$

where ζ is the friction coefficient of a chain segment determined by c and T. The dependence of ζ on c and T can be described well by the so-called free-volume theory. On the other hand, F is called the structural factor and it depends on both c and M. Recent studies[5] indicate that

$$F \propto (cM)^{3.4} \text{ for } M \geq M_e \tag{4a}$$

$$F \propto cM \text{ for } M < M_e \tag{4b}$$

M_e is called the critical molecular weight, which is approximately proportional to c^{-1} for many polymer–solvent systems, *i.e.*

$$cM_e = \text{constant} = M_{eo} \tag{5}$$

The material constant M_{eo} is determined by the unperturbed dimension and the specific volume of the polymer, and it assumes a value between 3×10^4 and 5×10^4 for polystyrene.[6] It is now widely accepted that eq 4a is characteristic of the system in which the entanglement coupling between molecules has a predominant effect on the viscosity.

As was noted in the preceding section, the viscosity of the present system was proportional to $M^{3.4}$ over the whole range of concentration investigated. This means that all the solutions studied are in the range that $M \geq M_e$, and they are classified as the entangled systems as far as the viscosity behavior is concerned.

Steady-Shear Compliance. According to Ferry and coworkers,[7] the steady-shear compliance of the same system as the present, *i.e.*, narrow-distribution polystyrene in chlorinated diphenyl, obeys the relationship (1) in the range of concentration 0.04~0.4 g/ml and of molecular weight higher than 8×10^4. The same behavior was also observed by Ashare.[8] Figure 5

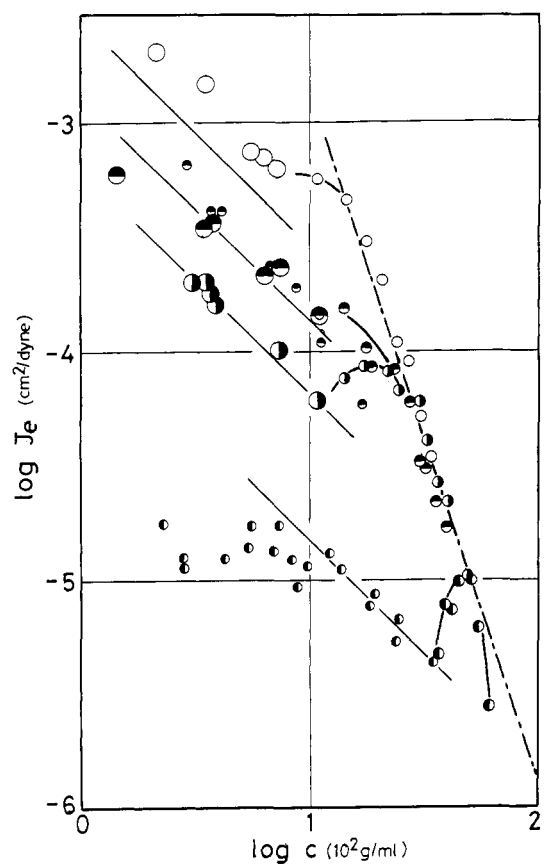

Figure 5. Steady-shear compliance J_e plotted against concentration c on a double logarithmic scale: ◓, polystyrene 6a (Holmes, *et al.*[7a]); ◐, S-102 (Holmes, *et al.*, and Kusamizu, *et al.* [7b]); ○, 14a (Ashare[8]); ◓, 6a (Ashare); ◑, 3a (Ashare); other designations are the same as in Figure 1. Thin lines, values calculated from eq 6.

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

(6) R. S. Porter and J. F. Johnson, *Chem. Rev.*, **66**, 1 (1966).

(7) (a) L. A. Holmes and J. D. Ferry, *J. Polym. Sci., Part C*, **23**, 291 (1968); (b) S. Kusamizu, L. A. Holmes, A. A. Moore, and J. D. Ferry, *Trans. Soc. Rheol.*, **12**, 559 (1968).

(8) E. Ashare, *ibid.*, **12**, 535 (1968).

illustrates this. The two types of small circles represent the date obtained by Holmes, *et al.*, for sample 6a and another sample S-102 with $M = 8.2 \times 10^4$ and the three types of large circles represent the data obtained by Ashare for samples 14a, 6a, and 3a. The thin lines represent the calculated values of J_e due to the modified Rouse theory[7a]

$$J_e = 0.4M/cRT \qquad (6)$$

where R is the gas constant. The temperature T was chosen as 30° and the molecular weight M as 1.80×10^6, 8.60×10^5, 4.11×10^5, and 9.72×10^4, respectively, from top to bottom in the figure. Agreement between the experimental values of J_e and the theoretical ones is satisfactory, except for low concentrations of sample S-102. Thus, based on this finding, these authors have suggested that eq 1 and 6 represents the typical behavior of J_e of the fully entangled systems. This point of view is also supported by the fact that J_e of some undiluted polymers, *e.g.*, poly(vinyl acetate), is proportional to M.[9]

On the other hand, Akovali,[10] Onogi, *et al.*,[11] and Nemoto[12] have found that J_e of undiluted polystyrene with narrow molecular weight distribution is independent of M unless the molecular weight is very low. The values of J_e obtained by these three groups were about 1.0×10^{-6}, 1.4×10^{-6}, and 1.9×10^{-6} cm²/dyn, respectively, and were roughly in agreement with one another. The independence of J_e on M also has been reported for concentrated solutions of thermally polymerized polystyrene in toluene.[13] These results present a sharp contrast to the prediction by the modified Rouse theory, eq 6.

Now, returning to Figure 5, we find that the present measurements just cover the range of concentration which has not been investigated so far. In the figure, the circles of middle size represent the present data for samples 14a, 6a, 3a, and 4a, which are reproduced from Figure 1. These data predict 1.4×10^{-6} cm²/dyn for J_e of the undiluted state if the extrapolation is made linearly toward the right ordinate as indicated by the chain line. (Note, the right ordinate roughly corresponds to the undiluted state.) This value is in good agreement with the value determined by Onogi, *et al.* The slope of the chain line is −3. One measurement at the highest concentration for sample 4a clearly deviates from the chain line. This may be due to the fact that the system is too close to the glass transition point. Hence we neglect this deviation, and conclude that J_e of polystyrene obeys the following relationship above a concentration c_d which is determined by the molecular weight of the polymer

$$J_e \propto 1/c^n, \text{ independent of } M \qquad (7)$$

The exponent n assumes a value about 3. This relationship is analogous to eq 2 except for the difference in the values of n.

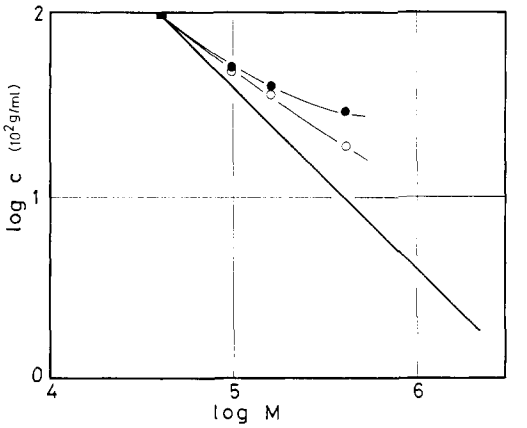

Figure 6. The "critical concentrations" c_d and c_m plotted against M on a double logarithmic scale. c_d is the concentration below which J_e deviates from the relation, $J_e \propto M^0/c^n$ and c_m is the concentration at which J_e displays a maximum. The square corresponds to the molecular weight above which J_e becomes independent of M in the undiluted state.[11] The thick line represents $cM = M_{c0} = 4 \times 10^4$.

Below the concentration c_d, the steady-shear compliance deviates from eq 7, but its behavior is very complicated as is seen in Figure 1 or 5. For the samples with relatively low molecular weights, the deviation occurs rather abruptly around c_d and the steady-shear compliance displays a distinct maximum at a concentration c_m. The shape of the maximum becomes broader and the ratio c_d/c_m becomes larger as the polymer molecular weight increases. However, for samples 14a and 6a with high molecular weights, the deviation from eq 7 occurs only gradually, and the maximum becomes obscure. Two concentrations c_d and c_m determined in this way are plotted against M in Figure 6 by black circles and white circles, respectively. Also the square indicates the molecular weight above which J_e of undiluted polystyrene becomes independent of M,[11] and the heavy line represents the relationship $cM_c = M_{c0} = 4 \times 10^4$. The region above this line corresponds to the so-called entangled region in which the viscosity obeys eq 3 and 4a. Now, the present study reveals that this region is further divided into two parts according to the behavior of J_e. One part located above c_d is the fully entangled region in which J_e obeys eq 7. The other part extends between c_d and the line, $cM_c = 4 \times 10^4$, in which J_e deviates from eq 7 but η still obeys the 3.4th power law, eq 4a. When M is large, the latter region extends over a fairly wide range of concentration, and J_e varies as $1/c^n$ with $n = 1 \sim 3$.

In this connection, we note that J_e of sample 14a obeys eq 2 in toluene in the range of concentration 0.07∼0.2 g/ml.[13] This observation does not conflict with the present one, for the exponent n generally tends to decrease with decreasing concentration. In fact, the value 2 is obtained from sample 14a in the present solvent in the range of concentration 0.1∼0.2 g/ml. However, the value of J_e obtained in this study is about twice as large as that obtained in toluene if comparison is made at the same concentration. This suggests the possibility that J_e depends on the type of solvent. However, more extensive measurements are necessary to clarify the solvent effect on J_e.

(9) Y. Oyanagi and J. D. Ferry, *J. Colloid Sci.*, **21**, 547 (1966).
(10) G. Akovali, *J. Polym. Sci., Part A-2*, **5**, 875 (1967): see also A. V. Tobolsky, J. J. Aklonis, and G. Akovali, *J. Chem. Phys.*, **42**, 723 (1965).
(11) S. Onogi, T. Masuda, and K. Kitagawa, *Macromolecules*, **3**, 109 (1970).
(12) N. Nemoto, *Polym. J.*, **1**, 485 (1970).
(13) M. Kurata, K. Osaki, and M. Tamura, *Bull. Inst. Chem. Res., Kyoto Univ.*, **46**, 87 (1968).

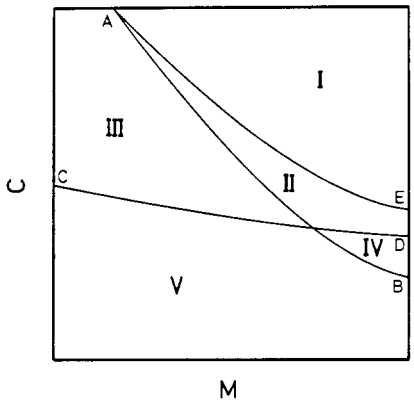

Figure 7. Five categories of polymer solutions based on the flow properties of polymer solutions as functions of molecular weight and concentration.

Classification of the Effects of M and c on J_e. It has been suggested by the present authors that polymer solutions can be classified into several regions of concentration and molecular weight according to the behavior of viscosity η and steady-shear compliance J_e.[14] These regions are (I) $\eta \propto M^{3.4}$ and $J_e \propto M^0/c^n$. This region is located at high concentration; (II) $\eta \propto M^{3.4}$. J_e increases with M and displays a maximum as a function of c. This type of behavior is observed in the concentration range a little higher than that corresponding to the relation $cM = M_{c0}$. The third region extends over the range of fairly high concentration c and low molecular weight M: (III) $\eta \propto M^{1.0}$. J_e is very low, increases with increasing M and is not very sensitive to c. This type of behavior is observed in solutions of low molecular weight polymers in the concentration range a little lower than that corresponding to the relation $cM = M_{c0}$. In addition, two other regions have been observed in earlier publications:[15,16] (IV) η is not proportional to a simple power of M. J_e varies in proportion to M^1/c^0. This behavior is observed in rather dilute solutions of polymers of very high molecular weight;[15] (V) the dynamic mechanical properties obey the predictions of the theories of dilute polymer solutions. This behavior is observed in extremely dilute solutions.[16]

These five regions may be distinguished by assuming three boundaries, AB, CD, and AE, as shown in Figure 7. Polymer chains have a tendency to entangle with each other in the region above the curve AB, *i.e.*, in regions I, II, and IV. The polymer chains may have contact with each other below the curve AB, but they are free of entanglement. This boundary AB may be represented by the relation $cM = M_{c0}$. The curve CD is the boundary between "dilute" and "concentrated" solutions. In the former, a polymer molecule may be surrounded predominantly by solvent molecules, and in the latter, by other polymer molecules. This boundary may be more or less diffuse, and the transition from one side to the other occurs gradually. Thus, regions IV and V belong to the category of "dilute" solutions and the viscosity is probably proportional to the viscosity of solvent. Furthermore, in region IV, polymer molecules tend to form entanglements due to their large dimensions. Thus, the concept of aggregated molecules seems to be applicable in this region as a working hypothesis. The line AE defines the region I in which the entanglement is so highly developed that a collective motion extending over many molecules will play a dominant role in determination of the flow behavior. Of course, this is only a conjecture until the theory of entanglement is developed in a form applicable not only to η but also to J_e.

Acknowledgment. The authors wish to thank Professor John D. Ferry for his helpful discussions during his stay at Kyoto University in 1968. This work was supported by a grant for scientific research from the Ministry of Education of our government.

(14) See, for example, T. Kotaka and K. Osaki, *J. Polym. Sci., Part C*, **15**, 453 (1966).
(15) K. Osaki, M. Kurata, and M. Tamura, *Polym. J.*, **1**, 334 (1970).
(16) See, for example, J. E. Frederick, N. W. Tschoegl, and J. D. Ferry, *J. Phys. Chem.*, **68**, 1974 (1964).