Non-Newtonian Flow of Concentrated Solutions of High Polymers*

SHIGEHARU ONOGI† *Department of Chemistry, University of Massachusetts, Amherst, Mass.,*

and

TADASHI KOBAYASHI, YASUHIRO KOJIMA, and YOSHISHIGE TANIGUCHI, *Department of Polymer Chemistry, Kyoto University, Kyoto, Japan*

INTRODUCTION

In the previous paper on viscoelastic properties of concentrated solutions of polyvinyl alcohol,[1] log–log plots of zero-shear viscosity versus concentration were represented by two straight lines having a slope of about 6 above the critical concentration 8.7% and a much lower slope below it. Because of restriction of the apparatus employed, the concentration dependency of the dynamic viscosity under various conditions could not be studied. In the study reported here the steady-flow viscosities of moderately concentrated solutions of polyvinyl alcohol and polystyrene were measured at various concentrations and temperatures by means of a capillary viscometer with continuously varying pressure head. The concentration dependency of the zero-shear viscosity is chiefly discussed.

EXPERIMENTAL

Materials

The polyvinyl alcohol (PVA) samples were very similar to those used in the previous viscoelastic study.[1] The viscosity-average degrees of polymerization calculated from the intrinsic viscosity in water were 640, 1100, 1600, 2000, and 2200.[2] Polystyrene (PS) samples, on the other hand, were polymerized from purified monomer for 100 hrs. at 80°C., 37 hrs. at 100°C., 8 hrs. at 115°C., and 8 hrs. at 130°C., giving the desired molecular weights.[3] The polymers obtained were dissolved at once in methyl ethyl ketone, and

then precipitated by gradual addition of the solution into toluene. In these processes, the fractions of very low and of high molecular weight were removed. The viscosity-average molecular weights for each sample, determined from intrinsic viscosities in toluene, were 1.57, 2.82, 5.87, and 11.9 $\times$ 10[5].[4,5]

Methods

Steady-flow viscosity was measured by means of a capillary viscometer with continuously varying pressure head, described by Maron et al.[6] Four capillaries having different dimensions were used. Dimensions of the other parts of the viscometer were not very different from those described by Maron and co-workers, and the measuring techniques were entirely the same as theirs. The apparent viscosity η_a was calculated by the following equation:

$$1/\eta_a = - (m/B) [1 + (1/9.212m^2) (dm/dt)$$

where $m = d (\log h)/dt$, $h =$ height of the mercury manometer from its equilibrium position, $t =$ time, and $B =$ apparatus constant.

RESULTS

Figure 1 shows a typical data of rate of shear dependence of the apparent viscosity at various temperatures. Other solutions of PVA and PS with
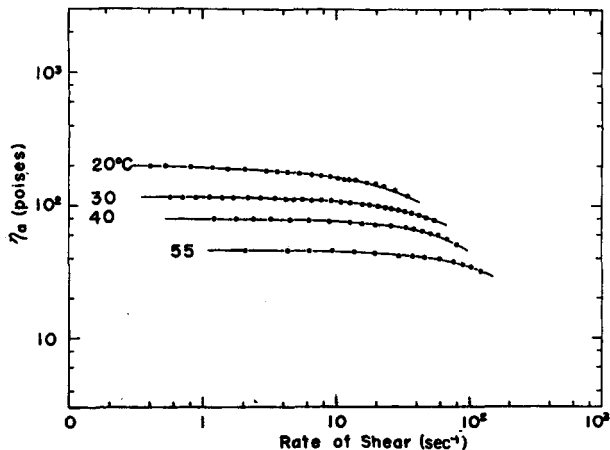

Fig. 1. Rate of shear dependence of the apparent viscosity of 12% solution of PVA having DP = 2000 at various temperatures.

different molecular weights show very similar behavior at different concentrations. For these data the so-called time–temperature superposition method can be applied. The shift factor log a_T obtained for the solution shown in Figure 1 is plotted against temperature in Figure 2. Its tempera-
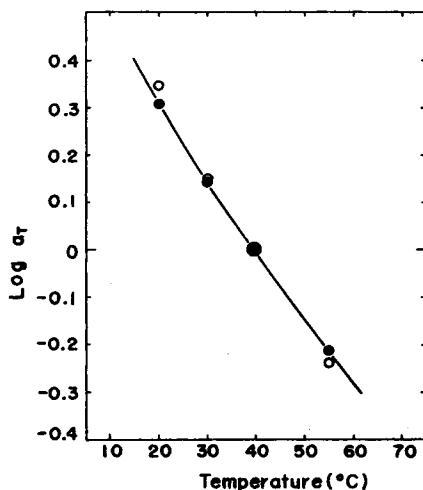
Fig. 2. Comparsion of shift factors obtained from steady-flow and dynamic data for PVA solutions: (O) from steady-flow data, DP = 2000; (●) from dynamic data, DP = 1600.
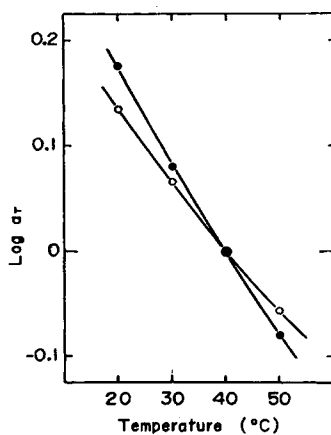

Fig. 3. Shift factor versus temperature for solutions of PS having $M = 2.82 \times 10^{5}$: (●) 19.4%; (O) 4.83%.

ture dependence is very similar to that found in dynamic data previously and can be represented by the following WLF type of equation:[7]

$$\log a_T = -4.50 \ (t\text{-}40)/(310 + t - 40)$$

where t is temperature in degrees centigrade.

The time–temperature superposition method and WLF-type equations can also be applied to the PS solutions studied. For instance, Figure 3 shows the shift factors plotted against temperature for 4.83 and 19.4% solutions of PS having a molecular weight of 2.82×10^{5}. Two constants in the WLF-type equation, c_1 and c_2, are 1.26 and 200 for the former and
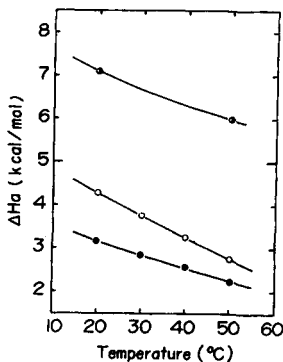
Fig. 4. Apparent activation energy as a function of temperature for PVA and PS solutions: (◐) PVA, 12%, DP = 1600; (O) PS, 19.4%, $M = 2.82 \times 10^5$; (●) PS, 4.83%, $M = 2.82 \times 10^5$.
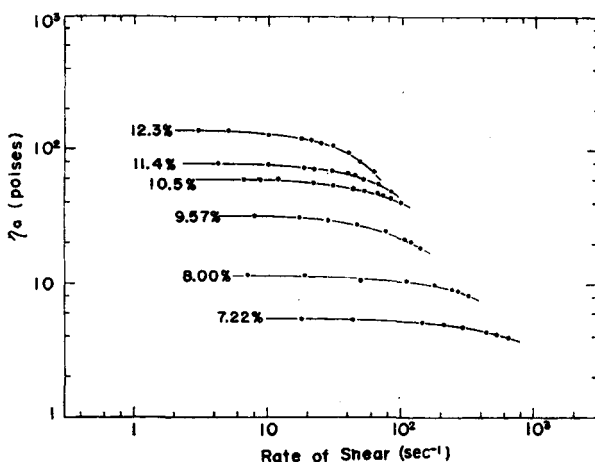

Fig. 5. Rate of shear dependence of the apparent viscosity of PVA solutions at 40°C. at different concentrations, DP = 2200.

2.16 and 260 for the latter. The apparent activation energies ΔH_a for these solutions, obtained from the shift factor, are plotted in Figure 4 against temperature.

The zero-shear viscosity for solutions of PVA as well as PS plotted logarithmically against the logarithm of molecular weight can be presented by a straight line having a slope of about 3.4.

Figures 5 and 6 show examples of rate of shear dependency of the apparent viscosity for solutions of PVA and PS at different concentrations. For these curves the usual time–concentration superposition methods described by Ferry[8] and by DeWitt et al.[9] cannot be applied. However, when we shift the curves by proper distances different from those described by Ferry and DeWitt, in vertical and horizontal directions, they can be superposed fairly well.
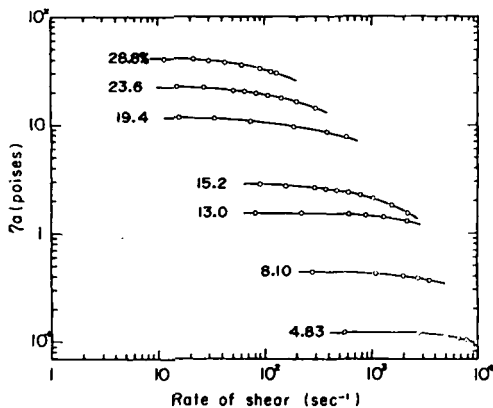
Fig. 6. Rate of shear dependence of the apparent viscosity of PS solutions at 40°C. at different concentrations.
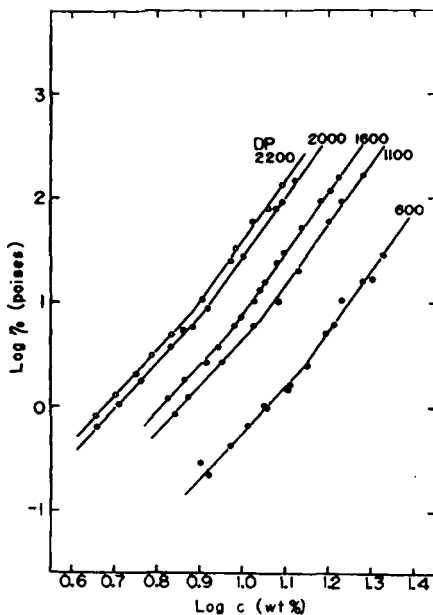
Fig. 7. Log–log plot of zero-shear viscosity versus concentration for PVA solutions at 40°C.

In Figures 7 and 8 the logarithm of zero-shear viscosity η_0 at 40°C. is plotted against the logarithm of concentration for solutions of PVA and PS having different molecular weights.   As seen from these figures, the curves can well be represented by two straight lines intersecting at critical concentration c_c, at least in the concentration range studied here.   The slope of the straight line below c_c is 4.4 for PVA solutions and 2.3 for PS solutions.   On the other hand, the slope above c_c is 6.0 for PVA solutions and 5.0 for PS

TABLE I
The Slopes of log η_0 versus log c Curves

System	Below c_c	Above c_c	Ref.
PVA–water	4.4	6.0	
PS–toluene	2.3	5.0	
PVC–cyclohexanone	3.3	5.0	11
PS–diethyl benzene	2.3	6.0	10

solutions. Similar features can be found in experimental results with PS in diethyl benzene studied by Bueche,[10] and have been reported recently by Asai[11] for polyvinyl chloride (PVC) in cyclohexanone. The slopes below and above c_c are listed in Table I.
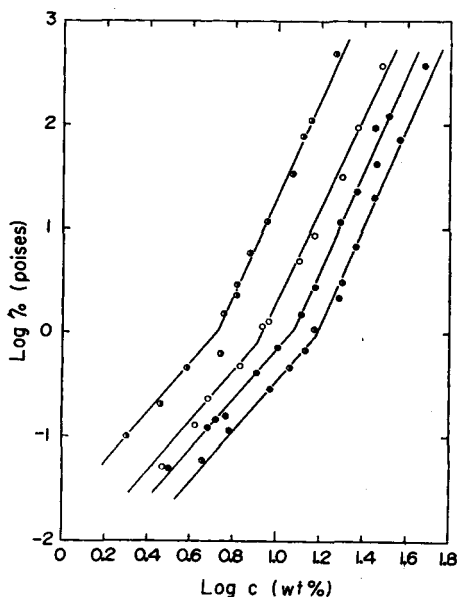
Fig. 8. Log–log plot of zero-shear viscosity versus concentration for PS solutions at 40°C.: M = (◑) 1.23 × 10⁶; (○) 5.87 × 10⁵; (●) 2.82 × 10⁵; (◍) 1.57 × 10⁵.

The critical concentration c_c seems very similar to the critical chain length Z_c in log η_0 vs. log Z plots for many polymer systems, including concentrated solutions and melts, as mentioned by Fox et al.[12,13] This critical concentration c_c depends, of course, very much upon the molecular weight of the solute polymers, but the product of the chain length and the critical concentration in the volume fraction of polymers in solution, v_{2c}, is not constant but changes with the chain length, showing a difference from the prediction made by Bueche.[10,14] In Figure 9 c_c and v_{2c} for PVA and c_c for PS solutions are plotted against the reciprocal chain length Z^{-1}. The critical concentration increases with decreasing chain length, but the rela-
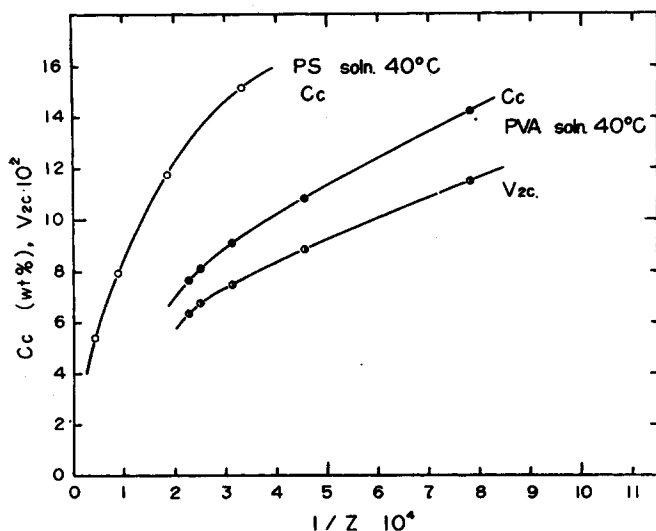
Fig. 9. Critical concentration c_c (wt.-%) and v_{2c} (volume fraction) plotted against reciprocal chain length for PVA and PS solutions at 40°C.

tion between them is not at all linear. It is very interesting to notice that PVA has much lower critical concentration than PS having the same chain length. In other words, a polar polymer reaches the critical concentration

TABLE II
Some Characteristics of the Critical Concentration

Z	c_c, wt.-%	V_{2c} in vol. fract., $\times 10^{-2}$	$v_{2c}Z$	$c_c\rho Z^{1/2}$
		PVA, 40°C.		
4400	7.67	6.38	281	517
4000	8.13	6.75	270	522
3200	9.13	7.49	240	526
2200	10.8	8.84	195	508
1280	14.3	11.5	147	526
			Mean 520	
		PS, 40°C.		
23,700	5.37	4.24	1004	710
11,300	7.94	6.13	693	728
5,420	11.8	9.52	516	753
3,020	15.1	12.3	371	729
			Mean 730	
		PVC, 30°C.		
3300	9.86	6.67	220	548
2500	11.27	7.68	192	547
1940	12.74	8.74	170	548
1480	14.39	10.3	152	547
			Mean 548	

sooner than a nonpolar polymer when the concentration is increased.   Furthermore, the order of magnitude of the product $v_{2c}Z$ is quite the same as that of the product v_2Z_r in the case of $\log \eta$ versus $\log \eta Z$ plots.   That is, $v_{2c}Z$ of PVA is very low (147–281) and of same order as v_2Z_c for polar polymers, while that of PS (371–1004) is of same order as v_2Z_c for nonpolar polymers.   The product $v_{2c}Z$ obtained by Asai for PVC also shows very low values and varies from 152 to 220, depending upon the molecular weight of the solute polymers.[11]   In Table II some characteristics of the critical concentrations for the above solutions are summarized.   It is worth noticing in this table that the product $c_c\rho Z^{1/2}$ (ρ is the density of the solution) in the last column has constant values independent of molecular weight or chain length.   This constancy of $c_c\rho Z^{1/2}$ and the significance of the critical concentration will be discussed.

DISCUSSION

First we consider that the solution can be represented by the equivalent sphere model, and the number of spheres in volume V is denoted by n, the radius by r, and the volume by v.

Now, we assume that the rapid increase in the apparent viscosity at the critical concentration c_c occurs when the volume fraction of spheres reaches a constant value v_0.   Then, at $c = c_c$ the following relation holds:

$$\frac{4\pi r^3 n}{3V} = v_0 \tag{1}$$

When the radius r of the sphere is proportional to the root of chain length Z, eq. (1) can be written as follows:

$$Z^{3/2}n/V = 3v_0/4\pi k^3 \tag{2}$$

where:

$$k = r/Z^{1/2} \tag{3}$$

since the concentration in weight-per cent, c, is given as:

$$c = 100\, nM/\rho N_0 V$$

where M = molecular weight of solute polymers, ρ = density of the solution, and N_0 = Avogadro's number, eq. (2) becomes:

$$N_0 Z^{3/2} c\rho/M = 300 v_0/4\pi k^3 \tag{4}$$

For vinyl polymers, Z can be given as

$$Z = 2M/M_0 \tag{5}$$

where M_0 is the molecular weight of monomer units.   Therefore, eq. (4) reduces to:

$$c\rho Z^{1/2} = 300 v_0 M_0/8\pi k^3 N_0$$

$$= K = \text{constant}\quad(\text{at constant temperature})\tag{6}$$

or

$$c'Z^{1/2} = K \quad \text{(at constant temperature)} \tag{6}$$

where c' is the concentration in grams per 100 milliliters.

The above result of the calculation can explain very well the constancy of $c\rho Z^{1/2}$ observed experimentally and suggests that the assumptions employed in the calculation are very probable. In other words, it is very probable that moderately concentrated polymer solutions can well be represented by the equivalent sphere model, and that at the critical concentration the volume fraction of the spheres is constant. Furthermore, chain molecules in the solution seem to be unperturbed, at least at the critical concentration: they are quite free from perturbation owing to the long-range effect.

Now, we can calculate the volume of spheres in the solution, v, by using eqs. (6) and (2), when we assume a suitable value for v_0 and use K values obtained experimentally for each polymer. As an example, the values of v for the solutions of PVA, PS, and PVC have been calculated by assuming $v_0 = 0.5236$, which is a value for the cubical packing of spheres. The results are shown in the second column of Table III as v_c.

TABLE III
Volume of Equivalent Spheres

$Z^{1/2}$	v_c ($v_0 = 0.5236$)	v_c	v_c/v_e	v_1 ($v_0 = 1.00$)	v_1/v_c
		PVA			
66.4	10.8×10^{-19}			20.6×10^{-19}	
63.2	9.29 "			17.7 "	
56.6	6.68 "			12.8 "	
46.9	3.80 "			.29 "	
35.8	1.69 "			3.24 "	
		PS			
153.9	22.6×10^{-18}	45.1×10^{-18}	1/2.00	43.2×10^{-18}	1/1.04
106.3	7.45 "	14.9 "	1/2.00	14.2 "	1/1.05
73.6	2.47 "	4.97 "	1/2.01	4.73 "	1/1.05
55.0	1.03 "	2.06 "	1/2.00	1.97 "	1/1.05
		PVC			
57.4	9.37×10^{-19}			17.9×10^{-19}	
50.0	6.20 "			11.9 "	
44.0	4.23 "			8.08 "	
38.5	2.83 "			5.41 "	

Unfortunately, however, we have no way of deciding the reasonableness of the value of v_c. To proceed further, therefore, we shall compare v_c with the extension of chain molecules in dilute solutions.

According to the results of the hydrodynamic treatment of Kirkwood and

Reiseman, the molecular frictional coefficient f_0 is related to the mean square length of chain, $\overline{r^2}$, by the following equation:[15,16]

$$f_0/\eta_s = 5.11 \sqrt{\overline{r^2}} \tag{7}$$

where η_s is the viscosity of the solvent. When the molecules are unperturbed and, hence, the molecular expansion factor α is equal to unity, $\overline{r^2}$ in eq. (7) can be replaced by the unperturbed dimensions $\overline{r_0^2}$. Therefore, we can obtain:

$$f_0/\eta_s = 5.11 \sqrt{\overline{r_0^2}} \tag{8}$$

Now, the unperturbed molecular expansions $(\overline{r_0^2}/M)^{1/2}$ of several polymers are known. For polystyrene it is given as:[16]

$$(\overline{r_0^2}/M)^{1/2} = 735 \times 10^{-11} \text{ at about } 25°C.$$

Substituting this value into eq. (8) we obtain for PS:

$$f_0/\eta_s = 6\pi \times 1.993 \times 10^{-9} M^{1/2}$$

Therefore, the volume of spheres of molecules, v_e, can be given by:

$$v_e = 3.316 \times 10^{-23} M^{3/2} \tag{9}$$

The calculated values of V_e for PS solutions are shown in the third column in Table III. In the fourth column the ratio of v_c to v_e is given. It is very surprising to see that the values of this ratio are just equal to $^1/_2$ for four samples of PS used by us; v_c is much smaller than v_e.

However, if we consider a remarkable increase in the viscosity of polymer solutions with increasing concentration, a great decrease in the volume of spheres in concentrated solutions from that in dilute solutions is difficult to accept. Accordingly, it seems rather reasonable for us to take the volume of spheres in concentrated solutions as large as possible. And its upper limit is a value corresponding to $v_0 = 1.00$. This value, v_1, was calculated in the same manners as before; it is given in the fifth column of Table III, and its ratio to v_e in the last column. It is very interesting to see that for PS samples this ratio is very close to unity.

From the above we are inclined to conclude that the critical concentration c_0 means a limiting case at which spheres of chain molecules are fully packed throughout the solution without any spaces between them, and that molecules at c_0 are in an unperturbed state. Moreover, this conclusion is extended to the case of $\log \eta$ versus $\log M$ plots, the critical chain length may have the same meaning as this c_0, and the product $c\rho Z_c^{1/2}$ at $Z = Z_c$ may have the same value as $c_c\rho Z^{1/2}$. Experimental results verifying this can be found in a paper by Bueche,[10] who has studied both the $\log \eta$ versus $\log M$ and the $\log \eta$ versus $\log c$ relations for the same PS–diethyl benzene system. According to his results, 44% solutions of PS having different chain lengths give $cZ_c^{1/2} = 2110$, and solutions of PS having $M_w = 7.2 \times 10^5$ at different concentrations give $c_c Z^{1/2} = 2124$. Allowing for a slight difference in density of the solutions, these two values are quite close to each other.

Now, if the above conclusion is true, we can evaluate the unperturbed molecular extension $(\overline{r_0^2}/M)^{1/2}$ by using the following relation obtained experimentally from the K value as a product $c_c\rho Z^{1/2}$ or $c\rho Z_c^{1/2}$.

$$(\overline{r_0^2}/M)^{1/2} = 11.92/(N_0 M_0^{1/2} K)^{1/3} \qquad (10)$$

This relation can easily be derived by combining eqs. (2) and (6) with eq. (8), after assuming $v_0 = 1$.

The evaluation was tried by applying this method both to our solutions and to Asai's. The results are summarized in Table IV, with the K values. The molecular extension in the case of free rotation about C—C bonds, $(\overline{r_{0f}^2}/M)^{1/2}$, and the ratio σ of $(\overline{r_0^2}/M)^{1/2}$ to $(\overline{r_{0f}^2}/M)^{1/2}$ are also tabulated. It is clear from this table that K values for PVC at different temperatures increase and hence the molecular extension decreases with increasing temperature, although the changes are rather slight. This result seems to be quite reasonable, because it is coincident with the results with dilute solutions. When such a dependence of the molecular extension on the temperature is taken into consideration, the value 722 for PS at 40°C. appears to be very reasonable, as compared with the value 735 at about 25°C. described by Flory.[16]

TABLE IV
Unperturbed Molecular Extension Evaluated from $K = c_0\rho Z^{1/2}$

Polymer	Temp., °C.	K	$((\overline{r_0^2}/M)^{1/2})$ $\times 10^{11}$	$((\overline{r_{0f}^2}/M)^{1/2})$ $\times 10^{11}$	$\sigma =$ $((\overline{r_0^2}/\overline{r_{0f}^2})^{1/2})$
PVA	40	520	828	463	1.79
PS	40	730	722	302	2.39
PVC	40	557	861	389	2.21
	30	548	866	389	2.23
	20	541	869	389	2.23

Unfortunately, a θ solvent for PVA and PVC has not yet been found. Therefore, we cannot evaluate the molecular extension for these polymers directly from the intrinsic-viscosity data at θ point. According to Kurata,[17] who has calculated the molecular extension of PVA and PVC from the existing data on the molecular weight dependence of intrinsic viscosity by means of Kurata's theory,[18] $\sigma = 1.9$–2.0 for PVA and $\sigma = 2.0$ for PVC. As is well known, these polymers show rather complicated behavior even in dilute solutions, and accurate measurements of their viscosities are very difficult to make. Nevertheless, the values of σ evaluated by Kurata and by us in quite different manners show surprisingly good agreement, indicating that the above result for PS is not accidental.

We hope that our findings on the critical concentration will make much clearer the picture of concentrated solutions or melts of high polymers.

References

1. Onogi, S., I. Hamana, H. Hirai, *J. Appl. Phys.*, **29**, 1503 (1958).

2. Nakajima, A., and K. Furutachi, *Chem. High Polymers, Tokyo*, **6**, 460 (1949).

3. Schulz, G. V., and E. Huseman, *Z. Phys. Chem.*, **B34**, 187 (1936).

4. Alfrey, T., A. Bartovics, and H. Mark, *J. Am. Chem. Soc.*, **65**, 2319 (1943).

5. Kuroiwa, T., and E. Wada, *Kobunshi Jikkengaku Koza*, Vol. 8-1, Maruzen, Tokyo, 1958, chap. 5.

6. Maron, S. H., I. M. Krieger, A. W. Sisko, *J. Appl. Phys.*, **25**, 971 (1954).

7. Williams, M. L., R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).

8. Ferry, J. D., *J. Am. Chem. Soc.*, **72**, 3746 (1950).

9. DeWitt, T. W., H. Markovitz, F. J. Paddon, and L. J. Zapas, *J. Colloid Sci.*, **10**, 174 (1955).

10. Bueche, F., *J. Appl. Phys.*, **24**, 423 (1953).

11. Asai, H., paper presented at the Annual Meeting of The Chemical Society of Japan, 1961; *Chem. High Polymers, Tokyo*, **19**, 19 (1962).

12. Fox, T. G, S. Loshaek, *J. Appl. Phys.*, **26**, 1080 (1955).

13. Fox, T. G, S. Gratch, and S. Loshaek, in Eirich, F. R., *Rheology*, Vol. 1, Academic Press, New York, 1956, p. 446.

14. Bueche, F., *J. Appl. Phys.*, **26**, 738 (1955).

15. Kirkwood, J. G., and J. Riseman, *J. Chem. Phys.*, **16**, 565 (1948).

16. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, 1953, p. 618.

17. Kurata, M., private communication.

18. Kurata, M., and W. H. Stockmayer, paper presented at the International Symposium on Macromolecular Chemistry, Montreal, Canada, Aug. 1, 1961.

19. Onogi, S., T. Kobayashi, and Y. Taniguchi, *J. Japan Soc. Testing Mater.*, **9**, 245 (1960).

20. Onogi, S., Y. Kojima, and Y. Taniguchi, *J. Japan Soc. Testing Mater.*, **10**, 357 (1961).

Synopsis

Non-Newtonian flow of moderately concentrated solutions of polyvinyl alcohol (PVA) in water and polystyrene (PS) in toluene were measured with a Maron-Krieger-Sisko viscometer at various temperatures and concentrations. The usual dependences of the apparent and zero-shear viscosities for two polymers on rate of shear, temperature, and molecular weight have been found. The log–log plot of zero-shear viscosity versus concentration can be represented by two straight lines intersecting at one point (critical concentration c_0). The critical concentration in volume fraction of polymer, v_{2c}, multiplied by the chain length Z is not constant but decreases with decreasing Z, although it has the same order of magnitude as the value of $Z_c v_2$ obtained from the log–log plots of viscosity versus Z for many systems of polar and nonpolar polymers. The product $c_0 \rho Z^{1/2}$ (ρ = density of the solution) is constant and independent of Z. To explain the constancy of this product, an equivalent sphere model is presented. When the volume fraction of spheres is assumed to be unity, the extension of molecules agrees very well with the unperturbed extension evaluated from intrinsic viscosity data in Θ solvent.

Résumé

On a mesuré l'écoulement non-Newtonien de solutions modérément concentrées d'alcool polyvinylique (PVA) dans l'eau et de polystyrene (PS) dans le toluène à l'acide d'un viscosimètre de Maron-Krieger-Sisko, è diverses températures et concentrations. On a retrouvé les relations habituelles entre les viscosités apparentes et de cisaillement nul pour deux polymères et la vitesse de cisaillement, la température et le poids moléculaire. Un diagramme logarithmique de la viscosité à cisaillement nul en fonction de la concentration peut être représenté par deux droites se coupant en un point (la concentration critique c_c). La concentration critique de la fraction en volume de polymère, v_{2c}, multipliée par la longueur de chaîne Z, n'est pas constante mais diminue lorsque Z diminue, bien qu'elle ait le même ordre de grandeur que le valeur de $Z_2 v_2$ obtenue aux dépens des diagrammes logarithmiques de la viscosité en fonction de Z pour de nombreux systèmes de polymères polaires et non-polaires. Le produit $c_c \rho Z^{1/2}$ (ρ = densité de la solution) est constant et indépendant de Z. Afin d'expliquer la constance de ce produit, on propose un modèle de sphère équivalent. Lorsque la fraction en volume des sphères est supposée unitaire l'extension des molécules correspond très bien avec l'extension non-perturbée évaluée à partir de la viscosité intrinsèque dans un solvant Θ en accord avec les théories habituelles.

Zusammenfassung

Das nicht-Newtonsche Fliessen von mässig konzentrierten Lösungen von Polyvinyl-alkohol (PVA) in Wasser und Polystyrol (PS) in Toluol wurde mit einem Maron-Krieger-Sisko-Viskosimeter bei verschiedenen Temperaturen und Konzentrationen gemessen. Es wurde die normale Abhängigkeit der scheinbaren Viskosität und der Viskosität für den Schub Null von Schergeschwindigkeit, Temperatur und Molekularge-wicht bei zwei Polymeren gefunden. Das doppeltlogarithmische Diagramm Viskosität bei Schub Null gegen Konzentration kann durch zwei Gerade dargestellt werden, die sich an einem Punkt (kritische Konzentration c_c) schneiden. Die kritische Konzentration, ausgedrückt als Volumbruch des Polymeren, v_{2c}, multipliziert mit der Kettenlänge Z ist nicht konstant, sondern nimmt mit fallendem Z ab, besitzt aber die gleiche Grossen-ordnung wie der aus dem doppeltlogarithmischen Viskositäts-Z-Diagramm bei vielen Systemen mit polaren un unpolaren Polymeren erhaltene $Z_c v_2$-Wert. Das Produkt $c_c \rho z^{1/2}$ (ρ = Dichte der Lösung) ist konstant und von Z unabhängig. Zur Erkärung der Konstanz dieses Produkts, wurde ein Äquivalent-Kugel-Modell angegeben. Unter der Annahme, dass der Volumbruch der Kugeln eins ist, stimmt die Ausdehnung der Moleküle sehr gut mit der aus den Viskositätszahldaten in einem Θ-Lösungsmittel nach den bekannten Theorien berechneten ungestörten Ausdehnung überein.