Sedimentation, Diffusion and Viscosimetric Measurements on Polymethyl Methacrylate Fractions Obtained at Different Degrees of Conversion

A. FREDRIK V. ERIKSSON

Institute of Physical Chemistry, University of Uppsala, Uppsala, Sweden

It has been found from the nature of the relations between the sedimentation constant s , the intrinsic viscosity $[\eta]$ and the molecular weight M that polymethyl methacrylate molecules formed at higher degrees of conversion do not have the same configuration as those molecules obtained during the stationary stage of the polymerisation. The relations between s , $[\eta]$ and M obtained for polymer molecules prepared at low degrees of conversion have been compared with Flory's theory for chain molecules. Slight systematic deviations of the experimental values from the theoretically expected relations have been observed.

The work reported in this paper is a part of an investigation of the molecular weight distribution in polymethyl methacrylate. The purpose of the present part has been to determine empirical relations between the sedimentation constant, the intrinsic viscosity and the molecular weight of polymethyl methacrylate molecules.

MATERIAL

The monomer methyl methacrylate has been polymerised in nitrogen atmosphere with various amounts of benzoylperoxide as initiator. The polymerisation temperature was 60° C for samples B(704) and B(720) and 80° C for samples B(714) and B(712). The degrees of conversion are 18, 72, 14, and 47 % for B(704), B(720), B(714), and B(712), respectively. A detailed account of the polymerisation technique and the method of fractionation will be given elsewhere¹. Ethyl acetate has been used as solvent for all measurements. The quality of the ethyl acetate was "Baker Analyzed Reagent" and it was used without further purification.

VISCOSITY MEASUREMENTS

The intrinsic viscosity $[\eta]$ has been determined by means of an Ostwald viscometer at 20° C in ethyl acetate. The value of $[\eta]$ was obtained by extrapolating η_{sp}/c to infinite dilution, the reduced viscosity η_{sp}/c being determined for four concentrations (c). The

extrapolation was facilitated by the fact that η_{sp}/c is a linear function of concentration in the concentration range used. All measurements were made at concentrations lower than 0.4 g/100 ml.

SEDIMENTATION MEASUREMENTS

Technique. The sedimentation measurements have been performed in an oilturbine ultracentrifuge of the Svedberg type. A detailed account of the ultracentrifuge process has been given in the monograph by Svedberg and Pedersen ² so only certain technical data will be mentioned here. The distance between the meniscus and the axis of rotation was 5.9 cm. The speed of the rotor was 800 revs/sec. for all measurements except for those on fractions of the sample B(704). In this latter case the rotor speed was only 600 revs/sec. For the observation of the sedimentation velocity Lamm's ³ scale method was used. The temperature of the rotor was regulated by cooling the turbine oil, and the temperature recorded by means of a thermocouple immediately adjacent to the rotor. The observed sedimentation coefficients have been corrected to 20.0° C and to 1 atm. pressure in the usual manner ⁴.

In order to test the reliability of the pressure correction formula

$$s_{1 \text{ atm.}} = s_p \frac{\eta_p(1 - V_1 \rho_1)}{\eta_1(1 - V_p \rho_p)}$$

in the case of the present system of polymer and solvent the sedimentation rate of a polymethyl methacrylate fraction was determined for three different rotor speeds and three different dilutions. The corrected value of the sedimentation coefficient was found to be independent of the rotor speed ⁵.

Dependence of the sedimentation coefficient on concentration. Because of the large extension of the flexible polymethyl methacrylate molecules the decrease of the sedimentation velocity with increasing concentration is considerable. At a concentration of about 0.8 g per 100 ml all fractions except the ones with molecular weights lower than about two hundred thousand sediment with the same velocity (Fig. 1). This means that they have entirely lost their individuality as molecules and sediment as a clouster. The usual formula

$$\frac{1}{s} = \frac{1}{s_0} (1 + k_s c) \quad (1)$$

has been used for the extrapolation of the sedimentation coefficient to infinite dilution. It was, however, found that the inverse value of the sedimentation coefficient is a linear function of concentrations only if the dilution is great. This can be seen from Table 1 where the values of s and k_s are given for twelve fractions. For samples with sedimentation constants higher than about 20 the sedimentation coefficient will increase with the dilution more rapidly than is predicted by eqn. (1). For the two fractions with the highest molecular weights the values of s and k_s are considerably greater if calculated from the concentration interval 0.03—0.20 than from the concentration interval 0.15—0.8. All values have of course been obtained by means of the method of least squares. In order to avoid any systematical error from the method of extrapolating $1/s$ to infinite dilution, concentrations higher than 0.20 g per 100 ml have not been used. Six concentrations were used in carrying out the extrapolation.

Reproducibility of the determination of the sedimentation constant. In order to investigate the reliability of the determined values of the sedimentation

Fig. 1. The dependence of the sedimentation coefficient on concentration for samples B(720) I, B(713) IV, B(709) X, B(709) XIII and B(712) XIV respectively.

Table 1, showing how the value of the sedimentation constant s at infinite dilution and the value of the constant k_s , as obtained from a linear extrapolation of $1/s$, depend on the concentration range, from which the extrapolation is performed.

Sample	Concentrations lower than 0.2 g per 100 ml			Concentrations between 0.15 and 0.8 g per 100 ml			Concentrations between 0.4 and 1.0 g per 100 ml			All concentrations		
	s	k_s	No. of conc.	s	k_s	No. of conc.	s	k_s	No. of conc.	s	k_s	No. of conc.
B(720) I	51.1	7.42	7	41.0	4.94	5	—	—	—	46.1	5.78	10
B(720) II	46.8	7.49	10	35.2	4.36	5	—	—	—	43.4	6.15	12
B(709) II	34.8	5.04	8	30.1	3.80	5	—	—	—	33.6	4.53	11
B(713) IV	32.6	4.25	5	28.4	3.11	6	—	—	—	30.4	3.44	9
B(713) VI	26.6	2.94	5	27.6	3.16	5	—	—	—	27.1	3.06	9
B(713) VIII	23.5	2.64	6	21.9	2.02	6	21.8	2.01	3	22.4	2.12	12
B(704) IV	22.9	2.44	7	21.7	1.99	5	—	—	—	22.3	2.10	10
B(720) VIII	22.1	1.99	6	22.2	2.04	6	—	—	—	22.2	2.06	10
B(713) X	20.9	2.01	9	20.4	1.76	5	—	—	—	20.6	1.81	12
B(704) VI	18.3	1.83	6	17.3	1.41	5	—	—	—	17.7	1.48	9
B(709) X	16.3	1.30	10	16.3	1.32	6	16.4	1.34	5	16.4	1.34	16
B(709) XIII	10.7	0.86	6	10.2	0.56	5	10.4	0.62	3	10.5	0.64	10

Table 2, showing the reproducibility of the determination of the sedimentation constant when done at different times and on different parts of the same fraction.

Sample	Sedimentation constant at infinite dilution		Mean value $\bar{s}$	Mean deviation $\frac{[s_1 - s_2]}{2 \bar{s}}$ in per cent
	s_1	s_2		
B(704) IV	22.0	22.9	22.5	2.0
B(704) VI	18.0	18.3	18.2	0.8
B(720) I	49.0	51.1	50.1	2.1
B(720) II	43.1	46.8	45.0	4.2
B(720) VI	25.4	25.8	25.6	0.8
B(720) VIII	22.3	22.1	22.2	0.5
Mean error in per cent				1.7

constant, double determinations have been performed for six fractions, the two centrifugal runs for the same sample being made on different parts of the fraction and at a time interval of at least one year. The results are given in Table 2. From this it can be seen that the mean error is less than 2 %. This is, however, not a value of the reproducibility of the sedimentation coefficient itself which is considerably greater. The main part of the deviation is due to inhomogeneity of the sample and variations of the solvent used.

DIFFUSION MEASUREMENTS

Technique. The diffusion coefficient was determined in ethyl acetate at 20° C. The diffusion cell used was of the old Claesson ⁶ type. (During the course of this investigation a new diffusion cell with increased reproducibility has been constructed by Claesson *et al.*⁷) The diffusion was followed by means of Lamm's scale method ⁸.

Dependence of the diffusion coefficient on concentration. Because of the strong dependence of the sedimentation velocity on concentration it was considered essential to use as low concentrations as possible for the diffusion measurements. In the initial experiments the highest concentration was 0.4 g/100 ml ⁵. Later, however, the concentration range was extended to 0.6 in order to increase the reliability of the determination and to be able to study the concentration dependence of the diffusion coefficient itself. Within the experimental accuracy this coefficient was found to be a linear function of the concentration as can be seen from Fig. 2, where D_m and D_A are plotted against the original concentration of the solution. When the diffusion coefficient is dependent on concentration the experimental curves will no longer be symmetrical around the position of the original boundary between solution and solvent. If, as in this case, the diffusion coefficient increases with increasing concentration the maximum of the diffusion curve must be displaced to the pure solvent side of the boundary ^{8,9} — the negative side — according to the theory of Boltzmann ⁸. The experimentally obtained diffusion curves were also found to be

Fig. 2. The dependence of the diffusion coefficient on concentration. Circles represent D_m and crosses D_A values. The figures on the ordinate mark the zero points of the fractions indicated by corresponding numbers on the right. The distance between each scale line is 10^{-13} units of D .

Fig. 3. The normalized diffusion curve. The different symbols represent points from five different exposures taken from 14.6 to 35.6 hours after the start of the diffusion process. The black circles give the Gaussian curve. Sample B(720)VIII. Conc. 0.411 g/100 ml.

Fig. 4. The dependence of the diffusion coefficient on concentration obtained by Boltzmann analyses. The straight lines at the end of the figures indicate the concentration dependence calculated from the skewness of the diffusion curves according to the method of Gillis et al.

skew and with a negative displacement of the maximum. This is illustrated in Fig. 3 where the normalized diffusion curves³ from five exposures taken during the same diffusion experiment from 14.6 to 35.6 hours after the start of the diffusion process are given. The experimental points from the five normalized curves fall on the same curve.

Method of extrapolation of the diffusion coefficients. Unfortunately the spread of the D_m and D_A values is rather large at the low concentration — D_m and D_A being, respectively, the diffusion coefficients determined with the method of moments and areas. Two different methods have been used to determine the constant k_D in the equation:

$$D(c) = D_0 (1 + k_D c) \quad (2)$$

Method 1. According to the theory of Boltzmann⁸⁻¹⁰ it is possible to determine the value of D for every value of the concentration (c) from zero to the initial concentration (c_0) of the solution, $D(c)$ being given by the expression:

$$D(c) = -D_m \cdot \frac{1}{dc/dz} \int_{-\infty}^z z \cdot \frac{dc}{dz} \cdot dz \quad (3)$$

where D_m is the obtained value of the diffusion coefficient determined in the usual way by the moment method, dc/dz and z the coordinates of the normalized diffusion curve. In the derivation of eqn. (3) it has been assumed that the diffusing material is monodisperse. As has been shown by Beckmann and Rosenberg¹⁰ the experimentally obtained relation between $D(c)$ and c will show a minimum near the concentration $c = c_0/2$ if eqn. (3) is applied to the diffusion curve of a polydisperse sample.

In Fig. 4 the results of Boltzmann's analyses are shown for two different fractions L(6)F(2) II and B(720) VIII and at three different concentrations. All six curves have minima in the vicinity of $c = c_0/2$. Owing to uncertainty

in the determination of D_m the three curves are also at little displaced parallel to one another. However, they all show the same tendency. An average value of D_0 at infinite dilution and of k_D for the different molecules in the fraction has been defined by the equations

$$D_0 \cdot k_D \frac{c_0}{2} = \frac{\int_0^{c_0} D(c) dc}{c_0/2} - \frac{\int_0^{c_0/2} D(c) dc}{c_0/2} \quad (4)$$

$$D_m = D_0 \left(1 + k_D \frac{c_0}{2} \right) \quad (5)$$

The last equation ^{9, 11} can be obtained if one integrates $D(c)$ over the whole concentration interval remembering eqns. (2) and (3).

$$\frac{\int_0^{c_0} D(c) dc}{c_0} = \frac{\int_0^{c_0} D_0(1 + k_D c) dc}{c_0} = D_0 \left(1 + \frac{1}{2} k_D c_0 \right) \quad (6)$$

or

$$\begin{aligned} \frac{\int_0^{c_0} D(c) dc}{c_0} &= \frac{\int_{-\infty}^{+\infty} D_m dz \int_{-\infty}^z \frac{dc}{dz} dz}{c_0} = \\ &= \frac{D_m}{c_0} \int_{-\infty}^{+\infty} z^2 \frac{dc}{dz} dz - \frac{D_m}{c_0} \left[z \int_{-\infty}^z \frac{dc}{dz} dz \right]_{-\infty}^{+\infty} = D_m \end{aligned} \quad (7)$$

It may be worth-while to point out that eqn. (7) does not imply that D_m , the diffusion coefficient calculated by the moment method, is a weight average. The whole derivation is strictly valid only for a monodisperse sample. Eqn. (7) expresses only a relation between D_m and the concentration dependence of $D(c)$.

Method 2. The second method used to determine k_D and D_0 is given by Gillis and Kedam ¹¹. Assuming

$$D(c) = D_0 (1 + k_D c) \quad (8)$$

they have solved the Fick equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D(c) \frac{\partial c}{\partial x} \right) \quad (9)$$

in an approximate manner and calculated the relation between the product $k_D \times c_0$ and the ratio ρ of the slope of the diffusion curve at the two points where $dc/dz = \frac{1}{2}(dc/dz)_{\max}$, $(dc/dz)_{\max}$ denoting the maximum value of the diffusion curve. After having determined k_D from the ratio ρ one obtains D_0

Fig. 5. The dependence of k_D on the diffusion constant D_0 . The circles are calculated from the skewness of the diffusion curves, the crosses from analyses according to Boltzmann.

from eqn. (5). The derivations are rather complicated and cannot be reproduced here; for further details reference must be made to the original work¹¹. The derivations are of course only strictly valid for a monodisperse sample. Gillis and Kedam have also calculated the dependence of $(dc/dz)_{\max}$ on the ratio ρ . The results of these calculations are expressed in the form of a table. This table has been used to correct the diffusion coefficients D_A determined in the present investigation. The value of the ratio ρ has been evaluated from the normalized diffusion curve obtained from about five or six different exposures during the diffusion process.

The results of the two methods to determine k_D and D_0 are given in Fig. 5, where the obtained values of k_D are plotted against the corresponding D_0 . The crosses are obtained by method one, the circles by method two. The line corresponds to the equation $k_D = 2.24 \cdot 1/D_0^2$. The constant 2.24 has been determined by applying the method of least squares to the values of k_D and D_0 obtained by method two. After having established this relation between k_D and D_0 , the D_0 of each fraction has been calculated by the equation:

$$\frac{\Sigma D_m}{n} = D_0 + \frac{1}{2} k_D D_0 \frac{\Sigma c}{n} \quad (10)$$

$$k_D = 2.24 \frac{1}{D_0^2} \quad (11)$$

where $\frac{\Sigma D_m}{n}$ and $\frac{\Sigma c}{n}$ are, respectively, the average value of the diffusion coefficient D_m at finite concentrations and the average concentrations used. The lines drawn in Fig. 2 have been obtained with the aid of eqns. (10) and (11).

MOLECULAR WEIGHT DETERMINATIONS

The molecular weights M_{SD_m} and M_{SD_A} of the different fractions have been calculated with the aid of Svedberg's formula²

$$M = \frac{RT s}{D(1 - V\varrho)} \quad (12)$$

Table 3, summarizing the main properties of the different polymethyl methacrylate fractions. In each series the linear and nonlinear regions in the $\log s - \log [\eta]$ plot are separated from each other by a line.

Fraction	$[\eta]$	$s_0 10^{13}$	k_s	$M_{sD_m} \times 10^{-3}$	$M_{sDA} \cdot 10^{-3}$	$(\Phi^{1/3} P^{-1}) \cdot 10^{-6}$ from M_{sD_m} from M_{sDA}		$M_{calc} \times 10^{-3}$	$\frac{M_{calc}}{M_{sDA}}$	$\frac{k_s}{[\eta]}$
Polymer B(704)										
I	2.10	—	—	—	—	—	—	—	—	—
II	1.83	26.7	2.03	1 425	1 324	2.43	2.55	1 117	0.84	1.11
III	1.44	25.2	2.23	1 200	1 135	2.37	2.46	1 074	0.95	1.55
IV	1.24	22.0	1.78	834	834	2.51	2.51	783	0.94	1.44
V	1.03	19.7	1.53	671	645	2.45	2.50	615	0.95	1.49
VI	0.95	18.0	1.44	506	515	2.63	2.59	521	1.01	1.52
VII	0.81	16.8	1.19	447	462	2.52	2.47	427	0.92	1.47
VIII	0.74	15.0	0.96	402	375	2.34	2.46	324	0.86	1.30
IX	0.65	14.0	0.98	364	357	2.24	2.27	295	0.83	1.51
X	0.54	11.9	0.58	269	269	2.18	2.18	178	0.66	1.07
						Mean for III-X	Mean for III-X			
						2.41	2.43			
Polymer B(720)										
I	3.73	49.0	7.67	—	—	—	—	5 400	—	2.06
II	3.23	43.1	6.83	—	—	—	—	4 204	—	2.11
III	3.07	34.0	3.61	1 965	2 316	2.97	2.66	2 141	0.92	1.18
IV	2.37	31.0	3.06	1 584	1 634	2.87	2.81	1 717	1.05	1.29
V	1.93	28.8	3.26	1 304	1 395	2.82	2.70	1 587	1.14	1.69
VI	1.65	25.6	2.66	1 021	1 141	2.81	2.61	1 201	1.05	1.61
VII	1.43	—	—	—	—	—	—	—	—	—
VIII	1.21	22.3	2.13	894	898	2.41	2.40	874	0.97	1.76
IX	1.08	19.5	1.46	678	631	2.44	2.56	592	0.94	1.35
X	0.96	18.2	1.12	555	553	2.50	2.50	467	0.84	1.17
XI	0.87	17.4	1.06	433	456	2.73	2.64	425	0.93	1.22
XII	0.68	14.4	0.92	353	356	2.38	2.37	298	0.84	1.35
XIII	0.47	9.86	0.59	180	185	2.26	2.22	135	0.73	1.25
						Mean for VIII-XIII	Mean for VIII-XIII			
						2.45	2.45			
Polymer B(714)										
I	2.05	28.5	3.53	—	—	—	—	1 625	—	1.72
II	1.34	23.6	2.67	879	907	2.66	2.62	1 065	1.17	1.99
III	1.22	21.8	2.37	—	—	—	—	891	—	1.94
IV	1.09	21.4	2.13	770	763	2.47	2.49	821	1.08	1.95
V	0.92	19.2	1.92	633	621	2.38	2.41	663	1.07	2.09
VI	0.82	18.5	1.89	527	550	2.50	2.43	622	1.13	2.30
VII										
VIII	0.81	17.4	1.79	457	461	2.57	2.56	552	1.20	2.21
IX	0.67	14.6	0.85	360	338	2.38	2.48	292	0.86	1.27
X	0.61	13.7	0.98	290	286	2.50	2.52	285	1.00	1.61
XI	0.52	12.8	0.88	264	272	2.35	2.31	244	0.90	1.69
XII	0.43	10.8	0.69	180	182	2.41	2.39	168	0.92	1.60
XIII	0.29	8.11	0.50	103	102	2.30	2.32	93	0.91	1.72
						Mean for IV-XIII	Mean for IV-XIII			
						2.43	2.43			

Polymer B(712)

I	1.74	24.8	2.03	975	1 082	2.85	2.66	1 000	0.92	1.17
II	1.36	22.3	1.98	753	785	2.82	2.73	842	1.07	1.46
III	1.00	21.4	2.02	590	608	2.86	2.81	800	1.32	2.02
IV	0.95	19.3	1.83	571	578	2.60	2.57	652	1.13	1.93
V	0.74	16.1	1.35	393	408	2.56	2.50	427	1.05	1.83
VI	0.67	15.2	1.50	369	354	2.44	2.50	413	1.17	2.24
VII	0.61	13.3	1.03	291	284	2.42	2.46	280	0.99	1.69
VIII	0.53	12.1	0.68	228	233	2.47	2.43	197	0.85	1.28
IX	0.50	11.6	0.69	214	214	2.42	2.42	187	0.87	1.38
X	0.43	10.7	0.65	177	176	2.41	2.42	161	0.92	1.51
XI	0.38	9.54	0.69	130	128	2.53	2.56	139	1.09	1.82
XII	0.31	8.41	0.43	109	108	2.35	2.36	91	0.84	1.39
XIII	0.28	7.06	—	—	—	—	—	—	—	—
XIV	0.21	6.29	0.29	65	62	2.18	2.25	48	0.77	1.38
						Mean for	Mean for			
						III—	III—			
						XIV	XIV			
						2.48	2.48			

where T = the absolute temperature
 R = the universal gas-constant
 V = the partial specific volume of the polymer
 ρ = the density of the solvent
 The value $\frac{1}{2}$ 0.787 has been used for V .

The molecular weights calculated from the values of $(D_m)_0$ and $(D_A)_0$ at zero concentration can be found in Table 3.

DISCUSSION

(Relations between intrinsic viscosity, sedimentation constants and molecular weights.) According to the current theories¹² describing the hydrodynamic behaviour of flexible polymer molecules, the dependence of the intrinsic viscosity $[\eta]$ and of the frictional coefficient, f_0 , of the chain molecule at infinite dilution on the molecular weight M can be expressed by the equations

$$[\eta] = \Phi \left(\frac{r_0^2}{M} \right)^{3/2} M^{1/2} \alpha_\eta^3 \quad (13)$$

and

$$f_0 = \eta_0 P \left(\frac{r_0^2}{M} \right)^{1/2} M^{1/2} \alpha_f \quad (14)$$

where α_η and α_f represent the ratio of r the effective radius of the molecule in the given solvent to r_0 the root mean square distance between the ends of the polymer chain in a solvent where the second and higher osmotic virial coefficients are zero. Φ and P are universal constants for all flexible polymers irrespective of molecular weight, temperature or solvent used. The sedimentation constant at infinite dilution is further connected with the frictional coefficient f_0 by the expression

$$s_0 = \frac{(1 - V_e)M}{Nf_0} \quad (15)$$

where N is Avogadro's number.

Inserting the value of f_0 given by eqn. (14) in eqn. (15) gives

$$s_0 = \frac{(1-V\rho)}{\eta_0 N P} \cdot \frac{1}{\left(\frac{r_0^2}{M}\right)^{\frac{1}{2}}} \frac{M^{\frac{1}{2}}}{\alpha_t} \quad (16)$$

By combining (13) and (16) one obtains

$$\frac{s_0[\eta]^{\frac{1}{2}}}{M^{2/3}} \cdot \frac{\eta_0 \cdot N}{(1-V\rho)} = \Phi^{1/3} P^{-1} \frac{\alpha_\eta}{\alpha_t} \quad (17)$$

In the above equations it is generally assumed that $\alpha_\eta = \alpha_t = \alpha$. A statistical treatment of the long-range intramolecular interaction gives the expression

$$\alpha^5 - \alpha^3 = C_T M^{\frac{1}{2}} \quad (18)$$

where C_T is a constant for a given polymer-solvent system. For a not too large molecular weight interval it is therefore possible to assume that

$$[\eta] = K_\eta M^{a_1} \quad (19)$$

and

$$s = K_s M^{a_2} \quad (20)$$

where a_1 and a_2 take into account the extension of the molecule over that which would be obtained by random flight. A $\log s - \log [\eta]$ plot of the values for the different fractions does not give a straight line as predicted by eqns. (19) and (20), see Fig. 6. The points for the highest molecular weight fractions tend to lie below the straight line. This is most clearly seen for the series B(720) and B(712) for which the polymerization reaction had passed the first stationary stage. The direction of the deviation in the $\log s - \log [\eta]$ curve indicates that the polymers with the highest molecular weight, which have been formed during the second "explosive" stage of the polymerization, have a more extended configuration. Two explanations are possible, either the molecules are

Fig. 6. $\log s$ plotted against $\log 10 [\eta]$. The upper curve has been displaced 0.2 units upward. The straight lines are drawn with the aid of the equation $\log s = 0.74 \log [\eta] + 1.29$.

connected by branching or so tightly entangled with one another that they never behave freely in the dissolved stage. The problem will be treated in detail elsewhere¹ so it will not be discussed further here. The points on the curved part of the line have been excluded in the determination of the constants in the equations describing the relations between sedimentation constant, intrinsic viscosity and molecular weight given in Table 4. In these calculations both M_{sD_m} and M_{sD_A} , the molecular weights obtained from D_m and D_A respectively, have been used. As can be seen from the last row in the table these two kinds of molecular weights give exactly the same relation with s and $[\eta]$ in spite of the fact that for a polydisperse sample D_A must be lower than D_m ^{3,9}. The reason for the high values of D_A may be an undercorrection of the concentration effect. In extrapolating the experimentally obtained values of the diffusion coefficients, in accordance with the calculations by Gillis and Kedam, a lower concentration dependence has been assumed for D_A than for D_m . This causes $(D_A)_0$ at infinite dilution to be nearly equal to $(D_m)_0$ although the measured value of the former is lower at finite concentrations (See Fig. 2).

A calculation of $\Phi^{1/3}P^{-1}\frac{\alpha\eta}{\alpha_f} \times 10^{-6}$ from expression (17) gives lower values for the last fractions in each series. From an analysis of all 34 values in the region where $\log s$ is a linear function of $\log [\eta]$, one obtains the following mean values 2.37, 2.44 and 2.52 for the molecular weight intervals $<2.5 \times 10^5$, 2.5×10^5 to 5×10^5 and $>5 \times 10^5$, respectively. The number of fractions in each region is 9, 13 and 12, respectively. The values of $\Phi^{1/3}P^{-1}$ calculated for polymethyl methacrylate in acetone from data obtained by Meyerhoff show the same trend to increase for the lowest molecular weights¹³. The average value of $\Phi^{1/3}P^{-1}$ calculated from different polymers in different solvents, is $(2.5 \pm 0.1) \times 10^{-6}$. The reason for the low value obtained for the last fractions can be either that these have a different degree of heterogeneity from the others

Table 4, giving the relations between the quantities s , $[\eta]$, M_{sD_m} and M_{sD_A} .

	No. of frac- tion	$\log s =$		$\log s =$		$\log [\eta] =$		$\log [\eta] =$		$\log s =$	
		$a \log M_{sD_m} - b$		$a \log M_{sD_A} - b$		$a \log M_{sD_m} - b$		$a \log M_{sD_A} - b$		$a \log [\eta] + b$	
		a	b	a	b	a	b	a	b	a	b
B(704)	8	0.50	1.63	0.51	1.70	0.67	3.89	0.69	3.98	0.74	1.28
B(720)	6	0.51	1.64	0.53	1.76	0.61	3.53	0.63	3.65	0.83	1.28
B(714)	9	0.48	1.51	0.48	1.51	0.65	3.76	0.64	3.75	0.75	1.31
B(712)	11	0.52	1.70	0.51	1.63	0.68	3.92	0.66	3.84	0.78	1.31
All fractions	34	0.48 ⁴	1.51 ⁶	0.48 ⁴	1.51 ⁸	0.65 ⁹	3.82 ⁴	0.65 ⁹	3.82 ²	0.73 ⁹	1.29 ¹

Fig. 7. s_0 and $10[\eta]$ as functions of $M_s D_A$. The solid lines are the curves obtained from the constants in Table 4. The dotted lines are drawn through points that give a curved $\log s - \log [\eta]$ line. Upper curve s , lower curve $[\eta]$.

or that the shapes of the polymer chains are such that they can not be approximated with an equivalent effective sphere, giving $\alpha_\eta/\alpha_t \neq 1$. (See Ref. 1).

The dependence of the sedimentation constant, the intrinsic viscosity, and the constant $\Phi^{1/3} P^{-1}$ on molecular weight is graphically represented in Figs. 7 and 8. The solid lines in Fig. 7 are the curves obtained from the constants in Table 4. The dotted lines are drawn through points that give a curved $\log s - \log [\eta]$ line. This figure shows that the anomalies in intrinsic viscosity occurs at a lower molecular weight for polymers prepared at 80°C — B(712) and B(714) — than those at 60°C — B(704) and B(720). The deviation of the observed sedimentation constants from the solid line at high molecular weights is not so pronounced as in the case of intrinsic viscosity. This must also be expected from eqns. (13) and (16), s being inversely proportional to α and $[\eta]$ directly proportional to the third power of α .

Fig. 8. $\Phi^{1/3} P^{-1}$ as a function of $M_s D_A$.

(The concentration dependence of the sedimentation coefficient.) The effect of the concentration on the sedimentation velocity of chain molecules has been investigated by Wales and Holde¹⁴. In their treatment the coiled polymer is considered as a sphere obeying Stokes' law

$$6\pi\eta_0 a = \eta_0 P r \quad (21)$$

where r is the effective radius of the equivalent sphere and

$$r = r_0 \alpha_t \quad (22)$$

The concentration dependence of the sedimentation coefficient of spherical particles is given by Burgers' relation

$$\frac{1}{s} = \frac{1}{s_0} \left(1 + \frac{55}{8} n v \right) \quad (23)$$

where n is the number of molecules in unit volume and v the volume of a molecule. Eqns. (13)—(15) and (21)—(23) together with the empirically found relation for the concentration dependence of the sedimentation coefficient

$$\frac{1}{s} = \frac{1}{s_0} (1 + k_s c) \quad (24)$$

give

$$\frac{k_s}{[\eta]} = \frac{55 N}{8} (\Phi^{1/3} P^{-1})^{-3} \quad (25)$$

and

$$M = \pi N \left(\frac{16\,200}{55} \right)^{1/2} k_s^{1/2} \left(\frac{s_0 \eta_0}{(1 - V\rho)} \right)^{3/2} \quad (26)$$

If the value of $\Phi^{1/3} P^{-1}$ is considered to be 2.5×10^{-6} one obtains

$$k_s / [\eta] = 1.66 \quad (27)$$

As is seen from Table 3 there is a spread in the individual values of $k_s / [\eta]$ for the different polymethyl methacrylate fractions. However, the average value of $k_s / [\eta]$ in the three molecular weight intervals $< 2.5 \times 10^5$, $2.5 \times 10^5 - 5 \times 10^5$ and $> 5 \times 10^5$ are 1.48, 1.57 and 1.71, respectively, the number of values in each interval being 9, 13 and 12. As can be seen from these figures $k_s / [\eta]$ gives approximately the value predicted by Wales and Holde, but increases slowly with increasing molecular weight. Thus both $k_s / [\eta]$ and $\Phi^{1/3} P^{-1}$ increase with molecular weight contrary to the predictions of eqn. (25).

The molecular weights, M_{calc} , of the different fractions calculated by eqn. (26) are given in Table 3. These are in fairly good agreement with those obtained by direct determination of the molecular weight M_{sD_A} . An analysis of the values in the three molecular weight intervals previously used shows that $M_{\text{calc}} / M_{sD_A}$ is about 88, 94 and 103 % and increases with increasing M_{sD_A} . The nature of the average obtained by eqn. (26) is very complicated. It has been

found by the present author that for a symmetrical distribution of s the value of k_s is not very much influenced by the width of the distribution (unpublished work). This means that under the given assumption the average obtained by eqn. (25) would be equal to that calculated by inserting a weight average of s and a weight average of $1/D$ in eqn. (12). As the harmonic mean is less than the arithmetic mean this results in a molecular weight greater than $M_{s,D}$ calculated from a weight average of both s and D .

This investigation has been financially supported by grants from *Statens Tekniska Forskningsråd* and *Stiftelsen Svensk Gummiforskning* (Ab. Sieverts Kabelverk, AB. Liljeholmens Kabelfabrik, Goodyear Gummifabriks AB., Svenska Gummifabriks AB., Viskafors Gummifabriks AB.).

The author wishes to acknowledge his indebtedness to Professor The Svedberg and Professor Stig Claesson for their very kind interest and for the many facilities which have been put at his disposal.

The author also wishes to thank Dr. P.-O. Kinell and Assistant Evald Hellman for their interest in this study and for many valuable discussions.

REFERENCES

1. Eriksson, A. F. V. *Svensk Kem. Tidskr.* (in English) **68** (1956). *In press.*
2. Svedberg, T. and Pedersen, K. O. *The Ultracentrifuge*, Oxford 1940.
3. Lamm, O. *Nova Acta Regiae Soc. Sci. Upsaliensis* **10** (1937) No. 6.
4. Mosimann, H. and Signer, R. *Helv. Chim. Acta* **27** (1944) 1123.
5. Eriksson, A. F. V. *Acta Chem. Scand.* **7** (1953) 623.
6. Claesson, S. *Nature* **158** (1946) 834.
7. Claesson, S. and Sahlman, Y. *Unpublished.*
8. Boltzmann, L. *Ann. Physik* **53** (1894) 959.
9. Gralén, N. *Sedimentation and Diffusion Measurements on Cellulose and Cellulose Derivatives*, Thesis, Uppsala 1944.
10. Beckmann, C. O. and Rosenberg, Y. L. *Ann. N. Y. Acad. Sci.* **46** (1945) 329.
11. Gillis, J. and Kedem, O. *J. Polymer Sci.* **11** (1953) 545.
12. Flory, P. J. *Principles of Polymer Chemistry*, New York 1953.
13. Fox, T. G. and Mandelkern, L. *J. Chem. Phys.* **21** (1953) 187; Meyerhoff, G. and Schulz, G. V. *Makromol. Chem.* **7** (1952) 294.
14. Wales, M. and van Holde, K. E. *J. Polymer Sci.* **14** (1954) 81.
15. Burgers, J. M. *Proc. Acad. Sci. Amsterdam* **45** (1942) 9.

Received January 24, 1956.