The Distribution of Sizes of Particles in Some Polymeric Methyl Methacrylates *

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By the sedimentation of polydisperse substances in the ultracentrifuge a concentration gradient will appear in the cell due to the various sedimentation velocities of particles with different molecular weights. The shape of the concentration gradient curve will depend upon the nature of the frequency function of the sedimentation constants or — as the sedimentation constant is some function of the molecular weight — the frequency function of the molecular weights. From a sedimentation diagram, therefore, it must be possible to deduce the distribution of sizes of particles in a polydisperse substance.

Since the development of the ultracentrifugal technique this method has been used by Rinde [1] to obtain the frequency curves for the particles in gold sols, by Nichols *et. al.*[2] on suspensions of ferric oxides, barium sulphates, on emulsions and rubber latex etc. More recently Jullander [3] has thoroughly discussed different ways of obtaining frequency curves for cellulose nitrates. In this connection the work of Signer and Gross [4] on polystyrene can also be mentioned. The earlier work has mainly been concerned with substances, the frequency curves of which show only one maximum. Further their sedimentation has been almost independent upon the concentration; an exception is of course the behaviour of cellulose nitrate and polystyrene.

When the frequency curve of the substance under investigation has more than one maximum and when the sedimentation velocity is dependent upon the concentration, the problem of obtaining the frequency curve from the sedimentation diagram is very complicated. In this paper some of the prob-

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* Part of this investigation was presented at the XI:th International Congress of Pure and Applied Chemistry, London, July 17—25, 1947 and at Sjätte Nordiska Kemistmötet, Lund, Aug. 25—29, 1947.

Table 1. Sedimentation measurements in acetone solution.

Sample B			Sample E		
c	s	dB/dx	c	s	dB/dx
0.500	22.1		0.500	26.0	0.27
0.330	24.3		0.333	30.5	0.34
0.314	25.1	0.58	0.200	40.9	0.50
0.280	27.8		0.100	49.6	0.82
0.250	27.9		0	58.2	1.23
0.221	30.0				
0.214	28.7	0.89			
0.165	27.8				
0.125	28.1				
0.105	31.8	1.22			
0.054	30.4	1.49			
0	37.2	1.80			

lems involved are discussed in connection with an ultracentrifugal investigation of polymeric methyl methacrylate. The sedimentation diagrams at low concentrations are compared with frequency curves obtained from fractions of the samples used.

SEDIMENTATION AND DIFFUSION MEASUREMENTS ON UNFRACTIONATED SAMPLES

The samples used for this investigation were two commercial methyl methacrylates, here called sample B and E. These samples were characterized by means of sedimentation and diffusion measurements. The sedimentation measurements are given in Table 1 (for details about the ultracentrifugal technique, *cf.* reference 2). They were performed in acetone solution and the values obtained for the sedimentation constant, s, are given in S-units and refer to a temperature of 20° C. The s-values have been corrected for the influence of the increased hydrostatic pressure in the cell due to the high compressibility of acetone (Mosimann and Signer [5]). The concentrations, c, are given in g/100 ml. For concentrations lower than 0.1 g/100 ml it has been very difficult to calculate reliable s-values because the width of the curve in the sedimentation diagram is very large and it has been almost impossible to determine the true maximum of the curve. In Table 1 the values of dB/dx are also given. These have been calculated according to Gralén [6] and show how the width, B, of the sedimentation curve varies .with the distance, x

Table 2. Sedimentation measurements in ethyl acetate solution.

Sample B		Sample E	
c	s	c	s
0.500	11.0	0.507	12.8
0.333	13.4	0.406	13.8
0.200	14.8	0.203	19.5
0	17.7	0.101	25.3
		0	32.2

from the centre of rotation (B is the ratio between the area of the curve and the maximum height). The values extrapolated to zero concentration indicate a very high polydispersity. In order to check the s-values obtained in acetone solution the samples were also measured in ethyl acetate solution. The results follow from Table 2. Using the formula given by Kraemer and Nichols [7]

$$[s]_0 = \frac{\eta V s_0}{1 - V\varrho} \tag{1}$$

we can calculate the intrinsic sedimentation constant, *i.e.* the sedimentation constant reduced to a common basis involving only the volume of the sedimenting particle and shape factors (η is the viscosity and ϱ the density of the solvent; V the partial specific volume of the solute). The following values are obtained:

	s_0	$[s]_0$*
Sample B, acetone	37.2	26.9
ethyl acetate	17.7	23.1
Sample E, acetone	58.2	42.0
ethyl acetate	32.2	42.1

The agreement is satisfactory and hence the results from the sedimentation measurements quite reliable.

To get the molecular weights of the samples the diffusion constants were determined in acetone solution at 20° C by means of Lamm's [8] scale method. Both of the samples gave skew diffusion curves and a reduction to zero concentration was made according to Gralén (*l. c.*). The results are given in Table 3, where the area value, D_A, the moment value, D_m, and the reduced

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* $[s]_0$ is expressed in units of 10^{-15} cgs.

Table 3. Diffusion measurements in acetone solution.

Sample	c	D_A	D_m	D_0
B	0.494	4.36	4.78	4.31
E	0.382	3.23	3.87	3.32
	0.255	3.14	3.29	3.29
				3.31

value, D_0, of the diffusion constants are given in units of 10^{-7} cgs. The centrations are given in g/100 ml.

From Svedberg's formula

$$M = \frac{RTs_0}{(1 - V\varrho)D_0}$$ (2)

with $V = 0.80$ the following molecular weights have been calculated: sample B, $M = 570000$; sample E, $M = 1170000$. It is to be emphasized that these values are not well defined averages. According to Jullander [9] the values obtained from equ. (2) in the way used above are close to a $M_{w,w}$-value obtained by using a weight average value of s instead of s_0.

The sedimentation diagrams of the two samples are shown in Figs. 1 and 2. Here the scale line displacement, Z, divided by the scale distance, b, and the concentration, c, is given as a function of the distance from the centre of rotation at different times, t, of sedimentation. The diagrams show that the polydispersity of the samples is high and that the gradient curves tend to distribute themselves over almost the whole cell.

Furthermore the irregularities to the left and right of the main peak (sample B: $c = 0.105$ g/100 ml, $t = 40$ min; sample E: $c = 0.100$ g/100 ml, $t = 15$ and 25 min) indicate that the frequency curves of the substances have at least three maxima. Attempts to measure the substances at still lower concentrations indicate a possibility of a better resolution of the peaks.

FRACTIONATION OF THE SAMPLES

In order to get the frequency curves of the samples in another way they were divided into fractions by means of fractional precipitation. The precipitation was made with cyclohexane from benzene solution according to Schulz and Dinglinger [10] and was performed in a thermostat at 20° C. The cyclohexane
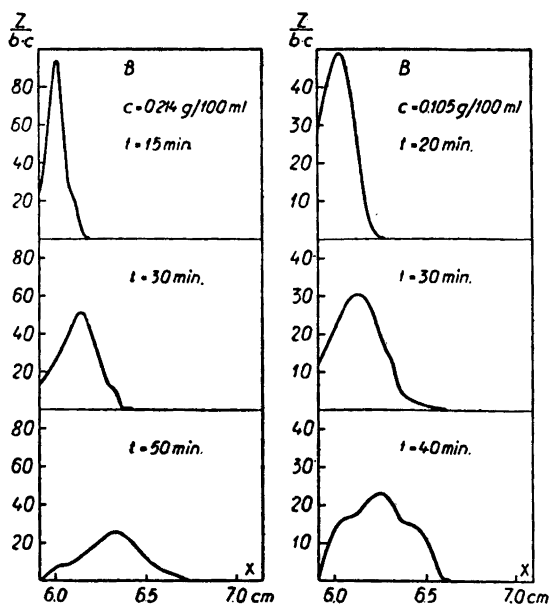
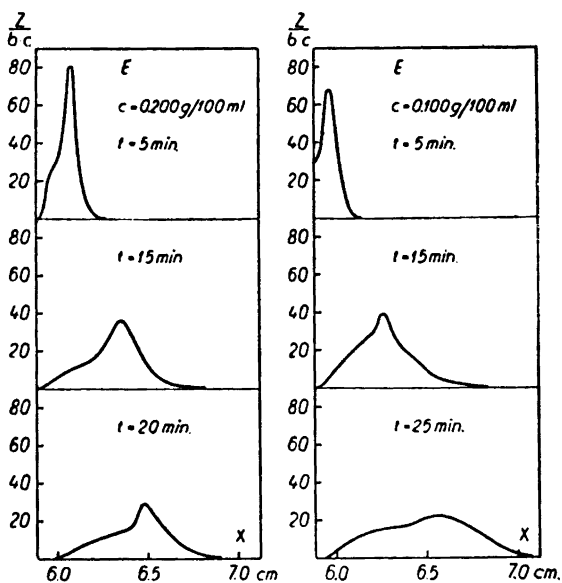Fig. 1. Sedimentation diagram of sample B at different concentrations and different times.

Fig. 2. Sedimentation diagram of sample E at different concentrations and different times.

was added to the benzene solution very slowly (about 1 ml/min) and under intensive stirring until the critical composition of the solvent/non solvent system was almost reached. Then the cyclohexane was added drop by drop until the solution became turbid. The temperature of the thermostat was slowly raised to about 30° C and in this way the precipitate was dissolved. By lowering the temperature slowly it precipitated again and the precipitate formed a gel which could easily be removed. From the supernatant liquid a new fraction could be obtained. In this way, it was possible to get about 10 fractions. The concentration of the original solution was about 2 %. This is a little high and certainly it has had an effect upon the sharpness of the fractions (cf. Scott and Magat [11] and Scott [12]). The sample B was not completely soluble in benzene. After 10 days an insoluble residue of about 25 % remained; hence only one fractionation of this sample was performed. On sample E, five independent fractionations were made in all. The sum of the weights of the fractions corresponded within 5—10 % to the original amount of substance. The loss is due to the difficulties involved in working quantitatively with the small original amounts of substance (about 5 g). The fractions were characterized by means of viscosity measurements in benzene and/or acetone solution. In Table 4 the data for the fractions are given. The amount of a fraction in per cent is based on the total weight of all the fractions in one experiment. The intrinsic viscosity has been calculated with the concentration expressed in g/ml for B (1) and E (1)—E (2) and in g/g for E (3)—E (5). In the table are also given for fractionations E (3) and E (4), the k'-values defined by the equation

$$\frac{\overline{\eta_{sp}}}{c} = [\eta] (1 + k' [\eta]c) \tag{3}$$

As to the notations of the fractions E (4) III means the third fraction of sample E in the fourth fractionation experiment.

In Fig. 3 the distribution and frequency curves are drawn according to Schulz [13]. The former have been obtained by plotting the quantity $(\sum_{1}^{n-1} p_\nu + \frac{1}{2} p_n)$, were p_ν denotes the percentage amount of the ν:th fraction, against the intrinsic viscosity $[\eta]_n$. The latter have been constructed by taking the derivatives of the distribution curves at a number of points.

All the frequency curves have distinct maxima. Sample B has three maxima at the intrinsic viscosities 60, 120 and 180 respectively. Sample E in acetone has four maxima at the intrinsic viscosities 60, 120, 180 and 280 respectively. The third maximum is the highest one. In benzene we have four maxima for E (3) and E (4); E (5) does not show the first small maximum

Table 4. Fractionation experiments. (The intrinsic viscosities for B (1), E (1)—(2) measured in acetone and for E (3)—(5) in benzene).

Fraction	Amount %	$[\eta]$	Fraction	Amount %	$[\eta]$	k'
B (1) I *	24.6	120	E (3) I	16.3	446	0.38
II	14.2	228	II	23.6	369	0.32
III	16.3	174	III	9.6	352	0.31
IV	14.0	149	IV	9.9	303	0.34
V	5.6	129	V	3.6	283	0.32
VI	10.1	122	VI	16.6	253	0.36
VII	5.4	106	VII	7.3	200	0.37
VIII	4.9	80	VIII	5.1	170	0.40
IX	5.1	56	IX	4.0	142	0.34
			X	4.0	86	0.27
E (1) I	58.3	202				
II	13.6	130	E (4) I	27.9	425	0.36
III	2.5	94	II	17.0	388	0.34
IV	19.9	71	III	17.7	321	0.33
V	5.7	43	IV	19.0	264	0.34
			V	6.6	202	0.32
E (2) I	23.4	282	IV	4.2	171	0.29
II	21.2	240	VII	3.1	82	0.27
III	12.7	191	VIII	4.6	79	0.28
IV	14.5	175				
V	9.5	136	E (5) I	20.5	358	
VI	6.0	120	II	26.8	352	
VII	7.1	105	III	14.0	303	
VIII	4.7	74	IV	11.5	222	
IX	3.4	58	V	11.9	202	
			VI	5.2	183	
			VII	4.5	151	
			VIII	2.4	134	
			IX	1.8	110	
			X	1.4	87	

* In benzene insoluble part.

In this case the fourth (third for E (5)) is the highest one. As regards the quantity of substance represented by the maxima, however, it seems to correspond to the fourth maximum for E (2). The discrepancy between the heights of the maxima in the two solvents certainly depends upon the relation between intrinsic viscosity and molecular weight.
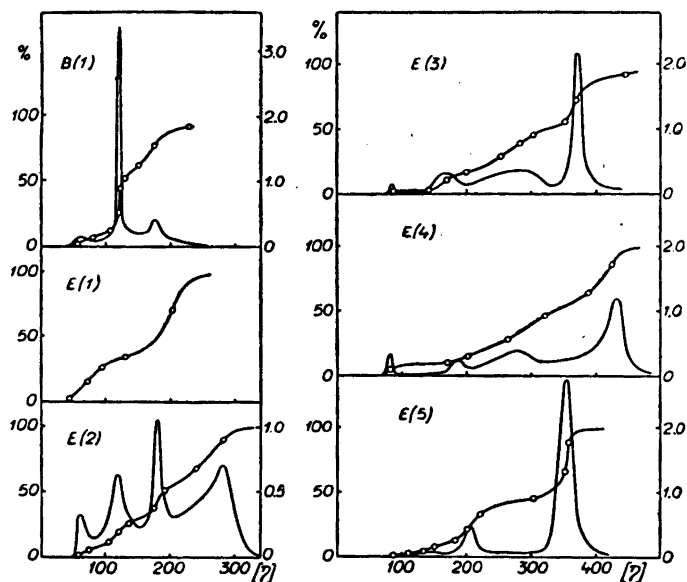
Fig. 3. Distribution and frequency curves from viscosity data.

SEDIMENTATION MEASUREMENTS ON FRACTIONS

In order to give further evidence for the frequency curves shown in the preceding section, the sedimentation constants for the fractions B (1) I—IX and E (2) I—IX have been determined in acetone solution. The results obtained are given in Table 5. There is also given for E (2) the k_s-values

Table 5. Sedimentation measurements on fractions.

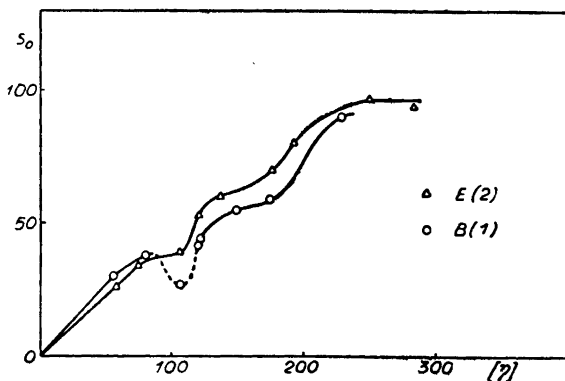| Fraction	s_0	Fraction	s_0	k_s
B (1) I	42	E (2) I	94	7.3
II	90	II	97	9.4
III	59	III	80	4.7
IV	55	IV	70	—
V	51	V	60	—
VI	44	VI	53	—
VII	27	VII	39	1.7
VIII	38	VIII	34	1.6
IX	30	IX	26	1.1

Fig. 4. The relation between sedimentation constant and intrinsic viscosity.

(c expressed in g/100 ml) of those fractions whose concentration dependence of s follows the relation.

$$s = \frac{s_0}{1 + k_s \cdot c}$$

(cf. Gralén, l. c.). The k_s-values show that the concentration dependence for the highest fractions is very pronounced.

Before we discuss the frequency curves, it is interesting to study the sedimentation constants as functions of the intrinsic viscosity. This last quantity is a simple algebraic function of the molecular weight and hence in this way we get an idea of the general behaviour of the molecules during the sedimentation. In Fig. 4 the s_0-values are plotted against the corresponding $[\eta]$-values. In their treatment of different hydrodynamical models Kuhn and Kuhn [14] have discussed two limiting cases of chain-like molecules: free draining coils and matted coils. The frictional resistance of the first type is proportional to the molecular weight M and that of the second proportional to $M^{\frac{1}{2}}$. As the sedimentation constant according to Svedberg [15] is defined by the relation

$$s = \frac{M(1 - V\varrho)}{f} \tag{5}$$

where f is the molar frictional coefficient, s for the free draining type is independent of M and for the matted coil proportional to $M^{\frac{1}{2}}$. If the molecules were built up in the same way the curves in Fig. 4 should indicate that the folding of the molecule depends very much on the molecular weight. In the regions $[\eta] = 80$—110, 130—170 and > 230 the molecules should behave
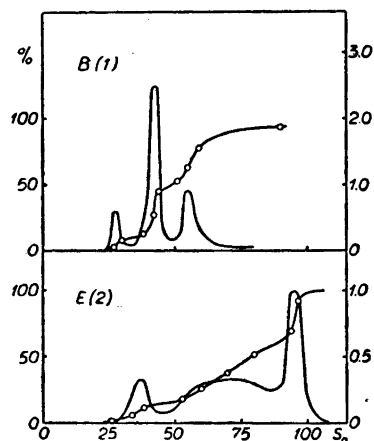
Fig. 5. Distribution and frequency curves from sedimentation data.

as free draining coils and between these regions more as matted coils. In this case, however, where we have synthetic polymers, the behaviour of the molecules may depend upon the internal structure and not only on the folding of the chain. Especially, branching of the chains may have a large effect on the frictional resistance. The k'-values in Table 4 give some evidence that structural differences really exist. According to Ewart [16], linear molecules in good solvents should give k'-values of about 0.38. Since we can assume benzene to be a good solvent for linear molecules of polymethyl methacrylates independently of their molecular weights, the only reason for the change in the k' values must be changes in structure. At high intrinsic viscosities we have values near to 0.38; then they decrease with decreasing viscosity but have for $[\eta] < 300$ a tendency to increase; finally they decrease to values below 0.30. Alfrey, Bartovics and Mark [17] have shown that polystyrene polymerized at the temperatures 60, 120 and 180° C gives decreasing k'-values: 0.42, 0.33 and 0.21. Probably a higher temperature gives molecules which are more branched or more cross-linked.

From the s_0-values in Table 5 and the percentage amount of fractions B (1) I—IX and E (2) I—IX in Table 4, the distribution and frequency curves for the sedimentation constants have been drawn (Fig. 5). The frequency curve for B (1) shows three maxima. These occur for the s_0-values 27, 42 and 55 S. The frequency curve for E (2) also shows three maxima; the corresponding s_0-values are 36, 70 and 95 S.

It is possible to get the frequency curve for an unfractionated substance by adding the frequency curves for each fraction. This method has been tried for sample E assuming that the frequency curves of the sedimentation con-

stants for the fractions can be approximated with a logarithmic frequency function (given by Lansing and Kraemer [18] for the molecular weights):

$$\frac{dc}{ds_0} = K_s \cdot e^{-\frac{1}{\gamma_s^2} \log^2 s_0/s_1} \tag{6}$$

where γ_s is a distribution coefficient, K_s, the maximum height, and s_1, the s_0-value at the maximum. By knowing the dB/dx-values, it is possible to calculate γ_s according to the relation

$$\frac{dB}{dx} = \gamma_s \cdot e^{\frac{1}{4}\gamma_s^2} \sqrt{\pi} \tag{7}$$

and K_s from

$$K_s = \frac{\text{Area}}{s_0 \cdot (dB/dx)} \tag{8}$$

If the areas are taken equal to the fractional amount of each fraction, we get the values in Table 6 for the fractions E (2) I—IX. The frequency curve of sample E obtained in this way is drawn in Fig. 6. It shows only one maximum, but there are two irregularities on the left side of the curve. These indicate the existence of at least another two maxima (dotted lines).

Still another method has been used to get the frequency curve of sample E. In this the fractions have been assumed to have a symmetrical triangular frequency curve, the height of which is equal to K_s and the base equal to

Table 6. Data corresponding to frequency curves given in Figs. 6 and 7.

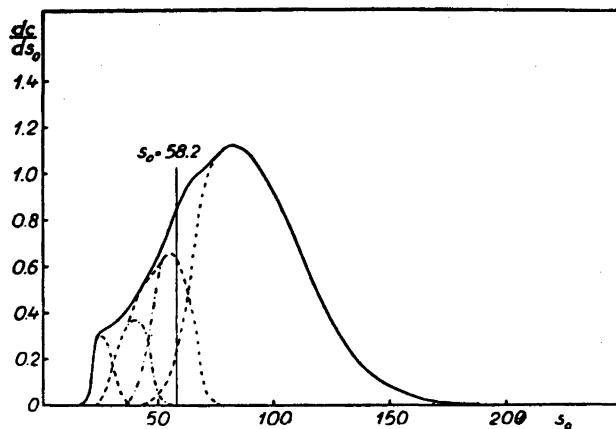| Fraction		s_1	dB/dx	Area	γ_s	$K_s \cdot 10^2$
E (2)	I	94	0.58	0.234	0.319	0.430
	II	97	0.56	0.212	0.309	0.394
	III	80	0.60	0.127	0.330	0.265
	IV	70	0.53	0.145	0.293	0.391
	V	60	0.43	0.095	0.239	0.368
	VI	53	0.42	0.060	0.234	0.269
	VII	39	0.44	0.071	0.245	0.413
	VIII	34	0.51	0.047	0.282	0.272
	IX	26	0.40	0.034	0.223	0.327

Fig. 6. Frequency curve obtained by adding the frequency curves of the fractions (logarithmic frequency curve).

$2s_0 \cdot (dB/dx)$. The frequency curve obtained (Fig. 7) shows two maxima, for $s_0 = 27$ S and $s_0 = 70$ S.

DISCUSSION

The results presented in the previous sections give evidence that the two samples of polymethyl methacrylate should have frequency curves with at least three maxima. This follows from the sedimentation diagrams and the curves in Figs. 3 and 5. The attempt to add the logarithmic frequency curves for the fractions does not give any clear cut decision. One of the reasons for
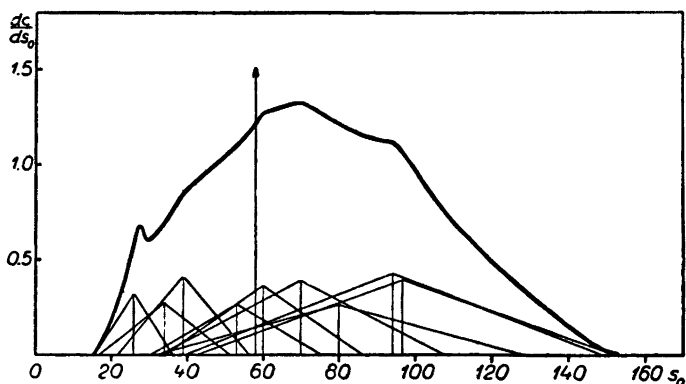

Fig. 7. Frequency curve obtained by adding the frequency curves of the fractions (symmetrical triangular curve).

this is certainly connected with the nature of the logarithmic frequency function. It will distribute too much substance towards higher s_0-values. From a theoretical point of view the fractions should have a tail towards smaller s_0-values instead (*cf.* Scott *l. c.*). A better result is obtained by adding the triangular frequency curves (Fig. 7). The two maxima correspond very well to the first and the third maxima of the viscosity frequency curve E (2) in Fig. 3 (the s_0-values for the peaks are according to the relation in Fig. 4, $s_0 =$ 27, 53, 72 and 96 S). Between 90 and 100 S the curve shows a tendency to form a third maximum corresponding to the fourth maximum in Fig. 3. The large maximum of the curve probably contains the two maxima shown in this region in Fig. 3. The agreement with the second and the third maxima in Fig. 5 is also good. As regards the curve in Fig. 7 its shape can depend upon the conditions under which the fractionation is performed. In some work on cellulose nitrate Rånby [19] has shown that the sharpness of the fractions depends upon the solvent/non solvent system used in the fractionation and that the frequency curve obtained is the more rich in details the sharper the fractions.

Examining Figs. 6 and 7 we see that the determined s_0-value of 58 S for the unfractionated sample E does not correspond to the highest maximum. From Fig. 5 it is seen that $s_0 = 58$ S corresponds to the left side of the middle maximum. This discrepancy may have two reasons. It has been shown by Kinell [20] that for polydisperse substances, the sedimentation of which is not dependent upon the concentration of the solute, the determined s_0-values does not correspond to the maximum of the original frequency curve except for the time $t = 0$. The higher the polydispersity the larger the difference between the observed value and the original maximum value for a given time. On the other hand the dilution with the sector shape of the cell causes an increase in the s-values. The combination of these two effects for a polydisperse, concentration dependent substance may cause the measurements to give an s_0-value which is too low. The other explanation of this may be found in the discussion given by Johnston and Ogston [21]. If two components with different sedimentation constants sediment in the ultracentrifuge, the slower moving component will show an increase in amount if the sedimentation velocity changes when the substance passes the boundary. (This effect was first observed by McFarlane [22] and Pedersen [23] in mixtures of proteins; it has also been studied on mixtures of fractions of cellulose nitrate by Sihtola [24]). For a substance which has a frequency curve with several maxima, it is very likely that in the sedimentation the heights of the maxima may change considerably according to this boundary effect. If this is the case here the maximum of the sedimentation curve should not correspond to the highest maximum of the

frequency curve. With decreasing concentration the effect should be less pronounced and disappear completely at zero concentration. It is not possible to run concentrations lower than 0.1 g/100 ml, when the concentration dependence is still quite considerable, and hence it is not excluded that, according to the boundary effect, the extrapolation gives an s_0-value which is too low. (An experimental error in the s_0-value must be excluded in this case where the agreement between the $[s]_0$-values is very good). A final decision as regards the reason for the observed discrepancy is not possible.

In this paper mainly the frequency curve of the sedimentation constants has been discussed. It is to be emphasized that conclusions as to the frequency curve of the molecular weights can be drawn from the sedimentation diagram only if we are dealing with molecules having certain sedimentation properties. If the molecules are of the free-draining type only a very bad or no resolution at all will be obtained in the ultracentrifuge, because the sedimentation constant is the same for all molecular weights. In this case nothing can be said about the distribution of the molecular weights without other methods being applied.

Finally, it can be emphasized that a synthetic high polymer giving a frequency curve of the shape shown in this paper must have been formed by a rather complicated mechanism of reaction. At least sample B is known to have been prepared by bulk polymerisation with a peroxide catalyst. This process should, therefore, be much more complicated than, for instances, the polymerisation in a reduction-oxidation system used by Baxendale, Bywater and Evans [25]. They get a frequency curve with only one maximum and in good agreement with the curve corresponding to the assumed simple reaction mechanism. A preliminary result from the investigations of Eriksson and Kinell [26] is that in bulk polymerisation a frequency curve with at least two maxima appears after quite a short time of polymerisation. The positions and the heights of the maxima is then changed as the polymerisation proceeds.

SUMMARY

Two samples of polymeric methyl methacrylate have been characterized by means of sedimentation and diffusion measurements. The samples have been divided into a series of fractions by fractional precipitation. The fractions have been characterized by viscosity and sedimentation measurements. From the data obtained, frequency curves have been constructed and it follows that each of the samples probably has three maxima. This is also in agreement with the conclusions which can be drawn from the sedimentation diagrams. The relation between sedimentation constant and intrinsic viscosity suggests

that the molecules have different structures (branching) or that the folding of the molecules depends on the molecular weight. This fact makes it difficult to draw definite conclusions about the distribution of molecular weights from the sedimentation diagram alone.

This investigation was started as part of some research work carried out at the request of *A B. Bofors Nobelkrut*, Bofors.

The author wishes to express his sincere thanks to Professor The Svedberg for his very kind interest and for the many facilities put at the author's disposal.

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