The Molecular Weight Distribution in Polymethyl Methacrylate Prepared by Redox Polymerisation in Water Phase. II

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In an earlier article¹, the kinetic aspects of the redox polymerisation of methyl methacrylate in aqueous solution in the presence of a ferrous sulphate-hydrogen peroxide initiator were considered. The theoretical molecular weight distribution was derived on the assumption of the deactivation of active radicals either by disproportionation or by combination, and in each case it was compared with the distributions determined experimentally for different polymers by fractionation and viscosity measurements. In that connection, the degree of reproducibility with which the molecular weight distribution of polymethyl methacrylate can be determined by this method was also investigated. This paper gives an account of some sedimentation and diffusion measurements, and of viscosity determinations carried out on a fractionated polymer prepared by the method mentioned above, and conclusions are drawn regarding the polymolecularity of both the individual fractions and the original unfractionated product, as well as the shape of the molecules in the dissolved state. Reference may be made to the earlier paper for details concerning the conditions of polymerisation¹.

SEDIMENTATION MEASUREMENTS

A detailed account of the ultracentrifuge process is given in the monograph by Svedberg and Pedersen². Only certain technical data will be mentioned here. A Svedberg oil-turbine ultracentrifuge was used. The distance between the meniscus and the axis of rotation was 5.9 cm. The speed of the rotor was in most cases 45 000 revs./min. Under these conditions the centrifugal field at the actual meniscus is 134 000 g. Lamm's scale method³ was used for the observation of the sedimentation velocity. 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 mean value of the difference between the highest and lowest temperatures during any one running period was 0.23° C. The highest temperature measured was 21.8° C, and the lowest 19.2° C. The sedimentation constants have been corrected to a temperature of 20.0° C according to the relation:

$$s_{20} = s_t \frac{\eta_t}{\eta_{20}} \frac{(1 - V_{20}\rho_{20})}{(1 - V_t\rho_t)}$$

where s_{20} and s_t are the sedimentation constants at 20° and t° respectively, and η_{20} , η_t and ρ_{20} , ρ_t the viscosities and densities of the solvent at the corresponding temperatures. V is the partial specific volume of the solute. The last factor can be put equal to 1 for the temperature interval used. Since the hydrostatic pressure varies from about 1 atm. at the meniscus to 200–400 atm. at the bottom of the cell, depending on the density of the solvent, changes in the viscosity and density of the solvent at different cell levels must be taken into account. The sedimentation constant has been reduced to the value at 1 atm. by means of the formula³

$$s_1 = s_p \frac{\eta_p (1 - V_1\rho_1)}{\eta_1 (1 - V_p\rho_p)}$$

where all symbols have their usual significance. The indexes 1 and p refer to pressures of 1 and p atm. There are no available data about the variation of the partial specific volume of polymethyl methacrylate with pressure, but as it is generally assumed that this variation is small, V_p has been put equal to V_1 . The solvent used was ethyl acetate. For the part of the cell used the correction factor varies from 1.02 to 1.10.

In order to test the reliability of the correction formula, $s_1 = s_p \frac{\eta_p (1 - V_1\rho_1)}{\eta_1 (1 - V_p\rho_p)}$, the sedimentation rate of a polymethyl methacrylate fraction was determined for three different rotor speeds and three different dilutions. Table 1 gives the values of s_{20} which were obtained. The uncorrected value of s_{20} shows a definite trend for all concentrations, while the corrected value shows no systematic variation with rotor speed. This is most clearly indicated by the figures in the last two columns, where Σs_{20} for all three concentrations is given for the three rotor speeds. The table also gives the magnitude of the mean deviation from the mean $\bar{s}$ defined as $\frac{\Sigma |s - \bar{s}|}{n}$, for the different sedimentation constants.

The deviation thus defined is of the order of 1 % for the corrected s_{20} values.

Table 1. The effect of the speed of rotation on the sedimentation constant.

Rotor speed	Conc. 0.1629 g/ml		Conc. 0.1091 g/ml		Conc. 0.0561 g/ml		All three dilutions	
	s_{20} uncorr.	s_{20} corr.	s_{20} uncorr.	s_{20} corr.	s_{20} uncorr.	s_{20} corr.	Σs_{20} uncorr.	Σs_{20} corr.
600 revs/s	15.8	16.3	17.0	17.8	18.0	18.6	50.8	52.7
800 revs/s	15.0	16.2	16.0	17.3	17.2	18.8	48.2	52.3
1 000 revs/s	13.9	15.8	15.6	18.1	15.5	18.5	45.0	52.4
Mean	14.9	16.1	16.2	17.7	16.9	18.6		
Mean deviation	4.5 %	1.2 %	3.3 %	1.7 %	5.5 %	0.5 %		

Measurements were made on six different concentrations for each fraction. In extrapolating the sedimentation constants to infinite dilutions, the following relationship was used ⁵

$$s_{20} = s_{20}^0 - K \cdot s_{20} \cdot c$$

where s_{20} is the sedimentation constant measured at the concentration c , and s_{20}^0 the extrapolated value for zero concentration. The method of least squares has been used for the determination of s_{20}^0 and K . Figure 1 shows how s_{20} and $s_{20} \times c$ vary with the concentration. The sedimentation constant for polymethyl methacrylate exhibits a remarkably low concentration dependence in ethyl acetate, when compared with benzene for instance ⁶. For the first three fractions K is of the order of magnitude 5—6, whereas K for the lower fractions lies between 0.8 and 2.5. The concentration arbitrarily used here is that at the boundary between the solvent and the solution which has been put equal to half the initial concentration in the extrapolation formula (see Table 2).

CALCULATION OF THE HETEROGENEITY OF THE FRACTIONS

Gralén ⁷ introduced the width of the sedimentation curve as a measure of the polymolecularity of a substance. As the measure of the width (B) he used the ratio of the area of the curve to its maximum height

$$B(x_m) = \frac{\int_{x_0}^{\infty} \left(\frac{dc}{dx} \right) dx}{\left(\frac{dc}{dx} \right)_{\max}}$$

Fig. 1. The sedimentation constant s_{20} both as a function of concentration c and as a function of the product $s_{20} \times c$. The solvent used was ethyl acetate.

The width varies with the position of the maximum point in the cell (x_m). The derivative $\left(\frac{dB}{dx_m}\right)$ is in its turn a function of the solute's concentration (c), as long as this is not so low that the macromolecules sediment independently of one another. In determining $\left(\frac{dB}{dx_m}\right)$, the measured value of B is plotted against x_m , and the slope at the origin gives the value of $\lim_{x_m \rightarrow x_0} \left(\frac{dB}{dx_m}\right) = \lim_{c \rightarrow 0} \left(\frac{dB}{dx_m}\right) = \left(\frac{dB}{dx}\right)_c$. As this slope depends on the concentration, $\left(\frac{dB}{dx}\right)_c$ is determined for several dilutions, whereupon a value of $\left(\frac{dB}{dx}\right)_{c=0}$ may be obtained by extrapolation. The diffusion constant was so low for the substances for which Gralén⁷ and Rånby⁸ previously used this method of estimating the polymolecularity, that the broadening of the sedimentation curve could be attributed entirely to the different sedimentation rates of the solute particles (different s values). But the contribution of diffusion to the width of the curve is so large for the fractionated polymethyl methacrylates concerned here, that a correction is necessary.

The following assumptions are made:

1) Diffusion and sedimentation occur independently in the centrifuge cell. This is not quite true for higher concentrations of polymethyl methacrylate, but since $\left(\frac{dB}{dx}\right)_c$ is always extrapolated to 0, the assumption is probably justified.

Table 2. The sedimentation constant and $\left(\frac{dB}{dx}\right)$ for the different fractions in ethyl acetate solutions.

Concentration	s_{20} (corr.)	$\frac{dB}{dx}$	$\frac{dB}{dx}$ (corr.)	Concentration	s_{20} (corr.)	$\frac{dB}{dx}$	$\frac{dB}{dx}$ (corr.)
Fraction L(6) F(2) I				Fraction L(6) F(2) II			
0.2004	15.5	0.22	0.17	0.1995	14.0	0.26	0.17
0.1254	18.3	0.29	0.26	0.1499	15.9	0.30	0.24
0.0988	19.3	0.30	0.25	0.1012	17.0	0.30	0.27
0.0811	20.0	0.29	0.29	0.0833	17.8	0.30	0.25
0.0600	21.1	0.37	0.22	0.0578	19.6	0.35	0.30
0.0511	21.6	0.34	0.28	0.0502	17.8	0.42	0.37
0	25.0		0.27	0	21.5		0.30
$K = 6.0$				$K = 5.2$			
Fraction L(6) F(2) III				Fraction L(6) F(2) IV			
0.2000	12.4	0.14		0.1984	13.3	0.19	
0.1502	14.1	0.26		0.1487	13.4	0.29	0.24
0.1005	16.4	0.28	0.23	0.0994	14.7	0.37	0.31
0.0799	16.4	0.24	0.16	0.0760	15.2	0.30	0.20
0.0604	16.7	0.23	0.19	0.0595	15.2	0.32	0.25
0.0508	16.1	0.26	0.21	0.0499	15.2	0.30	0.23
0	19.4		0.21	0	16.3		0.27
$K = 5.2$				$K = 2.4$			
Fraction L(6) F(2) V				Fraction L(6) F(2) VI			
0.1986	11.8	0.25	0.14	0.1992	9.92	0.34	0.21
0.1512	12.4	0.31	0.17	0.1113	10.5	0.39	0.24
0.0995	13.0	0.33	0.22	0.0982	11.2	0.39	0.26
0.0787	13.2	0.30	0.24	0.0803	11.0	0.41	0.32
0.0615	13.3	0.32	0.24	0.0601	10.7	0.48	0.35
0.0513	13.4	0.37	0.31	0.0502	11.4	0.37	0.29
0	14.1		0.26	0	11.7		0.32
$K = 1.9$				$K = 1.8$			
Fraction L(6) F(2) VII				Fraction L(6) F(2) VIII			
0.2017	8.15	0.43	0.16	0.1989	5.97	0.72	0.27
0.1487	8.45	0.41	0.21	0.1468	6.48	0.69	0.22
0.1001	7.35	0.43	0.21	0.0999	6.92		
0.0815	8.41	0.46	0.17	0.0796	6.89	0.72	0.35
0.0606	8.70	0.42	0.27	0.0585	6.65	0.55	0.11
0.0525	8.64	0.41	0.17	0.0503	7.36	0.55	
0	8.8		0.22	0	7.6		0.25
$K = 0.8$				$K = 2.5$

Fig. 2. Sedimentation diagram for the sample L (6) F (2) III, dissolved in ethyl acetate at a concentration of 0.200 g/100 ml (upper diagram) and 0.051 g/ml (lower diagram). The times given for the exposures are times after the rotor attained full speed. The distance from the scale to the cell was 2.0 cm.

2) Each fraction is supposed to be such that the mass is distributed over the different s values in accordance with a Gaussian frequency curve with first moment $\bar{s}$, second moment p^2 and width

$$b = \frac{\int_0^{\infty} \left(\frac{dc_0}{ds} \right) ds}{\left(\frac{dc_0}{ds} \right)_{\max}}$$

This assumption is rather arbitrary, but may be regarded as permissible in view of the fact that it is only an estimation of the fraction's polymolecularity which is required, and in view of the actual appearance of the experimental curves (Fig. 2).

Symbols used:

- σ_{total}^2 = the total second moment of the experimental sedimentation diagram,
 $\sigma_{\text{sed.}}^2$ = the second moment if only sedimentation occurred,
 $\sigma_{\text{diff.}}^2$ = the second moment if only diffusion occurred,
 s = the sedimentation constant,
 D = the diffusion constant,
 ω = the angular velocity of the rotor,
 t = time,
 x = position coordinate in the centrifuge cell,
 dc_0 = the concentration of substance with sedimentation constants in the interval s to $s + ds$ initially,
 dc = the concentration of substance with sedimentation constants in the interval s to $s + ds$ at time t and at the point x ,
 x_0 = the distance of the meniscus from the axis of rotation.

At time t , molecules with sedimentation constant s are at the level x given by

$$x = x_0 e^{\omega^2 s t} \quad (1)$$

On account of the cell's sector form there is a dilution², so that the concentration of molecules with sedimentation constants in the interval s to $s + ds$ at the level x and time t is

$$dc = dc_0 e^{-2\omega^2 s t} \quad (2)$$

On differentiating eq. (1) we get

$$dx = x_0 e^{\omega^2 s t} \omega^2 t ds \quad (3)$$

Furthermore, according to eq. (2),

$$dc = \left(\frac{dc}{dx} \right) dx = \left(\frac{dc_0}{ds} \right) (ds) e^{-2\omega^2 s t} \quad (4)$$

For the second moment we have

$$\sigma_{\text{sed}}^2 = \int_0^{\infty} (x_0 e^{\omega^2 s t} - x_0 e^{\omega^2 s t})^2 \left(\frac{dc}{dx} \right) dx \quad (5)$$

or

$$\sigma_{\text{sed}}^2 = \int_0^{\infty} (x_0 e^{\omega^2 (s-s)t} - x_0)^2 \left(\frac{dc_0}{ds} \right) ds \quad (6)$$

Expansion in series gives

$$\sigma_{\text{sed}}^2 = \int_0^\infty x_0^2 \left\{ \omega^2(\bar{s}-s)t + \frac{\omega^4(\bar{s}-s)^2 t^2}{2!} e^{\Theta \omega^3(\bar{s}-s)t} \right\}^2 \left(\frac{dc_0}{ds} \right) ds \quad (7)$$

and if we neglect the higher terms,

$$\sigma_{\text{sed}}^2 = x_0^2 \omega^4 t^2 \int_0^\infty (\bar{s}-s)^2 \left(\frac{dc_0}{ds} \right) ds = x_0^2 \omega^4 t^2 p^2 \quad (8)$$

According to assumption 1)

$$\sigma_{\text{total}}^2 = \sigma_{\text{diff}}^2 + \sigma_{\text{sed}}^2 \quad (9)$$

According to assumption 2) p^2 is the second moment of a Gaussian distribution; and under the conditions for which it can be justified to neglect the higher terms in equation (7) σ_{sed}^2 can also be considered to correspond to a Gaussian distribution. σ_{diff}^2 is the second moment of a Gaussian distribution according to the accepted theory of free diffusion³. Therefore, σ_{total}^2 must be the second moment of a Gaussian distribution. For such a parameter,

$$B^2 = 2\pi\sigma^2 \quad (10)$$

or, according to (9) and (10),

$$B_{\text{total}}^2 = B_{\text{diff}}^2 + B_{\text{sed}}^2 \quad (11)$$

and according to eqs. (8), (10) and (11)

$$B_{\text{sed}} = \sqrt{B_{\text{total}}^2 - B_{\text{diff}}^2} = x_0 \omega^2 t b \quad (12)$$

For B_{diff} we have

$$B_{\text{diff}}^2 = 4\pi Dt \quad (13)$$

so that

$$B_{\text{sed}} = \sqrt{B_{\text{total}}^2 - 4\pi Dt} \quad (14)$$

If eq. (12) is differentiated we get

$$\left(\frac{dB}{dx} \right) = \left(\frac{dB}{dt} \right) \left(\frac{dt}{dx} \right) = x_0 \omega^2 b \frac{1}{x_0 \omega \bar{s} e^{\omega^3 i}} \quad (15)$$

and

$$\lim_{\substack{x=x_0 \\ t=0}} \left(\frac{dB}{dx} \right) = \frac{b}{\bar{s}} \quad (16)$$

Formula (14) has been used for correcting the width, t being taken as time after the rotor attained its full speed. Table 2 gives both the corrected and uncorrected values of $\left(\frac{dB}{dx}\right)_c$ for all concentrations and fractions, for comparison purposes.

DIFFUSION MEASUREMENTS

The diffusion constants were determined at 20° C. Unless otherwise stated, the diffusion cell was of the Claesson type²; in some cases a Svedberg cell was used³. The diffusion was followed by means of Lamm's scale method³. The diffusion constant was as a

Table 3. Diffusion constants for sample L(6) F(2) V in ethyl acetate solutions.

Concentration		Diffusion cell	D_A	D_m
Higher	Lower			
0.40	0	Claesson (1')	4.22	4.56
		» (1'')	4.14	4.18
		» (2)	3.29	3.23
		» (2)	3.76	3.35
		Svedberg	3.39	3.27
			<u>3.76</u>	<u>3.72</u>
0.30	0	Claesson (1')	3.96	4.00
		» (1'')	4.13	4.21
		» (2)	3.75	4.22
		Svedberg	3.46	3.25
			<u>3.83</u>	<u>3.92</u>
0.25	0	Claesson (1')	3.36	3.13
		» (1'')	3.68	3.59
		» (2)	3.45	3.49
			<u>3.50</u>	<u>3.40</u>
0.60	0.40	Claesson	3.78	3.60
0.50	0.30	Claesson	4.15	4.23
0.30	0.10	Claesson	3.67	3.67
Mean		$\bar{D}$	3.75	3.73
Mean deviation = $\frac{ D-\bar{D} }{n}$			0.26	0.40

Table 4. Diffusion constants for sample L(6) F(2) VI in ethyl acetate.

Concentration		D_A	D_m
Higher	Lower		
0.60	0.40	4.48	4.10
0.50	0.30	4.65	4.52
		5.10	4.50
0.40	0.20	4.69	4.30
Mean $\bar{D}$		4.73	4.36

rule calculated for three or four different concentrations. In some indicated cases the differential diffusion constant was measured. As may be seen from Tables 3, 4 and 5, the reproducibility was poor, probably due to the fact that no suitable sealing substance was found. As no systematic trend of the diffusion constant with concentration could be detected, the mean value of the diffusion constants for all concentrations used in the experiments was used in the calculation of the molecular weights*.

Table 5. Diffusion constants for different fractions of polymer L(6) in ethyl acetate solutions.

Concentration	L(6)F(2) I		L(6)F(2) II		L(6)F(2) III		L(6)F(2) IV		L(6)F(2) V		L(6)F(2) VI		L(6)F(2) VII		L(6)F(2) VIII	
	D_A	D_m	D_A	D_m	D_A	D_m	D_A	D_m	D_A	D_m	D_A	D_m	D_A	D_m	D_A	D_m
0.40	2.41	2.41	2.37	2.33	3.44	3.38	3.51	3.56					5.68	5.84		
0.30	2.38	2.35	2.58	2.61			—	—					5.59	5.08		
0.25	2.23	2.25	—	—			3.87	4.46	See Table 3		See Table 4		6.09	5.75		
0.20	1.99	—	2.75	2.69			3.36	3.34					5.90	5.97	8.10	7.21
Mean value	2.25	2.34	2.57	2.54	3.44	3.38	3.58	3.79	3.75	3.73	4.73	4.36	5.82	5.66	8.10	7.21

DETERMINATION OF THE PARTIAL SPECIFIC VOLUME

It is necessary to know the partial specific volume of the substance dissolved in the solvent used when calculating the molecular weight from measurements of sedimentation and diffusion. For this purpose two 30 ml pycnometer flasks as near as possible identical

* This decision also takes into account a large number of diffusion measurements which have not yet been published.

were used, the solution and the solvent being introduced into the respective flasks by means of a syringe. One of the flasks was used just as a counterweight, and was filled with the pure solvent. The other pycnometer contained either pure solvent to begin with, in which case the concentration of polymer was increased by removing some of the solution and replacing with concentrated solution, or concentrated solution initially, in which case the concentration was diminished in an analogous manner. In measurement series 3, the dry polymethyl methacrylate was introduced into the pycnometer through an extra side tube, which was then sealed off.

The calculation of the partial specific volume V_1 of the solute involves the relation

$$V_1 = V + \omega_2 \frac{\partial V}{\partial \omega_1}$$

where V is the specific volume of the solution, and ω_1, ω_2 the weight fractions for solute and solvent respectively. The derivative $\frac{\partial V}{\partial \omega_1}$ may be taken to be constant in the concentration interval concerned and was determined by the method of least squares (Table 6).

Table 6 a. The partial specific volume of polymethyl methacrylate dissolved in ethyl acetate.

Measurement series	$-\frac{dV}{dc}$	Partial spec. volume
1.	0.236	0.785
2.	0.316	0.795
3.	0.330	0.781
	Mean	0.787

Table 6 b. The partial specific volume of polymethyl methacrylate dissolved in benzene.

Measurement series	$-\frac{dV}{dc}$	Partial spec. volume
1.	0.321	0.818

MOLECULAR WEIGHT DETERMINATIONS

The molecular weights M_{Ds} of the different fractions were calculated with the aid of Svedberg's formula ²

$$M_{Ds} = \frac{RTs}{D(1-V\rho)}$$

where T = the absolute temperature,

R = the universal gas-constant,

V = the partial specific volume of the polymer,

ρ = the density of the solvent.

See Table 7.

VISCOSITY MEASUREMENTS

The intrinsic viscosity $[\eta]$ was determined by means of an Ostwald viscometer at 20.0° C. The solvent was either ethyl acetate or benzene. The reduced viscosity $\frac{\eta_{sp}}{c}$ was determined for the following concentrations (c): 0.40, 0.30, 0.20, and 0.10 g of dry solute in 100 ml solution. The intrinsic viscosity was obtained by extrapolating $\frac{\eta_{sp}}{c}$ to infinite dilution. This extrapolation was facilitated by the fact that $\frac{\eta_{sp}}{c}$ is a linear function of the concentration:

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c$$

Besides $[\eta]$, the constant k' was also determined. The molecular weight $(M)_{\eta}$ corresponding to the intrinsic viscosity $[\eta]$ was calculated by means of the formula ^{10 *}

$$(M)_{\eta} = 2.81 \cdot 10^5 [\eta]^{1.32}$$

See Table 7.

THE MASS DISTRIBUTION OF THE UNFRACTIONATED POLYMER

In constructing a curve of mass distribution for the unfractionated polymer product, it is possible to apply Schulz's method ¹¹ and assume that half the mass of a fraction has a s_0 value lower than the sedimentation constant determined for the fraction, the other half having a higher value, and that the fractions do not overlap. In this method it is not possible to take the polydispersity of the fractions into account, and it therefore gives an uncertain result when the fractions are broad. A construction more satisfactory in principle has been

* The constants in this formula are determined at 25.0° C and the molecular weights calculated from them here are consequently 2–3 % too low.

Fig. 3. Frequency curve and mass distribution curve for the unfractionated polymer together with the frequency curves for the separate fractions.

given by Rånby⁸ for the case where the fractions' $\left(\frac{dB}{dx}\right)$ values are known.

In this method each fraction's frequency curve is approximated to by a symmetrical triangular curve where the s_0 value for the apex of the triangle is put equal to the s_0 value determined for the fraction. In accordance with the definition of b , the base of the triangle is $2b = 2\bar{s}_0 \left(\frac{dB}{dx}\right)$ (formula 16). The value adopted for the height of the triangle is such that the area of the triangle is

proportional to the weight of the fraction. $\sigma = \frac{-\frac{dB}{dx}}{\sqrt{2\pi}}$, according to formulas

(10) and (16). It is therefore also possible to construct a Gaussian frequency curve for which the area is proportional to the weight of the fraction and σ equal to the σ value calculated for the fraction. The frequency curves constructed in this way for the various fractions are given in Fig. 3. The figure provides a good illustration of the polydispersity of the different fractions. It will also be seen from the figure that the different fractions overlap one another almost everywhere. Addition of all the ordinates for each of a series of s_0 values gives the frequency curve for the original unfractionated polymethyl methacrylate. As no measurements were made for fraction IX, which was merely an evaporation residue, the left of the frequency curve for the original product is indicated by a broken line. The three methods for obtaining the

Table 7.

Fraction	Weight in %	$M_{D_0} 10^{-3}$	$[\eta]_{\text{benzene}}$	k'_{benzene}	$M_{\eta_{\text{benzene}}} 10^{-3}$	$[\eta]_{\text{ethyl acetate}}$	$k'_{\text{ethyl acetate}}$	$\frac{M_{D_0}}{M_{\eta}}$
L(6)F(2) I	10.75	931	2.08	0.32	739	1.24	0.37	1.26
L(6)F(2) II	9.36	701	1.72	0.28	575	1.10	0.35	1.22
L(6)F(2) III	12.56	473	1.43	0.34	451	0.96	0.39	1.05
L(6)F(2) IV	11.50	381	1.30	0.30	397	0.77	0.54	0.96
L(6)F(2) V	18.75	315	1.00	0.42	281	0.64	0.64	1.12
L(6)F(2) VI	19.23	207	0.71	0.31	179	0.49	—	1.16
L(6)F(2) VII	6.39	127	—	—	—	0.37	—	—
L(6)F(2) VIII	7.00	79	0.26	—	48	0.27	—	1.65
L(6)F(2) IX	4.45							

mass distribution of the unfractionated polymer product give results in close agreement in this case (Table 8).

It will be seen from columns 3, 6 and 9 of Table 7 that the two methods for the determination of the molecular weight do not give the same result (*cf.* also footnote p. 634), as they give different kinds of averages for a poly-molecular fraction. Neither method gives a well-defined average, the nature of the average in each case being very complex and difficult to interpret. Determination of the molecular weight by means of the ultracentrifuge and diffusion measurements assigns greatest significance to the molecules for which the concentration by weight is largest. This uncertainty with regard to the nature of the average naturally makes it difficult to compare the mass distri-

Table 8. The mass distribution of the original sample calculated by a) Schulz's method, b) by Rånby's triangle method, and c) with the aid of Gaussian frequency curves.

Fraction	$\bar{S}_0$	Distribution according to		
		a)	b)	c)
L(6)F(2) I	25.0	94.6 %	93.6 %	93.5 %
L(6)F(2) II	21.5	84.6	84.3	84.2
L(6)F(2) III	19.4	73.6	75.4	75.0
L(6)F(2) IV	16.3	61.6	60.6	61.0
L(6)F(2) V	14.1	46.5	46.7	46.5
L(6)F(2) VI	11.7	27.5	28.6	28.5
L(6)F(2) VII	8.8	14.7	14.8	14.5
L(6)F(2) VIII	7.6	8.0	8.4	8.2

Fig. 4. Mass distributions for the unfractionated polymer.

- Curve I: theoretical, calculated on the basis of deactivation of the growing molecule through disproportionation¹.
 Curve II: theoretical, calculated on the basis of deactivation of the growing molecule through combination¹.
 Curve III: calculated from the sedimentation and diffusion constants on the assumption of Gaussian distributions for the separate fractions.
 Curve IV: calculated from the intrinsic viscosity of the fractions in accordance with Schulz's method.

bution of the unfractionated product as determined experimentally and as determined theoretically. However, it does appear that the weight average for a polydisperse fraction is to be preferred to the number average. Curve IV in Fig. 4 represents the mass distribution obtained from viscosity data according to Schulz's method, while curve III gives the corresponding distribution calculated from diffusion and sedimentation data. Curves I and II are theoretical curves based on the assumption that the growing radicals are rendered inactive by either disproportionation (I) or combination (II). As regards the theoretical calculations, see ¹.

THE MOLECULAR SHAPE AND FLEXIBILITY OF POLYMETHYL METHACRYLATE

The experimental data also give us some information about the shape and flexibility of the polymethyl methacrylate molecule in the dissolved state. The intrinsic viscosity of polymethyl methacrylate depends to a great extent on the particular solvent. In the poor solvent isobutyl acetate, for instance, it is about one eighth of what it is in chloroform⁶. This close dependence on the

Table 9. The dependence of the

Polymethyl methacrylate (I) in ethyl acetate					Polymethyl methacrylate (II) in ethyl acetate			
Temperature °C	20	30	40	Per cent/degree	20	30	40	Per cent/degree
Concentration <i>c</i>	0.3014	0.2970	0.2930		0.3971	0.3914	0.3861	
Specific viscosity η_{sp}	2.448	2.501	2.567	0.24	0.338	0.343	0.349	0.16
Reduced viscosity $\frac{\eta_{sp}}{c}$	8.12	8.42	8.76	0.39	0.85	0.88	0.90	0.29
Concentration <i>c</i>	0.1990	0.1962	0.1935		0.2985	0.2942	0.2902	
Specific viscosity η_{sp}	1.356	1.390	1.425	0.25	0.247	0.251	0.255	0.16
Reduced viscosity $\frac{\eta_{sp}}{c}$	6.81	7.09	7.36	0.40	0.83	0.85	0.88	0.30
Concentration <i>c</i>	0.1117	0.1101	0.1086		0.1984	0.1955	0.1929	
Specific viscosity η_{sp}	0.649	0.666	0.681	0.25	0.158	0.161	0.164	0.19
Reduced viscosity $\frac{\eta_{sp}}{c}$	5.81	6.05	6.27	0.40	0.80	0.82	0.85	0.31
Concentration <i>c</i>	0.0490	0.0483	0.0476		0.0995	0.0981	0.0968	
Specific viscosity η_{sp}	0.256	0.262	0.267	0.21	0.076	0.077		
Reduced viscosity $\frac{\eta_{sp}}{c}$	5.23	5.42	5.61	0.36	0.76	0.78		
Mean					0.24	Mean		
					0.39	0.17		
						0.30		

nature of the solvent indicates that the polymethyl methacrylate molecules are very flexible, assuming a shape which is more or less extended according as the affinity for the solvent is greater or less than the affinity between the different molecule segments of the polymer. Theoretical considerations^{12, 14} show that for a homologous series of polymers the intrinsic viscosity and the molecular weight M are related by the equation $[\eta] = KM^a$, where K and a are constants. In the limiting case where the molecules adopt a long, rigid form, $a = 1$, while in the other extreme case, where $a = 0.5$, the molecules assume a coiled shape. If the above relation is applied to the values obtained for M_{Ds} $[\eta]_{\text{benzene}}$ and $[\eta]_{\text{ethyl acetate}}$ given in Table 7, the following values for K and a result:

$$K = 2.11 \cdot 10^{-4}$$

$$K = 1.51 \cdot 10^{-4}$$

$$a = 0.64 \text{ for ethyl acetate}$$

$$a = 0.70 \text{ for benzene}$$

viscosity on temperature.

Polymethyl methacrylate (I) in benzene					Polymethyl methacrylate (II) in benzene			
Concentration c	0.3007	0.2969	0.2935		0.4011	0.3961	0.3915	
Specific viscosity η_{sp}	4.768	4.758	4.856	0.09	0.562	0.559	0.558	- 0.04
Reduced viscosity $\frac{\eta_{sp}}{c}$	15.86	16.03	16.54	0.21	1.40	1.41	1.43	0.10
Concentration c	0.2093	0.1991	0.1968		0.3033	0.2995	0.2961	
Specific viscosity η_{sp}	2.571	2.586	2.617	0.09	0.411	0.407	0.407	- 0.05
Reduced viscosity $\frac{\eta_{sp}}{c}$	12.76	12.99	13.30	0.21	1.35	1.36	1.37	0.07
Concentration c	0.1500	0.1481	0.1464		0.2009	0.1984	0.1961	
Specific viscosity η_{sp}	1.685	1.688	1.706	0.06	0.261	0.261	0.261	0
Reduced viscosity $\frac{\eta_{sp}}{c}$	11.24	11.40	11.65	0.18	1.30	1.32	1.33	0.12
Concentration c	0.0994	0.0981	0.0970		0.1004	0.0992	0.0980	
Specific viscosity η_{sp}	0.979	0.982	0.991	0.06	0.125	0.125	0.126	+ 0.04
Reduced viscosity $\frac{\eta_{sp}}{c}$	9.85	10.01	1.021	0.18	1.25	1.26	1.28	0.12
Concentration c	0.0498	0.0491	0.0486		Mean			
Specific viscosity η_{sp}	0.443	0.447	0.448	0.06				
Reduced viscosity $\frac{\eta_{sp}}{c}$	8.89	9.10	9.24	0.20				
Mean				0.08 0.19				

Meyerhoff and Schulz¹³ give the values $\alpha = 0.73$ for benzene and $\alpha = 0.80$ for chloroform. It is therefore clear that the molecules are more tightly coiled in ethyl acetate than in benzene. This conclusion is also in agreement with the fact that the dependence of $[\eta]$ on temperature is 2 to 3 times larger in the former solvent than in the latter (see Table 9).

The relation between s and M_{Ds} gives us further information about the shape of the polymethyl methacrylate molecule. According to Kirkwood and Riseman^{14,15}, a statistically coiled molecule experiences a frictional resistance to a translational movement which may be expressed by

$$f_T = \frac{Z \xi}{1 + \frac{8}{3} Z^{1/2} \lambda_0} \quad \lambda_0 = \frac{\xi}{\sqrt{6\pi^2 \eta_0 b}}$$

where ξ = the frictional coefficient describing the friction between the chain element and the surrounding liquid,
 b = the effective length of the segment,
 Z = the number of segments,
 η_0 = the viscosity of the solvent.

Furthermore,

$$s = \frac{\frac{dx}{dt}}{\omega^2 x} = \frac{M (1 - V_e)}{N f_T}$$

so that

$$s = \frac{M (1 - V_e)}{N Z \xi} \left(1 + \frac{8}{3} Z^{1/2} \lambda_0 \right)$$

Or, if half the molecular weight of the monomer is taken as the mean value of the molecular weight of the segment,

$$M = M_0 Z = 50 Z$$

$$s = \frac{M_0 (1 - V_e)}{N \xi} \left(1 + \frac{8}{3} Z^{1/2} \lambda_0 \right) = \frac{M_0 (1 - V_e)}{N \xi} \left(1 + \frac{8}{3} \frac{\lambda_0 M^{1/2}}{M_0^{1/2}} \right)$$

Table 10 gives the experimentally established relation between the sedimentation constant and the molecular weight, and the values of b and ξ calculated from them. For comparison, the corresponding relation has also been calculated for Meyerhoff and Schulz's¹³ data for acetone in the molecular weight interval 77 000–611 000, this being the interval which most nearly corresponds to that for the ethyl acetate solutions. The effective segment length is somewhat smaller in ethyl acetate than in acetone, but on the other hand ξ is larger.

Finally the partial specific volume for polymethyl methacrylate in ethyl acetate is only 0.787, while in benzene it is 0.818; in the solid state it is 0.84.

Table 10.

Solvent	$s = A + B \sqrt{M}$	b	ξ
Ethyl acetate	$s = -0.06 + 0.026 \sqrt{M}$	$5.6 \cdot 10^{-8}$	$> 24.2 \cdot 10^{-10}$
Acetone	$s = 1.64 + 0.0441 \sqrt{M}$	$5.9 \cdot 10^{-8}$	$1.87 \cdot 10^{-10}$

SUMMARY

The sedimentation and diffusion constants were determined for a complete series of polymethyl methacrylate fractions. The sedimentation constant for the solution in ethyl acetate is comparatively little dependent of the concentration. Values of s_{20} for zero concentration were obtained by extrapolation in accordance with the formula $\frac{1}{s_{20}} = \frac{1}{s_{20}^0} + \frac{K}{s_{20}^0} c$. No dependence on concentration was found for the diffusion constant, though the experimental error was large in this case.

The polydispersity of the separate fractions and of the unfractionated polymer were determined. A formula is suggested for the correction of the experimental $\left(\frac{dB}{dx}\right)$ values, to take the effect of diffusion into account. Different methods for determination of the molecular weight give somewhat different experimental mass distributions.

Polymethyl methacrylate molecules are very flexible, and assume a compact coiled shape in ethyl acetate solution.

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