250. *Magnetic Studies on Polymerisation. Part I. Magnetic Optical Rotatory Powers and Diamagnetic Susceptibilities of Certain Polymethyl Methacrylates.*

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The magneto-optic rotatory powers and diamagnetic susceptibilities of methyl methacrylate and the polymethyl methacrylates have been measured. The results may be employed to calculate the average molecular weights of the polymers, fair agreement being obtained with values determined by a viscosity method (Schulz and Blaschke).

The magnetic susceptibility method which Farquharson (*Trans. Faraday Soc.*, 1936, **32**, 219) employed to investigate the degree of polymerisation of 2 : 3-dimethylbutadiene and other substances, is used in the present investigation on the polymethyl methacrylates. In addition,

another method of molecular weight determination is proposed, which is based in the magneto-optical rotatory powers of the polymers concerned.

Melville and others (General Discussion, *Trans. Faraday Soc.*, 1944, **40**, 217—273) have surveyed the end-group, osmotic, and viscosity methods for the determination of the molecular weight of higher polymers; of these, Schulz and Dinglinger (*J. pr. Chem.*, 1940, **157**, 15), Schulz and Blaschke (*Z. physikal. Chem.*, 1942, *B*, **51**, 75), Baxendale, Bywater, and Evans (*J. Polymer Sci.*, 1946, **1**, 237), and Walling and Briggs (*J. Amer. Chem. Soc.*, 1946, **68**, 1141) have shown that the viscosity method can be usefully employed to find the molecular weights of the polymethyl methacrylates, using modifications of the Staudinger equation; the present results are compared with those obtained by Schulz and Blaschke in their detailed study of the benzoyl peroxide-catalysed polymerisation of methyl methacrylate.

Magnetic Optical Rotatory Powers.—Perkin (*J.*, 1884, **45**, 421 *et seq.*) deduced from measurements on many homologous series of organic compounds that the molecular magnetic rotation M of a substance could be expressed by

$$M = S + n\Delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Δ is the increase in rotation between successive members of an homologous series (the " CH_2 increment ") which Perkin found experimentally to have a mean value of 1·023; n is the number of carbon atoms in the molecule; S is the " series constant " which Perkin obtained by subtracting the value of $n\Delta$ from the total observed rotation, the resulting figure being approximately constant for an homologous series of compounds and different for different series.

It was proposed to make use of this relationship in the estimation of molecular weights of higher polymers.

It follows from the above equation that a monomer is related to its polymer thus :

$$M_p = n_a M_m + (n_a - 1)S_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where M_p, M_m are the molecular magnetic rotations of polymer and monomer respectively, n_a is the average number of units in the molecule of polymer, and S_1 is the " series constant ", which is in this case Perkin's constitutive correction for the formation of a new bond.

By definition,

$$M_p = \theta_p w_p/w; \quad M_m = \theta_m w_m/w$$
$$\theta_p = \alpha_p d/\alpha d_p; \quad \theta_m = \alpha_m d/\alpha d_m$$

where α_p, α_m, α are the observed rotations of polymer, monomer, and water respectively under the same conditions; θ_p, θ_m are the specific rotations of polymer and monomer, respectively; w_p, w_m, w are the molecular weights of polymer, monomer, and water, and d_p, d_m, d are the corresponding densities measured at the same temperature.

But $w_p = n_a \times w_m$, therefore

$$\theta_p n_a w_m/w = n_a \theta_m w_m/w + (n_a - 1)S_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Hence n_a may be calculated from the experimental results.

Diamagnetic Susceptibilities.—Farquharson's expression for the mass susceptibility of a polymer is

$$\chi_s = [n_a \chi_B + (n_a - 1)\lambda]/n_a w_m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where w_m is the molecular weight of the monomer, χ_s is the mass susceptibility of the polymer, χ_B is the molecular susceptibility of the monomer, n_a is the degree of polymerisation, and λ is Pascal's constitutive correction constant for the bond ruptured. This equation is used for the calculation of n_a.

Average Molecular Weights.—The following table has been drawn up from measurements of magneto-optic rotatory powers and diamagnetic susceptibility which are listed later (Tables I and II); t is the polymerisation time; n_a is the average number of units in the molecule of polymer, and w_p the corresponding average molecular weight, calculated from equations (3) and (4).

	Magneto-optic rotation.			Diamagnetic susceptibility.		
t (mins.).	n_a.	$n_a\theta_p$.	w_p.	n_a.	$n_a\chi_s$.	w_p.
0	1	1·093	100	1	0·5370	100
15	2	2·088	190	1—2	0·7521	130
30	2—3	2·535	240	2—3	1·248	220
45	4	4·279	410	3—4	2·192	380
60	5	5·556	550	5	2·904	500
75	14	13·77	1390	14	8·809	1380
180	68	66·80	6750	61 *	36·06	6110
				61 *	36·06	6110

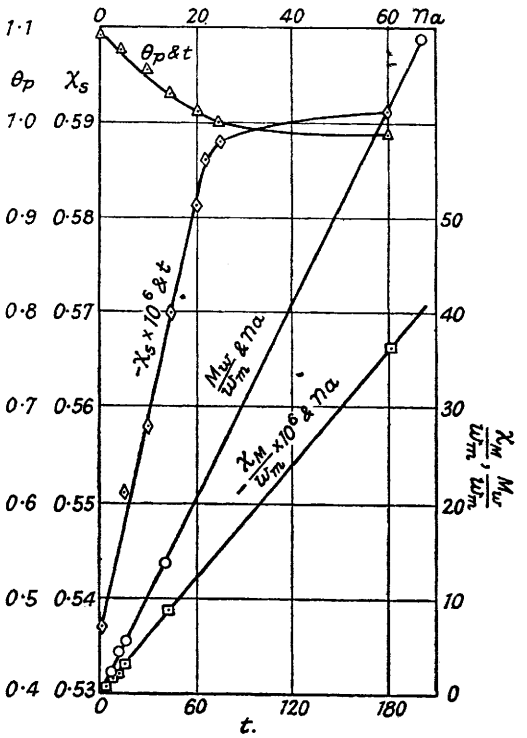
* Measurements on powder and solution, respectively.

A value of $-1{\cdot}112$ was used for S_1 in equation (3), by analogy with ethyl crotonate, for which Perkin found an increase of rotation of $1{\cdot}112$ compared with ethyl butyrate; λ was assumed to be $+5{\cdot}5$, which is Pascal's constitutive correction for the double bond.

The decrease in magneto-optic rotation and the increase in magnetic susceptibility which are found experimentally during polymerisation (Tables I and II) would be expected from the sign of the constants S_1 and λ above.

It will be seen that the figures for n_a and w_p obtained by the two methods agree very closely.

Extrapolation of the data of Schulz and Blaske to 80° and the benzoyl peroxide concentration used in the present investigation gives an upper limit of 5000—6000 for the molecular weight from viscosity measurements. Walling and Briggs quote higher figures in their determinations on benzoyl peroxide-free quinol-stabilised methyl methacrylate, and by analogy, an upper limit of 7000—8000 for the molecular weight may be estimated. The present figures (6750, 6110) are of the same order as the above, but from the calculation employed, it is obvious that decreasing accuracy is possible with polymers of molecular weights of the order 10^5 or higher.



Walling and Briggs found that, at 131°, concentrations of quinol of less than 1% had little effect on the molecular weight of the polymer, and it is doubtful whether the present concentration (0·03%) would cause alteration of the molecular weight to any appreciable extent at 80°.

Complete agreement is not to be expected, since both the present methods give the number-average molecular weight w_n, whereas the viscosity method gives the weight-average molecular weight w_w:

$$w_n = \Sigma w_i N_i / \Sigma N_i \text{ and } w_w = \Sigma w_i N_i / \Sigma w_i N_i$$

w_i is the molecular weight averaged over the number of particles, and N_i is the number of particles of chain length i (Mark and Raff, " Higher Polymeric Reactions," New York, 1941).

Course of Polymerisation.—The polymerisation of methyl methacrylate may be explained by a chain mechanism (Mark, " Physical Chemistry of Higher Polymeric Systems ", New York, 1940, 309). The methyl methacrylate molecule is thought to become activated, by heat, light, or catalyst, and in this condition it accumulates other methyl methacrylate molecules to form a long chain. Eventually the macro-molecule becomes deactivated by the saturation of the free valencies at the growing ends.

Alyea, Gartland, and Graham (*Ind. Eng. Chem.*, 1942, **34**, 458) have shown that benzoyl peroxide initiates these reaction chains, whereas quinol breaks the chains, and in doing so becomes oxidised to benzoquinone. Strain (*Ind. Eng. Chem.*, 1938, **30**, 345) has examined the polymerisation of methyl methacrylate in various organic solvents, using varying quantities of benzoyl peroxide as catalyst.

If the polymerisation is straightforward, χ_s and t will show a hyperbolic relationship (as Farquharson found to be the case with 2 : 3-dimethylbutadiene) and the curve for θ_p and t should also be a hyperbola. This was found to hold true in the present case (see Fig.). These results are consistent with Strain's hyperbolic percentage polymer yield–rate curves for 20% solutions of methyl methacrylate in benzene, acetone, and other solvents.

The figure also shows the linear relationships between $M_w/w_m(= n_a\theta_p)$ and n_a, and between $\chi_m/w_m(= n_a\chi_s)$ and n, in accordance with equations (3) and (4).

Experimental.

Measurement of Magneto-optic Rotations.—The apparatus used in these measurements has been described by Anderson, Bedwell, and Le Fèvre (this vol., p. 457). Methyl methacrylate was polymerised at 80° in the presence of a catalyst (1 mole of benzoyl peroxide to 500 moles of monomer). Samples were withdrawn at intervals, and the magneto-optic rotation measured at 20°. For the final determination, a 20% solution in methylene chloride was used. The results are shown in the figure and in Table I; t is the polymerisation time; w_1 is the weight fraction of the solute in the solution; d_{12} and a_{12} are the respective relative density and observed rotation of pure solute or solution.

By the additivity rule, $\theta_1 = (\theta_{12} - \theta_2)/w_1 + \theta_2$, where θ_1, θ_2, θ_{12} are the specific rotations of solute, solvent, and solution, respectively.

Table I.

t (mins.).	$100w_1$.	$(d_{12})^{20°}_{20°}$.	a_{12}.	a_{12}/a.	a_1/a.	θ_1.	
Water.							
0	0	0·99820	8·80	—	—	—	
Methylene chloride.							
0	0	1·33898	10·80	1·228	1·228	0·919	
Methyl methacrylate.							
0	100	0·96698	9·32	1·057	1·057	1·093	
15	100	0·97641	9·24	1·050	1·050	1·076	
30	100	0·98502	9·16	1·042	1·042	1·056	
45	100	0·99773	9·04	1·030	1·030	1·032	θ_p
60	100	1·00788	8·96	1·018	1·018	1·012	
75	100	1·01619	8·88	1·008	1·008	0·992	
180	20·04	1·31487 *	10·72	1·227	1·173	0·989	

* $(d_1)^{20°}_{20°} = 1·18630$.

Measurement of Magnetic Susceptibility.—Measurements were made at 20°, using the Gouy apparatus described by Anderson, Bedwell, and Le Fèvre (*loc. cit.*). The process of polymerisation was catalysed by benzoyl peroxide at 80°, as described in the previous section. Samples were withdrawn at intervals for measurement. The final polymer was measured both in 18% solution and in the finely powdered state. The results are shown in the figure and in Table II; t is the polymerisation time, and χ_s is the specific susceptibility of the polymerising substance.

Table II.

t (mins.)	0	15	30	45	60	66	75	180
χ_s	0·5370	0·5511	0·5670	0·5776	0·5809	0·5860	0·5881	0·5909 *
								0·5909 *

* Measurements on powder and solution respectively.

Purification of Methyl Methacrylate.—The methyl methacrylate was as supplied by I.C.I. Ltd. stabilised with quinol (0·5%). It was fractionally distilled under reduced pressure and the fraction retained ($n_D^{20°}$ 1·4143) was frozen at −70°, redistilled under high vacuum (after Walling and Briggs), and stored at −70° in the dark, with the addition of quinol as stabiliser, in the proportion of 1 mole of quinol to 4000 moles of methyl methacrylate.

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