349. *Molecular Polarisability: the Molar Kerr Constants of Methyl Methacrylate and its Polymers.*

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The apparent dipole moments, molar Kerr constants, etc., in benzene at 25° are reported for methyl methacrylate and eight of its polymers having (viscosity) molecular weights within the range 23×10^3 to 18×10^5. A conformation for the monomer is specified. The anisotropy of polarisability of the polymers diminishes as molecular weight increases. Scale models indicate that internal rotations within the polymer chain are strongly inhibited and that short segments must be relatively stiff; their ability to bend and twist slightly suggests that larger chains may tend to adopt curved or helical configurations such as have been proposed as a result of *X*-ray and other studies. Empirical relations between the degree of polymerisation and various observable properties are also noted.

THE present measurements are related to others (on polystyrenes, polyvinyl acetates, polyethylene glycols, polyvinyl chlorides, and polyvinyl bromides) already published.[1] They were begun in the hope that electric birefringence might provide information on the shapes and configurations of poly(methyl methacrylates) as solutes. Indications by other physical methods have not always been consistent among themselves.

EXPERIMENTAL

Solutes.—Methyl methacrylate was prepared by the depolymerisation [2] of " Perspex " at 300°. The redistilled fraction, b. p. 98—101°/759 mm., plus *ca.* 0·5% of quinol was stored in the dark. Before use the ester was purified [3] by washing with 5% sodium hydroxide solution, drying ($MgSO_4$), and distillation in nitrogen through a 20 cm. jacketed Widmer column. Middle cuts, b. p. 54·0°/148 mm., n_D^{25} 1·4115, d_4^{25} 0·9369, were collected and kept under nitrogen in sealed tubes at 0° in the dark until required.

Polymerisation was by an emulsion technique.[4,5] A mixture of water (oxygen-free, 2·5 l.), 2N-sulphuric acid (80 c.c.), trimethylcetylammonium bromide (" Cetavlon; " 3 g.), and methyl methacrylate (200 c.c.), was stirred vigorously while nitrogen slowly bubbled through it. Benzoyl peroxide (twice dissolved in chloroform and precipitated by methanol; 2 g.) was then added and the temperature maintained at 65° for 4·2 hr., after which the reaction was stopped with quinol. Pouring the emulsion into an excess of methanol–water gave the crude polymer which was repeatedly washed with methanol–water, then dried for 20 hr. at 60° and for 10 hr. in a vacuum at 50°. This heterogeneous preparation was fractionated twice from a 1·5% solution in benzene by using methanol as precipitant, being thus divided into nine fractions of which the four (samples I—IV) having relatively low molecular weights were taken for the present work. Polymer specimens V—VII were obtained by bulk polymerisation [6] of the monomer (with 1·5% of benzoyl peroxide) in sealed tubes under nitrogen for 75 min. at *ca.* 150°, 100°, and 75°, respectively. Fractionation was as with the emulsion-produced material. Sample VIII was commercial " Perspex " purified similarly.

The benzene used as solvent was from the sodium-dried stock [7] retained for dipole moment and Kerr effect purposes.

Molecular Weights of Polymers I *to* VIII.—These were estimated from measurements of the viscosities of solutions in benzene at 25°. The Ostwald–Fenske type of viscometer used had an efflux time for the solvent of 78·8 sec. The values given below for intrinsic viscosities $[\eta]$ have been obtained by plotting log (η_{sp}/c) against c (the concentration of solute per 100 c.c.

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[1] Le Fèvre, Le Fèvre, and Parkins, *J.*, 1958, 1468; 1960, 1814; Aroney, Le Fèvre, and Parkins, *J.*, 1960, 2890; Le Fèvre and Sundaram, *J.*, 1962, 1494, 4003.

[2] Vogel, " Practical Organic Chemistry," Longmans, London, 2nd edn., 1951.

[3] Scanlan, *Trans. Faraday Soc.*, 1954, **50**, 756.

[4] Chinai, Matlack, Resnick, and Samuels, *J. Polymer Sci.*, 1955, **17**, 391.

[5] Billmeyer and Stockmayer, *J. Polymer Sci.*, 1950, **5**, 121.

[6] Bovey and Tiers, *J. Polymer Sci.*, 1960, **44**, 173.

[7] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953.

TABLE 1.

Dielectric constants, birefringences, etc., observed for solutions of methyl methacrylate and eight polymers of it in benzene.

Solute: Methyl methacrylate.

10^5w_2 ...	1288	3652	6029	8191	10,413	12,400
$-10^4\Delta n$	14	35	54	69	89	107
$-10^4\Delta n^2$	42	105	162	208	268	321
ε^{12}	2·3076	2·3763	2·4457	2·5021	2·5665	2·6234
d^{12}	0·87454	0·87576	0·87704	0·87823	0·87946	0·88059

Whence $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}087_7$; $\Sigma\Delta n^2/\Sigma w_2 = -0{\cdot}264$;
$\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}82_7$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}0544$.

10^5w_2 ...	1288	2413	3652	6029	6914	8191
$10^7\Delta B$ ...	0·059	0·107	0·160	0·260	0·300	0·358

Whence $\Sigma\Delta B/\Sigma w_2 = 4{\cdot}36_7 \times 10^{-7}$.

Solute: Polymer I.

10^5w_2......	1160	1500	2546	3170
ε_{12}	2·2984	2·3071	2·3317	2·3463
d_{12}	0·87652	0·87749	0·88008	0·88163
$10^7\Delta B$ ...	0·0070	0·0094	0·0158	0·0198

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}326$;
$\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2466$;
$\Sigma\Delta B/\Sigma w_2 = 0{\cdot}624_8 \times 10^{-7}$.

10^4c	9690	13,164	22,409	27,946
$10^4\eta_{sp}$ ...	1771	2482	5136	7118

Whence $(\eta_{sp}/c)_{c\rightarrow 0} = 0{\cdot}1522$.

Solute: Polymer II.

10^5w_2 ...	1462	1704	2007	2297
ε_{12}	2·3060	2·3104	2·3182	2·3249
d_{12}	0·87743	0·87800	0·87876	0·87950
$10^7\Delta B$ ...	0·0077	0·0091	0·0110	0·0128

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}269$;
$\Sigma\Delta d/\Sigma w_2 = -0{\cdot}2475$;
$\Sigma\Delta B/\Sigma w_2 = 0{\cdot}543_5 \times 10^{-7}$.

10^4c	12,828	14,961	17,637	20,201
$10^4\eta_{sp}$ ...	3204	3814	4744	5664

Whence $(\eta_{sp}/c)_{c\rightarrow 0} = 0{\cdot}2139$.

Solute: Polymer III.

10^5w_2 ...	1389	1917	2648	3430	4267	4812
ε_{12}	2·3000	2·3104	2·3278	2·3429	2·3618	2·3721
d_{12}	0·87734	0·87863	0·88039	0·88224	0·88428	0·88605

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}058$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2499$.

10^5w_2 ...	3430	4267	4623	4812
$10^7\Delta B$ ...	0·012	0·019	0·024	0·027

Whence $\Sigma\Delta B/\Sigma w_2 = 0{\cdot}478_6 \times 10^{-7}$.

10^4c	12,182	23,309	37,735	42,639
$10^4\eta_{sp}$ ...	4029	8489	15,415	18,349

Whence $(\eta_{sp}/c)_{c\rightarrow 0} = 0{\cdot}2754$.

Solute: Polymer IV.

10^5w_2	1285	1551	3462	4371	4755	5297
ε_{12}	—	2·3050	2·3434	2·3614	2·3696	2·3800
d_{12}	0·87700	0·87763	0·88220	0·88490	0·88569	0·88722
$10^7\Delta B$	—	—	0·012	0·018	0·022	0·026

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}042$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2502$; $\Sigma\Delta B/\Sigma w_2 = 0{\cdot}436 \times 10^{-7}$.

10^4c	13,607	30,542	38,679	46,990
$10^4\eta_{sp}$	5665	16,291	23,735	29,300

Whence $(\eta_{sp}/c)_{c\rightarrow 0} = 0{\cdot}3467$.

Solute: Polymer V.

10^5w_2...	347	564	789	1164	1304	1497	1696
ε_{12}	2·2811	2·2866	2·2908	2·2982	2·3097	—	2·3164
d_{12}	0·87466	0·87516	0·87576	0·87668	0·87702	—	0·87802
$10^7\Delta B$	—	—	—	0·0050	0·0062	0·0080	0·0095

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}552$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2473$;
$\Sigma\Delta B/\Sigma w_2 = 0{\cdot}507 \times 10^{-7}$.

10^4c ...	6912	10,200	11,437	14,892
$10^4\eta_{sp}$...	3444	5368	6227	8448

Whence $(\eta_{sp}/c)_{c\rightarrow 0} = 0{\cdot}4519$.

Solute: Polymer VI.

10^5w_2 ...	1066	1634	1909	2608
ε_{12}	2·2965	2·3091	2·3118	2·3326
d_{12}	0·87640	0·87786	0·87914	0·88019
$10^7\Delta B$ ...	0·0034	0·0049	0·0059	0·0079

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}218$;
$\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2548$,
$\Sigma\Delta B/\Sigma w_2 = 0{\cdot}306 \times 10^{-7}$.

10^4c	9342	14,340	16,780	22,950
$10^4\eta_{sp}$ ...	20,965	40,780	55,007	95,000

Whence $(\eta_{sp}/c)_{c\rightarrow 0} = 1{\cdot}413$.

Solute: Polymer VII.

10^5w_2...	1428	1634	1889	2079	2219
ε_{12}	2·3036	2·3085	2·3152	2·3177	2·3208
d_{12}	0·87745	0·87803	0·87869	0·87910	0·87951
$10^7\Delta B$	0·0040	0·0047	0·0052	0·0056	0·0061

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}198$;
$\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2571$;
$\Sigma\Delta B/\Sigma w_2 = 0{\cdot}276_8 \times 10^{-7}$.

10^4c ...	12,530	16,597	18,277	19,517
$10^4\eta_{sp}$...	42,285	72,942	90,257	113,608

Whence $(\eta_{sp}/c)_{c\rightarrow 0} = 1{\cdot}5210$.

Solute: Polymer VIII.

10^5w_2 ...	392	537	920	1213	1556	1768
ε_{12}	—	2·2832	2·2903	2·2965	2·3031	2·3064
d_{12}	0·87488	0·87527	0·87629	0·87706	0·87812	0·87870
$10^7\Delta B$ ...	—	—	0·0013	0·0018	0·0024	0·0028

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 1{\cdot}969$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2750$;
$\Sigma\Delta B/\Sigma w_2 = 0{\cdot}152_1 \times 10^{-7}$.

10^4c	4699	8064	10,635	13,667
$10^4\eta_{sp}$ ...	56,012	201,732	460,432	1,189,531

Whence $(\eta_{sp}/c)_{c\rightarrow 0} = 4{\cdot}150$.

of solution) and extrapolation to infinite dilution. Relations for the calculation of " viscosity-molecular weights " in benzene are given in the literature by Baxendale *et al.*,[8] by Fattakhov, Tsvetkov, and Kallistov,[9] and by others cited by Fox *et al.*[10] who themselves propose two formulæ, one applicable to M's below and the other to M's above 44,000. In the present work the equation from ref. 8 has been adopted, producing apparent molecular weights as shown in Table 2. (The M's calculated by Baxendale's expression are, with one exception, always smaller than those by the alternatives, M_{Bax} being 0·6—0·7 of M_{Fatt}, or, for polymers III—VIII, 0·83 of M_{Fox}; for polymers I and II M_{Bax} is 1·1 and 0·87 of M_{Fox}, respectively. Such differences, however, while obviously changing the values of *molar* quantities listed in Table 2, do not affect the conclusions finally reached.)

Polarisations, Apparent Moments, Electric Birefringences, etc.—Apparatus and techniques for the measurement of these properties have been described before (refs. 1, 7, and 11). Observations and calculated information therefrom are given in Tables 1 and 2, respectively (for a summary of symbols used here, see Le Fèvre and Sundaram [12]).

TABLE 2.

Calculation of results.

Solute	Monomer	I	II	III	IV	V	VI	VII	VIII
$\alpha\varepsilon_1$ …………	2·827	2·326	2·269	2·058	2·042	2·552	2·218	2·198	1·970
β ……………	0·0623	0·2822	0·2838	0·2860	0·2863	0·2830	0·2916	0·2942	0·3147
γ ……………	−0·059	—	—	—	—	—	—	—	—
$\gamma' n^2$ ………	−0·264	—	—	—	—	—	—	—	—
δ ……………	10·65	1·524	1·326	1·167	1·064	1·237	0·747	0·675	0·371
${}_{\infty}p_2$ (c.c.) …	0·8514	0·6822	0·6710	0·6305	0·6274	0·7244	0·6586	0·6540	0·6041
${}_{\infty}r_2$ (c.c.) …	0·2639	0·2405	0·2401	0·2392	0·2391	0·2402	0·2374	0·2347	0·2296
${}_{\infty}({}_{s}K_2)10^{14}$	78·10	8·717	7·415	6·939	6·212	5·741	3·153	2·660	1·014
$(\eta_{sp}/c)_{c\rightarrow 0}$	—	0·1522	0·2139	0·2754	0·3467	0·4519	1·4130	1·5210	4·1500
M_2 …………	100	23,500	36,800	51,300	69,500	98,600	443,400	490,000	1,838,700
${}_{\infty}({}_{m}K_2)10^{12}$	78·1	2049	2729	3560	4317	5660	13,980	13,034	18,644
${}_{\infty}P_2$ (c.c.) …	85·1	16,030	24,690	32,350	43,610	71,430	292,050	320,460	1,110,810
R_D (c.c.) …	26·4	5650	8840	12,270	16,620	23,690	105,250	115,880	422,200
μ (D *) ……	$1{\cdot}67_5$	22	27	31	36	48	94	99	181

* With ${}_{D}P = 1{\cdot}05 R_D$.

DISCUSSION

Dipole Moment and Conformation of Methyl Methacrylate.—The dipole moment ($1{\cdot}67_5$ D) now found for this molecule in benzene at 25° is smaller than that (1·78 D) obtained by Mikhailov [13] in an unspecified solvent at an unspecified temperature. The slight lowering of moment from methyl isobutyrate (the corresponding saturated ester, which has [14] $\mu = 1{\cdot}80$ D) to methyl methacrylate can be attributed mainly to minor differences in the conformations of the two esters. [Conjugation effects are not clear: that conjugation exists is suggested by the fact that ν(C=O) (1718 cm.$^{-1}$) for methyl methacrylate is [15] some 20 cm.$^{-1}$ below ν(C=O) usual with saturated esters, but instead of μ(C=O) being raised [16] by conjugation the reverse appears to occur.] An *s-cis*-disposition of the C=O and O–Alkyl bonds in aliphatic esters has been shown [17] by many physical methods. Considerations of anisotropic polarisabilities [14] have recently indicated the

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[8] Baxendale, Bywater, and Evans, *J. Polymer Sci.*, 1946, **1**, 237.

[9] Fattakhov, Tsvetkov, and Kallistov, *Zhur. eksp. teor. Fiz.*, 1954, **26**, 351.

[10] Fox, Kinsinger, Mason, and Schuele, *Polymer*, 1962, **3**, 71, 97, 111.

[11] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261. Chap. XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, 3rd edn., Vol. I, p. 2459.

[12] Le Fèvre and Sundaram, *J.*, 1962, 1494.

[13] Mikhailov, *J. Polymer Sci.*, 1958, **30**, 605.

[14] Le Fèvre and Sundaram, *J.*, 1962, 3904.

[15] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, p. 181.

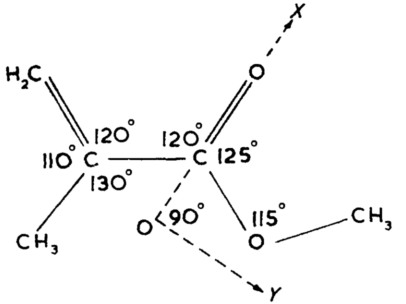
[16] Bentley, Everard, Marsden, and Sutton, *J.*, 1949, 2957; Le Fèvre and Maramba, *J.*, 1952, 235; Le Fèvre, Maramba, and Werner, *J.*, 1953, 2496.

[17] See ref. 12.

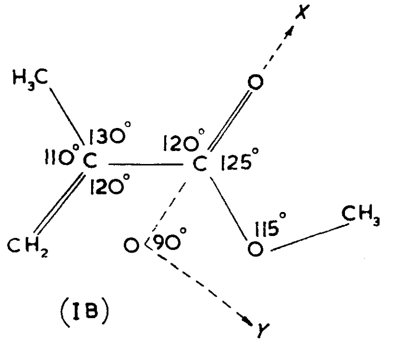
non-planar character of the methoxycarbonyl group, consistently with Ukaji's finding,[18] from electron diffraction, that in methyl methacrylate as a gas the planes containing the C–O–Me and CH_2=CMe·CO·O units are inclined at 25° ± 5°.

The polarity now reported for methyl methacrylate can be reconciled with the observations in refs. 14, 17, and 18. Let the inter-bond angles be as in Ukaji's paper, the moment components due to the C=O link and the C–O–C triangle be 2·7 and 1·28 D, respectively, and μ_{C-H} be regarded as negligibly small. The observed resultant then shows the components as interacting at $\theta = 152{\cdot}5°$, $\mu_{\text{resultant}}$ is located according to the relation $\tan \alpha = 1{\cdot}28 \sin \theta / 2{\cdot}7 + 1{\cdot}28 \cos \theta$, where α (the angle between $\mu_{\text{resultant}}$ and $\mu_{C=O}$) is 20° 42′. These estimates of θ and α are roughly those expected if the C–O–Me triangle is raised out of the flat configuration by a rotation about the C–O bond of *ca.* 30°.

Molar Kerr Constant and Conformation of Methyl Methacrylate.—Principal polarisabilities b_1, b_2, and b_3 are computed (by using the geometrical specifications of ref. 18, together with the longitudinal, transverse, and vertical polarisabilities of the involved bonds [11,14,19]) for four models: (IA and B), both planar but with the C=C and C=O links respectively *cis* and *trans* to each other, and (IC and D), which are non-planar variants of (IA and B) generated by rotating the C–O–Me triangles 30° above the planes of (IA and B). The mutually perpendicular arbitrary axes X, Y, and Z (used to define the locations of b_1, b_2, and b_3, and μ_1, μ_2, and μ_3) are chosen so that C=O is parallel to X, and Y is at 90° to X in the plane containing the CH_2=CMe·CO·O unit. From b_1, b_2, etc., and the directions and magnitudes of the moment components, μ_1, μ_2, and μ_3, the molar Kerr constant expected for each model is calculated (Table 3) and compared with the $_mK$ from experiment.



(IA)



(IB)

TABLE 3.

Principal polarisabilities and molar Kerr constants calculated for models (IA—D).

Conformation type	Principal axes *	Direction cosines with X	Y	Z	Dipole moment components †	$_m10^{12}K$ (calc.)
(IA)	$b_1 = 1{\cdot}180$	0·7547	−0·6561	0	$\mu_1 = 1{\cdot}264$	65·05
	$b_2 = 1{\cdot}059$	0·5651	0·7547	0	$\mu_2 = 1{\cdot}099$	
	$b_3 = 0{\cdot}768$	0	0	1	$\mu_3 = 0$	
(IB)	$b_1 = 1{\cdot}219$	1	0	0	$\mu_1 = 1{\cdot}675$	108·4
	$b_2 = 1{\cdot}020$	0	1	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}768$	0	0	1	$\mu_3 = 0$	
(IC)	$b_1 = 1{\cdot}189$	0·7548	−0·6559	−0·0085	$\mu_1 = 1{\cdot}185$	39·9
	$b_2 = 1{\cdot}041$	0·6549	0·7527	0·0680	$\mu_2 = 0{\cdot}983$	
	$b_3 = 0{\cdot}777$	−0·0382	−0·0569	0·9976	$\mu_3 = -0{\cdot}660$	
(ID)	$b_1 = 1{\cdot}217$	0·9975	−0·0688	0·0178	$\mu_1 = 1{\cdot}549$	77·5
	$b_2 = 1{\cdot}013$	0·0673	0·9951	0·0728	$\mu_2 = 0{\cdot}062$	
	$b_3 = 0{\cdot}777$	−0·0227	−0·0714	0·9972	$\mu_3 = -0{\cdot}635$	

* In 10^{-23} c.c. † In D.

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[18] Ukaji, *Bull. Chem. Soc. Japan*, 1959, **32**, 1275.

[19] Le Fèvre, Liversidge Lecture, *J. Proc. Roy. Soc. N.S.W.*, 1951, **85**, 1.

It is seen that a conformation as in (ID) provides satisfactory agreement with measurement.

Physical Properties and Molecular Weights of Poly(methyl Methacrylates).—As previously noted with other polymers,[1] most of the measured quantities tend to change smoothly with increasing molecular weight. Empirical equations may be fitted to the dielectric constant, density, and electric birefringence factors, to the specific polarisations, refractions, and Kerr constants, and to the apparent moments, whereby these data are expressed in terms of log ($M_{\text{polymer}}/M_{\text{monomer}}$), *i.e.*, of log (degree of polymerisation). Writing this logarithm as L, we have from Table 1:

$$\begin{aligned}
\alpha\varepsilon &= 3{\cdot}67 - 0{\cdot}795L + 0{\cdot}097L^2 \\
\beta d_1 &= 0{\cdot}2260 + 0{\cdot}0086L \\
10^7\delta\beta_1 &= 1{\cdot}868 - 0{\cdot}69L + 0{\cdot}068L^2 \\
{}_\infty p_2 &= 0{\cdot}7760 - 0{\cdot}0402L \\
{}_\infty r_2 &= 0{\cdot}2521 - 0{\cdot}00474L \\
10^{14}{}_\infty({}_sK_2) &= 17{\cdot}1 - 3{\cdot}774L \\
\mu\ (\text{D}) &= 2 - 32{\cdot}2L + 16{\cdot}1L^2
\end{aligned}$$

A comparison of calculated and observed values is given in Table 4. Some of the above equations may therefore be of possible use in the estimation of molecular weights, or degrees of polymerisation, as the measurements involved are no more difficult to make than those necessary in the conventional viscosity method; results, of course, will be on Baxendale's scale but division by $0{\cdot}6_5$ or 0·83 will bring them into near-correspondence with the scales of Fattakhov *et al.* or Fox *et al.*, respectively. As already noted, because Fox *et al.* use a viscosity relation for M's below 44,000 differing from that recommended when M exceeds this magnitude, M_{Bax} for polymer I is 23,500 in contrast with an M_{Fox} of 21,420; with polymer II M_{Bax} is less than M_{Fox}, as it is with polymers III—VIII. Of interest, therefore, is the fact that the equations still apply to polymer I satisfactorily even when M is taken as 21,420:

TABLE 4.

Calculated and observed values of $\alpha\varepsilon$, βd, etc.

Polymer	I	II	III	IV	V	VI	VII	VIII
$\alpha\varepsilon_1$ calc.	2·33	2·27	2·23	2·19	2·16	2·07	2·06	2·04
,, expt.	2·33	2·27	2·06	2·04	2·55	2·22	2·20	1·97
βd_1 calc.	0·2464	0·2481	0·2493	0·2504	0·2518	0·2574	0·2577	0·2627
,, expt.	0·2466	0·2475	0·2499	0·2502	0·2473	0·2548	0·2571	0·2750
$10^7\delta B_1$ calc.	0·614	0·546	0·497	0·456	0·412	0·256	0·249	0·162
,, expt.	0·625	0·544	0·479	0·436	0·507	0·306	0·277	0·152
${}_\infty p_2$ calc.	0·6807	0·6728	0·6671	0·6618	0·6557	0·6294	0·6277	0·6045
,, expt.	0·6822	0·6710	0·6305	0·6274	0·7244	0·6587	0·6540	0·6041
${}_\infty r_2$ calc.	0·2409	0·2399	0·2393	0·2386	0·2379	0·2348	0·2346	0·2319
,, expt.	0·2405	0·2401	0·2392	0·2391	0·2402	0·2374	0·2347	0·2296
$10^{14}{}_\infty({}_sK_2)$ calc....	8·15	7·42	6·87	6·43	5·80	3·34	3·17	1·00
,, expt.	8·72	7·42	6·94	6·21	5·74	3·15	2·66	1·01
μ (D) calc.	16	25	33	40	50	99	102	158
,, expt.	22	27	31	36	48	94	99	181

	$\alpha\varepsilon_1$	βd_1	δB_1	${}_\infty p_2$	${}_\infty r_2$	$10^{14}{}_\infty({}_sK_2)$	μ
Calc.	2·34	0·246	0·629	0·679	0·2410	8·30	14
Expt.	2·33	0·247	0·625	0·682	0·2405	8·72	22

From Table 4 it is seen that the observed dielectric constant and Kerr effect factors, and the specific polarisations, consistently exceed the calculated values for polymers V—VII. As V—VII were prepared by bulk polymerisation and I—IV by emulsion polymerisation, it seemed possible that the series I—VIII might not possess the same structural pattern throughout. Accordingly, infrared spectra (of films obtained by evaporation of solutions in chloroform on to rock-salt plates) were examined. No significant differences between the polymers could be thus detected.

Apparent Dipole Moments of Poly(methyl Methacrylates).—The last two lines of Table 4 illustrate the augmentation of apparent polarity accompanying added molecular weight. The observation is not novel, as the results of de Brouckère *et al.*[20] (who studied six polymer samples in benzene) show an analogous smooth increase of μ_{apparent} with M_{polymer}. When moments are plotted against log M_{polymer} the values in Table 2 produce a somewhat steeper curve than do those from ref. 20 (*e.g.*, for our preparation with $M = 490{,}000$, μ_{apparent} is 99 D; for a polymer with $M = 500{,}000$ de Brouckère *et al.* give $\mu = 83$ D). Such a divergence is explicable in various ways. Since at 25° we take μ_{apparent} as $0{\cdot}2211\,[M(p_2 - r_2)]^{0\cdot5}$, the apparent polarity depends upon the estimate of M which (cf. above and refs. 8 and 9), by viscometry, might differ between two workers; moreover, in ref. 20, Onsager's equation is used to extract μ directly from dielectric constants, refractivities thus being ignored. Further, Imamura reported[21] that when the moments of the polyester prepared in the presence of three different initiators were measured (in benzene at 30°) the " moment per monomeric unit," computed by using M_{monomer} throughout, is not constant, but 1·22, 1·37, and 1·45 D for the three specimens severally; there is thus a possibility that dissimilarities in preparative methods also contribute to the non-accord in question. On the basis of the same " monomeric unit " Kojima[22] had earlier given 1·3 D, and our work shows 1·45, 1·43, 1·36, 1·36, 1·52, 1·41, 1·41, and 1·33 D (mean, 1·41 D), respectively, for polymers I—VIII. Incidentally, we note that the moments just cited are less than that of the monomer ($1{\cdot}67_5$ D); this contradicts a previous statement by Mikhailov and Krasmer[23] and invalidates their deduction of high flexibility for this series of polymers.

Marchal *et al.*[24] have determined the Debye–Bueche[25] quotient ϕ in the equation $\mu^2 = n\phi\mu_0^2$, where μ_0 was taken as that of methyl propionate, although the last-named was not the nearest repeating unit of structure; they report for poly(methyl methacrylate) in benzene $\phi = 0{\cdot}62$. Using for μ_0 the value for methyl isobutyrate[12] (1·80 D) we find ϕ, for the data of Table 2, to lie between the extremes 0·72 and 0·55, with a mean value of 0·61, in satisfactory agreement with ref. 24 and with the results of Salovey[26] (if his $\mu_0 = 1{\cdot}6$ D is replaced by our 1·8 D). Salovey finds ϕ for atactic poly(methyl methacrylate) in benzene to rise from about 0·67 at 20° to nearly 0·82 at 70°. If we follow Debye and Bueche,[25] therefore, since none of these ϕ's reaches the 0·92 expected were internal rotations uninhibited within the free space available, a flexibility less than this must be inferred for the polymer solutes; that the flexibility should increase with temperature is, of course, reasonable.

The construction of (Leybold) scale models, however, reveals such a degree of interlocking that compact coiled configurations are clearly impossible from ordinary steric reasons. We note that several authors[27] have referred to the hindering of rotations by side-groups. Although Eriksson[28] earlier proposed that in ethyl acetate poly(methyl methacrylate) molecules are completely coiled, Schulz[29] considered these coils to have cylindrical shapes. In agreement with this, the molecular friction coefficient calculated

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[20] de Brouckère, Buess, and Van Beck, *J. Polymer Sci.*, 1957, **23**, 233.

[21] Imamura, *Nippon Kagaku Zasshi*, 1961, **82**, 554.

[22] Kojima, *J. Chem. Soc. Japan*, 1941, **62**, 1903.

[23] Mikhailov and Krasmer, *Zhur. tekh. Fiz.*, 1953, **23**, 1931.

[24] Marchal and Benoit, *J. Polymer Sci.*, 1957, **23**, 223; Marchal and Lapp, *ibid.*, 1958, **27**, 571.

[25] Debye and Bueche, *J. Chem. Phys.*, 1951, **19**, 589.

[26] Salovey, *J. Polymer Sci.*, 1961, **50**, S7.

[27] Chinai, Matlack, Resnick, and Samuels, *J. Polymer Sci.*, 1955, **17**, 391; Fox and Loshalk, *J. Appl. Phys.*, 1955, **26**, 1080; Silberberg, Eliassaf, and Katchalsky, *J. Polymer Sci.*, 1957, **23**, 259; Strella and Zand, *ibid.*, 1957, **25**, 97; Broens and Muller, *Kolloid. Z.*, 1950, **119**, 45; Chinai and Samuels, *J. Polymer Sci.*, 1956, **19**, 463; Chinai and Bondurant, *ibid.*, p. 555.

[28] Eriksson, *Acta Chem. Scand.*, 1953, **7**, 623.

[29] Schulz, *Makromol. Chem.*, 1953, **10**, 158.

from observations of the diffusion constant[30] and dynamic double refraction[31] in acetone solution had already suggested that the solute polymer was morphologically between a random coil and a rigid rod. Proton magnetic resonance is said[32] to indicate a regularity of structure, the most obvious form of which is helical.

From X-ray diffraction studies Koumalous[33] stated that the side-groups lie on alternate sides of a chain with limited flexibility, forty repeating units occurring in a helix of diameter 65 Å. Such ideas are quite compatible with the models. Other investigations[34] have shown like groups to be at maximum distances apart, while X-ray measurements[35] of crystalline poly(methyl methacrylate) have been interpreted in terms of a polymer chain coiled in 5-fold helices, associated with two different configurations: a 5 unit 2 turn (5_2) helix, requiring an isotactic chain conformation (because of the odd number of monomeric units per repeat distance), and a 10 unit 4 turn (10_4) helix, which would accommodate syndiotactic chains but would have twice the repeat distance; models and calculations show the 10_4 helix to be stiffer than the 5_2 helix. Salovey[26] has raised the possibility that isotactic poly(methyl methacrylate) may have helical conformations in benzene solutions and quotes Bovey and Tiers[36] for the suggestion that free-radical-induced polymerisation can favour the generation of syndiotactic polymers. These last are unlikely to be isotropically polarisable whatever their conformations. The possible anisotropy of this polymer has already been demonstrated. Specimens which had been stretched or compressed were anisotropic under the conditions for observing magnetic birefringence;[37] according to Tsvetkov *et al.*[38] the dynamic birefringences exhibited in various solvents can be described by an anisotropic micellar model; de Rosset,[39] also from flow-birefringence experiments, had previously recognised the solute particles as ellipsoids with major : minor axial ratios of about 2.

Apparent Anisotropic Polarisabilities of Poly(methyl Methacrylate) Solutes.—In the light of the above, the behaviour of this solute in electric fields becomes relevant. If we make the simplifying assumptions that the dissolved macromolecules possess polarisability ellipsoids of revolution and have their resultant moments acting along one of the major axes, the ${}_{\mathrm{m}}K$'s, R_{D}'s, and μ's of Table 2 lead to results as in Table 5.

TABLE 5.

Apparent semi-axes of polarisability * of polymers I—VIII.

Polymer	$+(b_1 - b_2)$	$b_1 + 2b_2$	b_1	b_2
I	0·04	638·31	212·80	212·76
II	0·03	998·61	332·89	332·86
III	0·03	1386·13	462·06	462·03
IV	0·03	1877·47	625·84	625·81
V	$0{\cdot}02_5$	2676·19	892·08	$892{\cdot}05_5$
VI	0·02	11,889·57	3963·20	3963·18
VII	0·02	13,090·33	4363·46	4363·44
VIII	$0{\cdot}01_5$	47,693·61	15,897·88	$15{,}897{\cdot}86_5$

* Calc. taking $b_1 - b_2$ as positive; negative values of $(b_1 - b_2)$ produce a similar low anisotropy, but with $b_2 > b_1$.

The anisotropies thus displayed are small and appear to diminish as M_2 increases; this diminution is also reflected in the specific Kerr constants, ${}_{\infty}({}_{\mathrm{s}}K_2)$, of Table 2, which drop from $8{\cdot}7 \times 10^{-14}$ to $1{\cdot}0 \times 10^{-14}$ as M_2 changes from 100 to 1,839,000. Since ${}_{\infty}({}_{\mathrm{s}}K_2)$ for

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[30] Meyerhoff and Schulz, *Makromol. Chem.*, 1952, **7**, 294.
[31] Tsvetkov and Petrova, *Zhur. fiz. Khim.*, 1949, **23**, 368.
[32] Odajima, Sohma, and Koike, *J. Chem. Phys.*, 1955, **23**, 1959.
[33] Koumalous, *Proc. Roy. Soc.*, 1944, *A*, **182**, 166.
[34] Arcus, *J.*, 1955, 2801.
[35] Stroupe and Hughes, *J. Amer. Chem. Soc.*, 1958, **80**, 2341.
[36] Bovey and Tiers, *J. Polymer Sci.*, 1960, **44**, 173.
[37] Ploquin, *Inst. recherches sci. et tech. Centre-Ouest*, 1954, **295**, 33.
[38] Tsvetkov, Firsman, and Mukhina, *Zhur. eksp. teor. Fiz.*, 1956, **30**, 649.
[39] de Rosset *J. Chem. Phys.*, 1941, **9**. 766.

$Me_2CH{\cdot}CO_2Me$ is[14] *ca.* 0·18 × 10^{-12} it seems improbable that the repeating monomer units in our polymers are themselves near-isotropic. We, therefore, conclude that either (*a*) the chains are flexible and contain these units in random arrangement or (*b*) the chains when short are stiff but when long enough can adopt curved configurations. Because models strongly counterindicate (*a*), we prefer (*b*) which qualitatively can be harmonised with helices of the type described in refs. 33 and 35.

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