594. *Molecular Polarisability. The Molar Kerr Constants, Apparent Dipole Moments, etc., of Methyl Acrylate and Five of its Polymers.*

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The dipole moment (1·67 D) and molar Kerr constant ($82·4 \times 10^{-12}$) now recorded for methyl acrylate as a solute in benzene are reconcilable with the structure assigned by Ukaji to the gaseous ester if the angle between the planes containing the C·OMe and CH_2:CH·CO·O units is about 30°. Five poly(methyl acrylates) of (viscosity) molecular weights between 2×10^4 and 183×10^4 display apparent dipole moments from 22 to 205 D. Slight signs that poly(methyl acrylates) are more flexible than poly(methyl methacrylates) are shown by the polarity, but not by the Kerr effect measurements, which are uninformative in this respect. Empirical equations, connecting degrees of polymerisation with dielectric constant, density, refractive index, etc., of solutions may be satisfactorily fitted, as previously noted with other polymers.

WE recently noted[1] that Leybold models of poly(methyl methacrylate) segments are relatively stiff, their atoms and groups being so interlocked that internal twisting about any C–C bond is restricted to a few degrees only. Flexibility is markedly improved by replacing each C–CH_3 by C–H. Accordingly it seemed of interest to repeat with a number of polyacrylates the measurements previously made[1] on polymethacrylates in the hope that features suggested by the models could be detected by polarity and polarisability observations of solutions in benzene.

EXPERIMENTAL

Methyl Acrylate.—As obtained from Eastman Organic Chemicals, Rochester, N.Y., this contained quinol; it was washed with 5% aqueous sodium hydroxide, dried ($MgSO_4$), and distilled under nitrogen through a jacketed Dufton column. The fraction with b. p. 80°, d_4^{20} 0·9535, n_D^{20} 1·4040, was collected, sealed with nitrogen, and stored at 0° in the dark until required.

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[1] Le Fèvre and Sundaram, (*a*) *J.*, 1963, 1880; (*b*) *J.*, 1962, 1494, (*c*) *J.*, 1962, 4003.

Polymerisation.—The ester and benzene in 1 : 1 proportion were heated at *ca.* 70° for 5 hr. under nitrogen in a sealed tube containing 0·02% of benzoyl peroxide (purified by twice dissolving it in chloroform and precipitating it with methanol). The polymerisation was stopped by pouring the viscous solution into an excess of methanol; the solid obtained was washed repeatedly with methanol and dried to constant weight *in vacuo* (yield *ca.* 68%).

Polymer Fractionation.—The total dry product, as a 1·5% solution in benzene, was fractionally precipitated by methanol, the temperature being lowered from 35° to 25° after each addition of non-solvent. Division of the original mixture into five portions was thus accomplished; these were separately redissolved, reprecipitated, and dried in a vacuum before molecular weight or other determinations were undertaken.

Molecular Weights.—Viscosities of solutions in benzene at 25° were measured in a viscometer of Ostwald–Fenske type in which the solvent had an efflux time of 78·8 sec. Graphical extrapolation of log (η_{sp}/c) against c (the concentration of polymer in g. per 100 c.c. of solution)

TABLE 1.

Dielectric constants, densities, refractive indexes, Kerr effects, and specific viscosities in benzene at 25°.

Solute: Methyl acrylate

10^5w_2	4100	6462	8777	11,722	13,594	16,056
$-10^4\Delta n$	42	65	83	119	138	161
$-10^4\Delta n^2$	126	195	249	357	414	482
ε_{12}	2·4067	2·4839	2·5600	2·6564	2·7174	2·7990
d_{12}	0·87654	0·87791	0·87894	0·88104	0·88208	0·88364

Whence $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}100$; $\Sigma\Delta n^2/\Sigma w_2 = -0{\cdot}300$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 3{\cdot}27_5$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}0615$.

10^5w_2	2014	3378	5219	7713	8709	9412
$10^{10}\Delta B$	109	182	282	418	471	510

Whence $\Sigma\Delta B/\Sigma w_2 = 5{\cdot}41 \times 10^{-7}$.

Solute: Polymer I

10^5w_2	2781	3324	4069	4743
ε_{12}	2·3463	2·3585	2·3792	2·3973
d_{12}	0·88015	0·88151	0·88312	0·88475
$10^{10}\Delta B$	51	62	77	89
10^4c	24,479	29,307	35,955	41,976
$10^5\eta_{sp}$	4857	6006	7991	10,062

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}623$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2301$; $\Sigma\Delta B/\Sigma w_2 = 1{\cdot}876 \times 10^{-7}$; $(\eta_{sp}/c)_{c\rightarrow 0} = 0{\cdot}1514$.

Solute: Polymer II

10^5w_2	1382	2087	2970	3650	5055
ε_{12}	—	2·3270	2·3489	2·3673	2·4028
d_{12}	0·87681	0·87872	0·88033	0·88236	0·88601
$10^{10}\Delta B$	30	33	41	51	71
10^4c	12,115	18,335	26,143	32,207	44,791
$10^5\eta_{sp}$	31,644	51,865	7,1960	102,343	163,530

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}586$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2326$; $\Sigma\Delta B/\Sigma w_2 = 1{\cdot}496 \times 10^{-7}$; $(\eta_{sp}/c)_{c\rightarrow 0} = 0{\cdot}2291$.

Solute: Polymer III

10^5w_2	2725	3269	4191	4695
ε_{12}	2·3425	2·3567	2·3806	2·3934
d_{12}	0·88024	0·88148	0·88386	0·88501
$10^{10}\Delta B$	37	44	57	64
10^4c	24,006	28,839	37,070	41,549
$10^5\eta_{sp}$	17,573	22,702	32,441	38,084

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}575$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2378$; $\Sigma\Delta B/\Sigma w_2 = 1{\cdot}361 \times 10^{-7}$; $(\eta_{sp}/c)_{c\rightarrow 0} = 0{\cdot}5370$.

Solute: Polymer IV

10^5w_2	1697	3020	3866	5153
ε_{12}	2·3159	2·3493	2·3716	2·4054
d_{12}	0·87785	0·88105	0·88317	0·88627
$10^{10}\Delta B$	22	39	50	66
10^4c	14,898	26,609	34,146	45,669
$10^5\eta_{sp}$	19,833	46,480	69,883	119,628

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}564$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2412$. $\Sigma\Delta B/\Sigma w_2 = 1{\cdot}286 \times 10^{-7}$; $(\eta_{sp}/c)_{c\rightarrow 0} = 0{\cdot}9452$.

Solute: Polymer V

10^5w_2	1625	2078	3495	4035
ε_{12}	2·3144	2·3257	2·3613	2·3742
d_{12}	0·87785	0·87906	0·88250	0·88383
$10^{10}\Delta B$	14	19	32	39
10^4c	14,267	18,258	30,829	35,645
$10^5\eta_{sp}$	103,420	156,696	462,580	729,297

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}543$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2496$; $\Sigma\Delta B/\Sigma w_2 = 0{\cdot}928 \times 10^{-7}$; $(\eta_{sp}/c)_{c\rightarrow 0} = 3{\cdot}802$.

to infinite dilution gave intrinsic viscosities $[\eta]$ from which molecular weights $[M]$ followed from the equation[2] $[\eta] = 1{\cdot}282 \times 10^4 M^{0{\cdot}7143}$. Results are included in Table 2.

Observations.—Dielectric constants ε_{12}, densities d_{12}, etc., for solutions containing weight fractions w_2 of solutes in benzene at 25° are listed in Table 1; polarisations, dipole moments, and molar Kerr constants, deduced from Table 1, follow in Table 2. Definitions of symbols used, descriptions of apparatus, and details of calculation procedures, being given in refs. 1, 3, and 4, are not repeated here. When $w_2 = 0$, $n_D = 1{\cdot}4973$, $\varepsilon = 2{\cdot}2725$, $d = 0{\cdot}87378$, and $B = 0{\cdot}410 \times 10^{-7}$.

TABLE 2.

Polarisations, refractions, molecular weights, dipole moments, and Kerr constants of poly(methyl acrylate) preparations.

Solute	Monomer	I	II	III	IV	V
$\alpha\varepsilon_1$	3·275	2·623	2·586	2·575	2·564	2·543
β	0·0704	0·2633	0·2662	0·2722	0·2761	0·2856
γ	−0·067	—	—	—	—	—
δ	13·20	4·575	3·649	3·319	3·136	2·262
$_\infty p_2$ (c.c.) ...	0·9329	0·7445	0·7366	0·7324	0·7290	0·7218
$_\infty r_2$ (c.c.) ...	0·2542	0·2468	0·2459	0·2438	0·2426	0·2394
$10^{14}\ _\infty({}_sK_2)$ ...	95·8	30·80	23·98	21·66	20·18	13·58
M_2	86·1	20,000	35,720	117,700	259,700	1,823,000
$10^{12}\ _\infty({}_mK_2)$ ...	82·4	6160	8566	25,494	52,407	247,618
$_TP$ (c.c.)	80·23	14,890	26,311	86,203	189,321	1,315,841
R_D (c.c.)	21·86	4936	8784	28,702	63,003	436,426
$_0P$ (c.c.)	57·28	9707	17,088	56,066	123,168	857,594
*μ (D)	$1{\cdot}67_3$	22	29	52	78	205

* $_DP = 1{\cdot}05R_D$.

DISCUSSION

Dipole Moment and Conformation of the Monomer.—The dipole moment now found (1·67 D) for methyl acrylate is slightly lower than the only previous value[5] (1·75 D, in an unspecified solvent at an unstated temperature). In electron-diffraction studies Ukaji[6] suggested a dihedral angle of 25° ± 5° for the out-of-plane disposition of the methoxy-group with respect to the plane of the $CH_2=CH\cdot CO\cdot O$ unit. The moment now obtained is consistent with such a structure if $\mu_{C=O} = 2{\cdot}7$ D, $\mu_{C-O-C} = 1{\cdot}28$ D, and inter-bond angles are taken as in ref. 6. The observed resultant then requires the two components to interact at 153°, with μ_{res} acting at 21° to $\mu_{C=O}$; these angles are roughly those expected if the C–O–Me triangle is raised out of the flat configuration by a rotation of *ca.* 30° about the C–O bond, *i.e.*, by the upper limit of Ukaji's estimate for the ester as a vapour.

Molar Kerr Constant and Conformation of the Monomer.—By using the anisotropic polarisabilities of the bonds involved,[1,3,6,7] the semi-axes of the molecular-polarisability ellipsoids expected for likely models of methyl acrylate are calculated in the usual way,[8] and the molar Kerr constants deduced therefrom compared with that found. For reasons cited when discussing methyl methacrylate,[1a] structures in which the O–Me and C=O group are *s-trans*-related are ignored and only four are considered. (A) and (B) are planar throughout, both having their O–Me and C=O groups *s-cis* to one another, differing in the *s-cis-* and *s-trans*-arrangements of C=C and C=O; (C) and (D) are non-planar variants of (A) and (B), respectively, in which the C–O–Me triangle has been rotated 30° above or

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[2] Sen, Chatterjee, and Palit, *J. Sci. Ind. Res., India*, 1952, **11**, *B*, 90.

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

[4] Le Fèvre, (*a*) " Dipole Moments," Methuen, London, 3rd edn., 1953, chapter 2; (*b*) *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1.

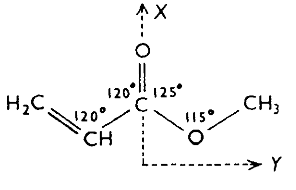
[5] Mikhailov, *J. Polymer Sci.*, 1958, **30**, 305.

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

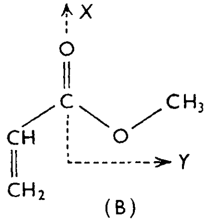
[7] Le Fèvre and (Mrs.) Sundaram, *J.*, 1962, 3904.

[8] Eckert and Le Fèvre, *J.*, 1962, 1081.

below the planes of (A) and (B), as noted in the preceding paragraph. Calculations are summarised in Table 3, reference axes X, Y, and Z (whereby the locations of the molecular principal axes b_1, b_2, and b_3 can be defined) being placed with X and Y, as shown in the CH–(CO)–O plane.



(A)



(B)

The experimental value of $_\infty({}_mK_2)$ is $82{\cdot}4 \times 10^{-12}$; to this, the $_mK$ forecast for conformation (D) is closest. Agreement is improved if the non-planarity of O–Me is made greater than 30° or if the $-CH{=}CH_2$ unit is rotated about the CH–(CO) bond; such adjustments, however, require only 1° or 2°. Alternatively, the solute may be viewed as a mixture containing a little (C) and much (D).

TABLE 3.

Principal polarisabilities, moment components, and molar Kerr constants for conformations (A—D) of methyl acrylate.

Conformation	Principal axes *	Direction cosines with X	Y	Z	Moment component	$10^{12}{}_mK$ (calc.)
A	$b_1 = 0{\cdot}862$	0·8434	0·5373	0	$\mu_1 = 1{\cdot}41_3$	41·42
	$b_2 = 0{\cdot}995$	−0·5373	0·8434	0	$\mu_2 = -0{\cdot}90$	
	$b_3 = 0{\cdot}613$	0	0	1	$\mu_3 = 0$	
B	$b_1 = 1{\cdot}059$	0·9945	0·1045	0	$\mu_1 = 1{\cdot}66_6$	115·7
	$b_2 = 0{\cdot}798$	−0·1045	0·9945	0	$\mu_2 = -0{\cdot}17_5$	
	$b_3 = 0{\cdot}613$	0	0	1	$\mu_3 = 0$	
C	$b_1 = 0{\cdot}846$	0·8134	0·5769	0·0741	$\mu_1 = 1{\cdot}22_7$	$20{\cdot}7_7$
	$b_2 = 1{\cdot}002$	−0·5796	0·8147	0·0201	$\mu_2 = -0{\cdot}91_7$	
	$b_3 = 0{\cdot}622$	−0·0488	−0·0593	0·9970	$\mu_3 = -0{\cdot}676$	
D	$b_1 = 1{\cdot}054$	0·9979	0·0603	0·0233	$\mu_1 = 1{\cdot}54_4$	85·11
	$b_2 = 0{\cdot}794$	−0·0622	0·9941	0·0887	$\mu_2 = -0{\cdot}15$	
	$b_3 = 0{\cdot}622$	−0·0178	−0·0899	0·9958	$\mu_3 = -0{\cdot}626$	

* Polarisabilities expressed here and throughout the paper in 10^{-23} c.c. units.

Physical Properties and Molecular Weights of Poly(methyl Acrylates).—As with poly(methyl methacrylates),[1a] empirical equations may be fitted to most of the measured quantities. Table 4 lists the relation between dielectric constant, density factors, etc., and $L = \log (M_{\text{polymer}}/M_{\text{monomer}})$.

The apparent polarities of poly(methyl acrylates) increase with molecular weight, as do those of poly(methyl methacrylates),[1a] and, over the ranges of L compared here and in ref. 1*a*, the polyacrylates seem to do so more rapidly than the polymethacrylates. Debye–Bueche quotients,[9] $\mu^2_{\text{app}}/x\mu_0^2$ (where x = degree of polymerisation and μ_0 is the moment of the repeating unit, taken in this instance to be 1·76 D, from methyl propionate [7]) emerge as

Polymer	I	II	III	IV	V
$\mu^2_{\text{app}}/x\mu_0^2$	0·67	0·66	0·64	0·65	0·64

These values would, of course,[9] be *ca.* 0·9 were the polymer chains highly flexible. Accordingly, comparison with our earlier data for poly(methyl methacrylates) suggests that the present polymers may in fact be slightly more flexible than the homologues: in the two

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

TABLE 4.

Empirical connections between physical properties and logarithms of the degrees of polymerisation of poly(methyl acrylate) preparations.

Dielectric constant factor	$\alpha\epsilon_1 = 2{\cdot}85 - 0{\cdot}131L + 0{\cdot}014L^2$
Density factor	$\beta d_1 = 0{\cdot}2063 + 0{\cdot}1005L$
Kerr effect factor	$\delta B_1 = 4{\cdot}70 - 1{\cdot}638L + 0{\cdot}18L^2$
Specific polarisation	$_\infty p_2 = 0{\cdot}7598 - 0{\cdot}0088L$
Specific refraction	$_\infty r_2 = 0{\cdot}2558 - 0{\cdot}0038L$
Specific Kerr constant	$_\infty(_sK_2) = 35{\cdot}6 - 4{\cdot}43L$
Dipole moment	$\mu = 5 - 46{\cdot}4L + 21{\cdot}1L^2$

D.P.*	233	415	1369	3020	21,200
$\alpha\epsilon_1$ (calc.)	2·618	2·603	2·577	2·564	2·545
(obs.)	2·623	2·586	2·575	2·564	2·543
βd_1 (calc.)	0·2301	0·2326	0·2378	0·2413	0·2498
(obs.)	0·2301	0·2326	0·2378	0·2413	0·2496
δB_1 (calc.)	1·832	1·646	1·334	1·180	0·983
(obs.)	1·876	1·496	1·361	1·286	0·928
$_\infty P_2$ (calc.)	0·7390	0·7368	0·7322	0·7292	0·7217
(obs.)	0·7445	0·7366	0·7324	0·7290	0·7218
$_\infty r_2$ (calc.)	0·2468	0·2459	0·2439	0·2426	0·2394
(obs.)	0·2468	0·2459	0·2439	0·2426	0·2394
$_\infty(_sK_2)$ (calc.)	25·2	24·0	21·7	20·2	16·4
(obs.)	30·8	24·0	21·7	20·2	13·6
μ (calc.)	23	28	67	99	200
(obs.)	22	29	52	78	205

* D.P. = Degree of polymerisation = $M_{\text{polymer}}/M_{\text{monomer}}$.

series studied the degrees of polymerisation ranged from 233 to 21,200 and from 235 to 18,390, respectively, but the Debye–Bueche quotients range from 0·67 to 0·64 and from 0·64 to 0·55, *i.e.*, they are numerically smaller with the poly(methyl methacrylates).

A similar indication is provided by the equations, $[\eta] = KM^\alpha$, for the intrinsic viscosities of polymer–benzene solutions: when macromolecular chains are more extended than for random kinking, α tends to have larger values;[10] since the α's are 0·714 and 0·77 for acrylates and methacrylates, respectively, the inference could be drawn that the former are more coiled. If the solutes are considered as ellipsoidal the treatments of Kuhn and Kuhn[11] and of Simha[12] show the length : diameter ratios to be proportional to M^α; thus for related M's the hydrodynamic lengths of polyacrylates should be less than those of polymethacrylates. Firm conclusions, however, are impossible because solvent immobilisation, demonstrated in model systems by Eirich,[13] might " affect viscosity in more ways than just by altering the geometry."

Table 5 summarises calculations made by assuming that the dissolved polyacrylates

TABLE 5.

Apparent semi-axes of polarisability * for polyacrylates I—V.

Polymer	$\pm(b_1 - b_2)$	$b_1 + 2b_2$	b_1	b_2
I	0·12	557·58	185·94	185·82
II	0·09	992·30	330·83	330·74
III	0·09	3242·31	1080·83	1080·74
IV	0·08	7117·12	2372·43	2372·35
V	0·04	49,300·68	16,433·59	16,433·55

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

have prolate polarisability ellipsoids of revolution, *i.e.*, that b_1 is greater than $b_2 = b_3$, that μ_{res} acts parallel to the b_1 axis, and that $_EP = 0{\cdot}95R_D$. The differences $(b_1 - b_2)$ are obtained from the measured $_\infty(_mK_2)$'s through a quadratic equation, hence the alter-

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[10] Huggins, *J. Phys. Chem.*, 1938, **42**, 911, 1939, **43**, 439; *J. Appl. Phys.*, 1939, **10**, 700; 1943, **14**, 246.

[11] Kuhn and Kuhn, *Helv. Chim. Acta*, 1943, **26**, 1324.

[12] Simha, *J. Chem. Phys.*, 1940, **44**, 25.

[13] Eirich, *Trans. Faraday Soc.*, 1946, **42***B*, 79.

native signs. Separate values for the principal axes then follow from the totals $(b_1 + 2b_2)$ which are, in turn, derived from ${}_{\mathrm{E}}P$.

The anisotropies thus revealed are low but appear to exceed corresponding estimates for polymethacrylates[1a] having the same range of molecular weights. There is nothing surprising in this for the presence of C–C links in the polymethacrylates in place of C–H links in the polyacrylates could cause the transverse polarisabilities in the former to be larger than in the latter, which therefore might be expected to have the greater anisotropy. If we accept that methyl isobutyrate and methyl propionate are models of the smallest repeating units in the polymethacrylate and polyacrylate, respectively, it is likely that the anisotropies of the polymers would tend to reflect those of these simple esters. Such indeed seems to be the case: from the semi-axes of the isobutyrate and propionate. recorded in ref. 7, the quantities $\delta^2 = [(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2/(b_1 + b_2 + b_3)^2$ appear[14] as 4×10^{-3} and 20×10^{-3}, respectively; from the $\pm(b_1 - b_2)$ data given in Table 5 of ref. 1*a* for polymethacrylate of molecular weight 23,500 and in Table 5 of this paper for polyacrylate of molecular weight 20,000 (two polymers with almost the same degrees of polymerisation) the corresponding δ^2's follow as $0{\cdot}8 \times 10^{-8}$ and $9{\cdot}3 \times 10^{-8}$, *i.e.*, although the anisotropies of the monomeric units are only 1 : 5, those of the polymers are about 1 : 12. This result is contrary to that foreseen from models: the more flexibly jointed the chain of anisotropic segments the more should the anisotropy of the whole chain be less than that of an individual segment. Perhaps the approximations and assumptions underlying the compiling of Table 5, although often valid for small molecules, are misleading in the present cases. We conclude, therefore, that, as used so far, the Kerr effect does not seem promising as a means of solving the difficult problem[15] of estimating chain flexibility reliably by experiment.

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[14] Le Fèvre and Rao, *J.*, 1947, 3644.

[15] Allen and Jones, *Ann. Reports*, 1960, **57**, 102.