361. *Molecular Polarisability. The Specific Kerr Constants and Polarisations of Vinyl Acetate and Various Polyvinyl Acetates dissolved in Carbon Tetrachloride or Benzene.*

By (Mrs.) C. G. Le Fèvre, R. J. W. Le Fèvre, and (Miss) G. M. Parkins.

Dipole moments, molar Kerr constants, and other measurements are reported for vinyl acetate and three polyvinyl acetates in benzene or carbon tetrachloride. It is concluded that the mean conformation of the monomer is non-planar with the long axes of the C=O and C=C bonds lying in mutually perpendicular planes. The polymers behave as near-isotropic solutes, probably as easily deformable macromolecular balls.

A survey of the applicability of polarisation and polarisability measurements to the stereochemistry of macromolecular solutes, begun recently for styrene and certain polystyrenes, is here continued for vinyl acetate and three polyvinyl acetates.

Experimental

Solutes.—Vinyl acetate (from the Polymer Corporation, Sydney) was redistilled (b. p. 73°/760 mm.) immediately before solutions were made up. Specimens of its polymers, presented by Monsanto Chemicals (Australia), Ltd., were used without further purification; only Gelva's 1·5, 2·5, and 7 were sufficiently soluble in carbon tetrachloride or benzene for our purposes. The " viscosity " (weight average) molecular weights (in benzene) of these samples were 10,000, 18,000, and 45,000 respectively.

Apparatus and Methods.—These have been described previously (see refs. 1—5, cited by

---

[1] Le Fèvre, Le Fèvre, and Parkins, *J.*, 1958, 1468.
[2] Le Fèvre and Rao, *J.*, 1957, 3644; 1958, 1465.
[3] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953, Chap. 3.
[4] Sakurada and Lee, *Z. phys. Chem.*, 1939, *B*, **43**, 245.
[5] Debye and Bueche, *J. Chem. Phys.*, 1951, **19**, 589.

Le Fèvre, Le Fèvre, and Parkins;[1] symbols now used and procedures for the calculation of results are explained in the first of these refs.).

Observations.—Tables 1—4 show, for solutions of weight fractions w_2, the differences (ΔB and Δn) between the Kerr constants and refractive indexes of the solutions and their solvents (carbon tetrachloride or benzene), together with dielectric constants (ε) and densities (d). Appropriate values for the pure solvents are given at the feet of the Tables. All measurements relate to 25°. Specific polarisations and specific Kerr constants at infinite dilution, ${}_{\infty}p_2$ and ${}_{\infty}({}_{\mathrm{S}}K_2)$ respectively, computed from data drawn from Tables 1—4, are included in Table 5.

Table 6 deals with the depolarisation factors for light transversely scattered by solutions of vinyl acetate in carbon tetrachloride; here solute concentrations are expressed as molar fractions (cf. Le Fèvre and Rao [2]), and observations were taken at room temperatures.

TABLE 1. *Kerr effects and refractive indexes for solutions in carbon tetrachloride * of vinyl acetate and polyvinyl acetates.*

Vinyl acetate

10^5w_2 ...	722	1545	2159	3168	3260
$10^7\Delta B$ ...	0·003	0·007	0·009	0·012	0·013
10^5w_2 ...	3338	5081	6800		
$10^4\Delta n$ ...	−42	−60	−80		

whence $10^7\Delta B = 0{\cdot}4767w_2 - 2{\cdot}70w_2^2$;
$\sum\Delta n/\sum w_2 = -0{\cdot}119_6$

Gelva V. 1·5

10^5w_2 ...	192	241	405	542
$10^7\Delta B$ ...	$0{\cdot}002_5$	$0{\cdot}002_5$	$0{\cdot}005_5$	$0{\cdot}005_5$
10^5w_2 ...	1009	1020	2041	
$10^4\Delta n$ ...	+2	+3	+3	

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 1{\cdot}16$;
$\sum\Delta n/\sum w_2 = 0{\cdot}019_7$

Gelva V. 1·5

10^5w_2	206	299	377	601	791
$10^7\Delta B$	0·002	0·004	0·005	0·009	0·012
10^5w_2	662	738	945		
$10^4\Delta n$	+2	+3	+4		

whence $10^7\Delta B = 1{\cdot}124w_2 + 52{\cdot}7w_2^2$; $\sum\Delta n/\sum w_2 = 0{\cdot}038_4$

* For $w_2 = 0$, $B_1 = 0{\cdot}070 \times 10^{-7}$, $n_{\mathrm{D}}^{25} = 1{\cdot}4575$.

TABLE 2. *Dielectric constants and densities for solutions in carbon tetrachloride * of vinyl acetate and polyvinyl acetates.*

Vinyl acetate

10^5w_2	413	424	812	845	1066	1496	1502
d_{12}	—	1·5795	—	1·5746	—	1·5671	—
ε_{12}	2·2531	2·2530	2·2766	2·2781	2·2921	2·3159	2·3157
10^5w_2	1624	2246	2402	3069	3443	4063	5360
d_{12}	—	1·5586	1·5565	1·5490	1·5451	1·5381	1·5242
ε_{12}	2·3251	2·3594	2·3719	2·4098	2·4282	—	—

whence graphically $\beta d_1 = -1{\cdot}188$ and $\alpha\varepsilon_1 = 6{\cdot}48$

Gelva V. 1·5

10^5w_2	188	191	217	236	306	361	385
d_{12}	1·5836	—	1·5834	—	—	1·5827	1·5826
ε_{12}	—	2·2393	2·2411	2·2416	2·2464	2·2492	2·2511
10^5w_2	398	423	632	637	641	854	972
d_{12}	1·5825	1·5824	1·5813	1·5813	1·5813	1·5802	1·5794
ε_{12}	—	2·2541	2·2659	2·2670	—	—	—

whence graphically $\beta d_1 = -0{\cdot}494$ and $\alpha\varepsilon_1 = 6{\cdot}38_8$

Gelva V. 2·5

10^5w_2	144	223	427	508	705	779	805	818	973	1153
d_{12}	—	1·5834	1·5824	1·5820	1·5810	1·5806	1·5805	1·5804	1·5796	1·5788
ε_{12}	2·2363	2·2409	2·2541	2·2593	2·2717	2·2765	2·2779	2·2785	2·2888	2·3004

whence graphically $\beta d_1 = -0{\cdot}4908$ and $\alpha\varepsilon_1 = 6{\cdot}341$

Gelva V. 7

10^5w_2	127	195	234	309	328	375	508	541
d_{12}	1·5839	1·5836	1·5833	1·5828	1·5829	1·5827	1·5816	1·5815
ε_{12}	2·2344	2·2391	2·2392	2·2466	—	2·2463	2·2595	2·2602

whence graphically $\beta d_1 = -0{\cdot}455$ and $\alpha\varepsilon_1 = 5{\cdot}65$

* For $w_2 = 0$, $d_1 = 1{\cdot}5845$, $\varepsilon_1 = 2{\cdot}2270$.

TABLE 3. *Kerr effects and refractive indexes for solutions in benzene * of vinyl acetate and polyvinyl acetates.*

Vinyl acetate

10^5w_2 ...	242	2898	3097	4163	6439	8633
$10^7\Delta B$ ...	—	0·010	0·013	0·014	0·028	0·033
$10^4\Delta n$ ...	−3	−33	−35	−47	−73	−77

whence $10^7\Delta B = 0{\cdot}379w_2 + 0{\cdot}185w_2^2$;

$\sum\Delta n/\sum w_2 = -0{\cdot}113$

Gelva V. 2·5

10^5w_2 ...	800	1172	1278	1534	2147	3545
$10^7\Delta B$ ...	—	0·007	0·008	0·012	0·018	—
$10^4\Delta n$ ...	−2	−3	−3	−4	−7	−11

whence $10^7\Delta B = 0{\cdot}422w_2 + 19{\cdot}3w_2^2$;

$\sum\Delta n/\sum w_2 = -0{\cdot}029$

Gelva V. 1·5

10^5w_2 ...	775	1235	1591	1715	2101	2327
$10^7\Delta B$ ...	0·005	0·008	0·013	0·013	0·018	0·022
10^5w_2 ...	1664	1818	1885			
$10^4\Delta n$ ...	−6	−7	−7			

whence $10^7\Delta B = 0{\cdot}415w_2 + 22{\cdot}0w_2^2$;

$\sum\Delta n/\sum w_2 = -0{\cdot}037$

Gelva V. 7

10^5w_2 ...	709	1259	2230	3125	3625	4191
$10^7\Delta B$ ...	0·003	0·008	0·010	0·017	0·020	0·025
10^5w_2 ...	1267	1420	1708	1824	2434	
$10^4\Delta n$ ...	−2	−3	−3	−3	−4	

whence $10^7\Delta B = 0{\cdot}428w_2 + 3{\cdot}7w_2^2$;

$\sum\Delta n/\sum w_2 = -0{\cdot}017_3$

* For $w_2 = 0$, $B_1 = 0{\cdot}410 \times 10^{-7}$, $n_D^{25} = 1{\cdot}4973$.

TABLE 4. *Dielectric constants and densities for solutions in benzene * of vinyl acetate and polyvinyl acetates.*

Vinyl acetate

10^5w_2	940	1160	1210	1400	1522	1687
d_{12}	0·87397	0·87402	0·87404	0·87409	0·87406	0·87410
ε_{12}	2·3075	2·3157	2·3172	2·3242	2·3293	2·3349

whence $\sum\Delta d/\sum w_2 = 0{\cdot}0187$; $\sum\Delta\varepsilon/\sum w_2 = 3{\cdot}710$

Gelva V. 1·5

10^5w_2	975	1235	1660	1883	2237
d_{12}	0·87609	0·87670	0·87768	0·87823	0·87902
ε_{12}	2·3077	2·3166	2·3329	2·3400	2·3525

whence $\sum\Delta d/\sum w_2 = 0{\cdot}2343$; $\sum\Delta\varepsilon/\Delta w_2 = 3{\cdot}594$

Gelva V. 2·5

10^5w_2	636	800	953	1172	1476	1534	2027	2147	3545
d_{12}	0·87531	0·87568	0·87609	0·87656	—	—	0·87857	—	0·88202
ε_{12}	2·2943	2·2999	—	2·3136	2·3222	2·3243	2·3416	2·3444	2·3951

whence $\sum\Delta d/\sum w_2 = 0{\cdot}2346$; $\sum\Delta\varepsilon/\sum w_2 = 3{\cdot}415$

Gelva V. 7

10^5w_2	709	1267	1420	1708	1824	2434
d_{12}	0·87547	0·87675	0·87721	0·87790	0·87815	0·87965
ε_{12}	2·2953	2·3148	2·3204	2·3320	2·3351	2·3569

whence $\sum\Delta d/\sum w_2 = 0{\cdot}2385$; $\Delta\varepsilon = 3{\cdot}246w_2 + 9{\cdot}83w_2^2$

* For $w_2 = 0$, $d_1 = 0{\cdot}87380$, $\varepsilon_1 = 2{\cdot}2725$.

TABLE 5. *Specific polarisations and specific Kerr constants of vinyl and polyvinyl acetates at infinite dilution.*

Solute	$(\alpha\varepsilon_1)_{w_2=0}$	$(\beta)_{w_2=0}$	γ	$(\delta)_{w_2=0}$	$_\infty P_2$ (c.c.)	$_\infty(_sK_2) \times 10^{12}$
			Solvent: Carbon tetrachloride			
Monomer	$6{\cdot}48_0$	$-0{\cdot}749_8$	−0·082	6·81	1·007	$0{\cdot}04_2$
Gelva V. 1·5	$6{\cdot}38_8$	$-0{\cdot}311_8$	+0·026	16·1	$0{\cdot}917_2$	$0{\cdot}10_7$
Gelva V. 2·5	$6{\cdot}34_1$	$-0{\cdot}309_8$	+0·013	16·6	$0{\cdot}911_8$	$0{\cdot}11_1$
Gelva V. 7	$5{\cdot}65_0$	$-0{\cdot}287_2$	—	—	$0{\cdot}834_5$	—
			Solvent: Benzene			
Monomer	$3{\cdot}71_0$	0·0214	−0·075	0·924	1·031	$0{\cdot}01_9$
Gelva V. 1·5	$3{\cdot}59_4$	0·2681	−0·025	1·01	$0{\cdot}925_4$	$0{\cdot}00_7$
Gelva V. 2·5	$3{\cdot}41_5$	0·2685	−0·019	1·03	$0{\cdot}891_7$	$0{\cdot}01_4$
Gelva V. 7	$3{\cdot}24_6$	0·2729	−0·012	1·04	$0{\cdot}858_4$	$0{\cdot}02_0$

DISCUSSION

Apparent Dipole Moments.—These are partly shown in Table 7, in which distortion polarisations have been taken as the R_2's deduced from the refractive indexes and densities given in Tables 1 and 3. For the pure monomer (n_D^{20} 1·3949, d_4^{20} 0·9287) R_D is 22·22 c.c.; with ${}_DP = 1{\cdot}05\ R_D$ the moment of vinyl acetate would appear as 1·76 D in carbon tetrachloride and as $1{\cdot}7_9$ D in benzene. (Usually solvent effects [3] cause μ_{CCl_4} to exceed $\mu_{benzene}$ slightly, but in the present case the conformation of the solute may not be quite the same in both media.) Sakurada and Lee [4] have reported the moment in benzene as 1·75 D.

TABLE 6. *Molecular anisotropy of vinyl acetate at infinite dilution in carbon tetrachloride.*

10^5f_2	3212	5993·5	8255	10,827	13,385
$10^3\Delta\Delta_{12}$	17·01	31·04	42·75	56·89	71·46

whence $\Delta\Delta_{12} = 0{\cdot}5054f_2 + 0{\cdot}20f_2^2$ and, with $D = 0{\cdot}6592$, ${}_\infty\delta_2^2 = 25{\cdot}5 \times 10^{-3}$

TABLE 7. *Polarisations and apparent moments.*

	Monomer	V. 1·5	V. 2·5	V. 7
Mol. wt.	86·1	10,000	18,000	45,000
		In carbon tetrachloride		
Specific refraction * (c.c.)	0·2745	0·234	0·230	—
${}_\infty({}_0P_2)$ (c.c.)	63·1	$6{\cdot}83 \times 10^3$	$12{\cdot}3 \times 10^3$	—
μ(D)	$1{\cdot}7_6$	18·3	24·5	—
		In benzene		
Specific refraction * (c.c.)	0·285	0·231	0·234	0·237
${}_\infty({}_0P_2)$ (c.c.)	64·3	$6{\cdot}9 \times 10^3$	$11{\cdot}8 \times 10^3$	$27{\cdot}9 \times 10^3$
μ(D)	$1{\cdot}7_7$	18·4	24·0	36·9

* Computed from the β and γ values in Table 5.

The Japanese authors also examined two polyvinyl acetates, of mol. wt. 24,200 and 60,000, finding moments of 28·7 and 44·4 D, respectively. That their results and ours are harmonious is shown by the fact that the four apparent moments from Table 7 and those from Sakurada and Lee form a smooth curve when plotted against log M. The total results can be represented by the equation: $\bar{\mu} = 1{\cdot}8 - 9{\cdot}8L + 8{\cdot}5L^2$ where $L = \log(M_{polymer}/M_{monomer})$. A comparison of calculated with observed moments is given in Table 8.

TABLE 8. *Moments of polyvinyl acetates calculated as* $1{\cdot}8 - 9{\cdot}8L + 8{\cdot}5L^2$.

Mol. wt. of polymer	10,000	18,000	24,200 *	45,000	60,000 *
$\bar{\mu}$ (calc.)	17·8	24·8	28·8	38·0	42·6
$\bar{\mu}$ (obs.)	18·3—18·4	24·0—24·5	28·7 *	36·9	44·4 *

* From Sakurada and Lee.[4]

An *a priori* approach to the polarities of these polymers may be made following Debye and Bueche [5] who considered a flexible chain of carbon atoms from alternate members of which a dipole moment μ_0 acts at angles β and γ respectively to the preceding and succeeding C–C bonds. Rotations around valency directions were assumed to be "free" save for restrictions imposed by interatomic distances and angles. With $\beta = 70°$ and $\gamma = 110°$, $\bar{\mu}^2 = 0{\cdot}92\,n\mu_0^2$, where n is the number of dipoles on the chain. In the present cases the repeating units may each be likened to ethyl acetate and μ_0 accordingly taken [6] as 1·8 D; predicted moments for the polymers listed in Table 8 are then obtained as 18·6, 25·0, 28·9, 39·5, and 45·6 D. Comparisons with the $\bar{\mu}$'s observed are satisfactory and suggest

---

[6] Wesson, "Tables of Electric Dipole Moments," Technology Press, Massachusetts Inst. Technology, 1948.

that flexibility of the polyvinyl acetates exceeds that of the polystyrenes[1] or the poly-*p*-chlorostyrenes,[5] for both of which series the quantity $\bar{\mu}^2/n\mu_0^2$ has been shown by experiment to be *ca.* 0·56, or for the polyvinyl chlorides,[7] for which the factor is *ca.* 0·75.

Anistropy of the Polyvinyl Acetates.—From the ${}_\infty({}_sK_2)$'s in Table 5 a small increase in anisotropy with molecular weight may be inferred; however, calculations indicate this effect to be extremely slight in terms of molecular semi-axes. Assuming that $b_1 > b_2 = b_3$, the differences, $10^{23}(b_1 - b_2)$, would only need to be *ca.* 0·002, 0·004, and 0·006 for Gelva's 1·5, 2·5, and 7 respectively to yield specific Kerr constants of the order found. Since total polarisabilities appear from the observed refractions to be 275, 501, and 1268 $\times 10^{-23}$ c.c., it is clear that these polyvinyl acetates behave in benzene or carbon tetrachloride as near-isotropic solutes.

Present results can be understood if the dissolved species adopt roughly globular forms having easy deformabilities. For a macromolecular ball, isotropy is to be expected; as *M* is increased, solvent impacts and solute–solvent forces should become more effective and make the mean conformation less isotropic; the imposition of external distorting influences should be detectable. The first two of these predictions are in accord with the data of Table 5, the third with observations by Hartmann and Jaenicke[8] (who found the dielectric constants of polyvinyl acetate solutions under streaming conditions to rise from the values at rest, and in a way which was strongly dependent on the flow gradient).

Conformation of Vinyl Acetate Monomer.—The molar Kerr constant of vinyl acetate is small ($3{\cdot}6_1 \times 10^{-12}$ in carbon tetrachloride; slightly less in benzene; cf. Table 5). The larger value, together with ${}_\infty\delta_2^2 = 0{\cdot}0255$ (Table 6), ${}_EP = 20{\cdot}78$ c.c. [calc. by totalling semi-axes of constituent bonds (cf. Table 9), this ${}_EP$ is $0{\cdot}935R_D$, which is reasonable], and $\mu_{\text{resultant}} = 1{\cdot}76$ D (Table 7) yields:

$$10^{23}b_1 = 0{\cdot}823,\ 10^{23}b_2 = 0{\cdot}985,\ 10^{23}b_3 = 0{\cdot}663$$

(provided that $\mu_{\text{resultant}}$ acts along the b_1 direction). The problem is now to reconcile such data with others computed *a priori* from the longitudinal, transverse, and " vertical " polarisabilities of the various bonds occurring in vinyl acetate. These are listed, together with certain geometrical details, in Table 9.

TABLE 9. *Anisotropic polarisabilities of bonds,* and intervalency angles used in calculations.*

	C–H	C–O	C=O	C–C	C=C
$10^{23}b_L$	0·064	0·081	0·230	0·099	0·280
$10^{23}b_T$	,,	0·039	0·140	0·027	0·073
$10^{23}b_V$	,,	0·039	0·046	0·027	0·077
Source	Ref. 9	Ref. 10	Ref. 11	Ref. 10	Ref. 12

* The suffixes L, T, and V are explained on p. 300 of ref. 9.

Angle Me–C=O taken † as 116°, cf. Me·CO_2Me	Angle O=C–O taken † as 124°, cf. Me·CO_2Me
,, C–O–C ,, 113° ,,	,, O–C=C ,, 121·5 ,, $(CH_2{:}CH)_2O$

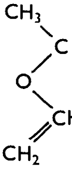
† Details for methyl acetate and divinyl ether, from ref. 13.

Inspection of models shows, of course, that a large number of conformations are possible between certain extremes, six of which are indicated by (I) to (IV) and Figs. *A* and *B*.

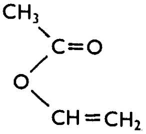
---

[7] Fuoss, *J. Amer. Chem. Soc.*, 1941, **63**, 2410.
[8] Hartmann and Jaenicke, *Z. phys. Chem.*, 1956, **6**, 220.
[9] Le Fèvre and Le Fèvre, *Revs. Pure Appl. Chem.*, 1955, **5**, 261.
[10] Le Fèvre and Le Fèvre, *J.*, 1956, 3549.
[11] Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 2340.
[12] Bramley, Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 1183.
[13] Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.

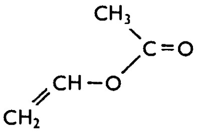
None of the planar forms gives predictions of molecular semi-axes of ${}_mK$'s which correspond to those from experiment (see Table 10). The molar Kerr constants calculated for them are all too large.



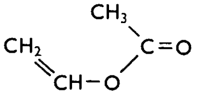
(I)



(II)



(III)



(IV)

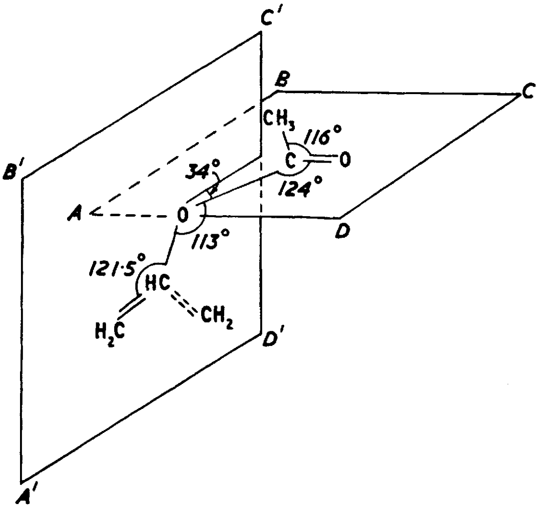


FIG. *A has* C=C *bond as full lines,* FIG. *B as broken lines; in both Figs. planes ABCD and A'B'C'D' are orthogonal, the* C=O *axis is normal to A'B'C'D' which contains the* $O{\cdot}CH{:}CH_2$ *triangles, and b_1 is taken parallel to $b_L{}^{C=O}$.*

To produce a b_1 of the order of that found the longitudinal polarisabilities of C=O and C=C need to be more at 90° to one another than they are in types (I)—(IV). Non-planar forms are therefore indicated, and of those tried the form *A* offers most promise. This is generated from (I) by twisting the CH_2=CH–O triangle about the acetyl–oxygen bond, and the CH_2=CH group about the vinyl–oxygen bond, until the CH_2=CH–O unit lies in a plane perpendicular to that containing the O•CO•Me fragment, and normal to the C=O long axis. Conformations *A* or *B* differ in that the olefinic linkage is disposed either *trans* or *cis* to a line at 34° to the Ac–O bond (see diagram); in both the vinyl–oxygen bond is at *ca.* 28° to the direction of $b_V{}^{C=O}$.

TABLE 10. *Semi-axes and molar Kerr constants expected for models* (I) *to* (IV) *and A and B.*

Structure	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10_m{}^{12}K$ (calc.)	Structure	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10^{12}{}_mK$ (calc.)
I	0·870	0·987	0·612	29·9	IV	$0{\cdot}890_5$	0·967	0·612	41·8
II	1·038	0·819	0·612	118	A	0·823	1·004	0·642	4·9
III	$0{\cdot}947_6$	0·926	0·612	68·1	B	0·823	0·851	0·795	0·1

Table 10 shows that *A* or *B* leads to a calc. b_1 identical with that from experiment, but consideration of the b_2's and b_3's strongly favours form *A*, which we accordingly propose as the effective conformation of vinyl acetate under our conditions.

The authors thank the Polymer Corporation Pty. Ltd. and Monsanto Chemicals (Australia) Ltd.

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA. [*Received, July 13th,* 1959.]