284. *Molecular Polarisability. Molar Kerr Constants and Dipole Moments of Vinyl Chloride and Six Polyvinyl Chlorides as Solutes in Dioxan.*

By R. J. W. Le Fèvre and K. M. S. Sundaram.

"Geon 101," by fractional extraction, gave six polyvinyl chlorides with viscosity molecular weights (in cyclohexanone) ranging from $3{\cdot}4 \times 10^4$ to $12{\cdot}6 \times 10^4$. The dielectric constants, densities, refractive indexes, Kerr effects, etc., of solutions in dioxan of these preparations can be related empirically to the logarithms of their degrees of polymerisation. Dipole-moment measurements indicate greater hindrance to internal rotations than was postulated in Debye and Bueche's general treatment. Anisotropies of polarisability, inferred from electric birefringences, are low; they allow the rejection of certain (unlikely) solute conformations among the infinitude possible. It is noted that an 8-link helix resembling Mumford's β-helix can provide a specifiable "equivalent structure" capable of satisfying observations of both the dipole moment and the Kerr effect.

The investigation of vinyl polymers through properties involving dipole moments and electric birefringence, begun recently [1] with polystyrenes and polyvinyl acetates, is here

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[1] Le Fèvre, Le Fèvre, and Parkins, *J.*, 1958, 1468; 1960, 1814.

continued with polyvinyl chlorides. Previous work relevant to ours appears non-existent except for one determination[2] of the polarity of vinyl chloride as a gas, and dielectric-constant and -loss studies by Fuoss and Kirkwood[3] on the solid (plasticised) systems polyvinyl chloride–biphenyl, polyvinyl chloride–tetrahydronaphthalene, etc. Ref. 3, which records estimates of the polarity of the $-CH_2{\cdot}CHCl-$ unit, is not included in Wesson's list.[4]

EXPERIMENTAL

Solutes.—Vinyl chloride was prepared[5] by dropping 1,2-dichloroethane into a warm 10% solution of potassium hydroxide in 1 : 1 water–ethanol and passing the gaseous monomer successively[6] over solid potassium hydroxide, anhydrous calcium chloride, and silica gel, and finally, for condensation, into a trap immersed in ethanol–solid carbon dioxide.

The polymers were obtained by " fractional extraction " according, in principle, to the methods of Desreux[7] and Cleland.[8] A commercial sample of polyvinyl chloride (PVC) resin (Geon 101) was extracted several times at 25° with acetone, dioxan, toluene, 1 : 3 carbon disulphide–acetone, and at 50° with dioxan and ethyl methyl ketone in a step-wise manner. The resulting viscous solutions were each filtered and poured into an excess of methanol with constant stirring. The solids thus separated were further purified by re-extraction with warm dioxan and reprecipitation by methanol; after filtration, washing with methanol, and air-drying, they were kept *in vacuo* until their weights were constant.

" Viscosity molecular weights " M were estimated in cyclohexanone at 25°, by using the equation $[\eta] = KM^a$ with $K = 1{\cdot}1 \times 10^{-5}$ and $a = 1$ as determined by Ciampa and Schwindt.[9] The values given in Table 1 for intrinsic viscosities have been obtained by plotting log (η_{sp}/C) against C (the concentration of polymer in g. per 100 c.c. of solution) and extrapolating the curve to infinite dilution. The six polymer samples, designated I—VI, showed molecular weights as follow:

Polymer	" Viscosity mol. wt."	Extractant	Polymer	" Viscosity mol. wt."	Extractant
I	33,650	Acetone at 25°	IV	60,340	CS_2–acetone (1 : 3) at 25°
II	43,020	Dioxan at 25°	V	99,100	Dioxan at 50°
III	53,230	Toluene at 25°	VI	126,400	Et Me ketone at 50°

Apparatus and Procedures.—Dielectric constants (ε), densities (d), refractive indexes (n), and Kerr constants (B) of solutions in dioxan containing weight fractions w of vinyl chloride or of polymers I—VI have been determined at 25° and with sodium light by methods described before.[10] In what follows, the suffixes 1, 2, or 12 are used to indicate, respectively, a property of the solvent, solute, or solution; the prefix Δ denotes a difference between solution and solvent, *e.g.*, $\Delta\varepsilon = \varepsilon_{12} - \varepsilon_1$, $\Delta d = d_{12} - d_1$, $\Delta n = n_{12} - n_1$, and $\Delta B = B_{12} - B_1$. The symbols α, β, γ, and δ are from the equations, $\varepsilon_{12} = \varepsilon_1(1 + \alpha w_2)$, $d_{12} = d_1(1 + \beta w_2)$, $n_{12} = n_1(1 + \gamma w_2)$, and $B_{12} = B_1(1 + \delta w_2)$, which are assumed to apply at low w_2's and to be usable whenever Δ(property) appears rectilinear with w_2; γ' refers to the square of the refractive index, $n_{12}^2 = n_1^2(1 + \gamma' w_2)$. Molar Kerr constants, total polarisations, etc., extrapolated to infinite dilution

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[2] Hugill, Coop, and Sutton, *Trans. Faraday Soc.*, 1938, **34**, 1518.

[3] Fuoss, *J. Amer. Chem. Soc.*, 1941, **63**, 2401, 2410; Fuoss and Kirkwood, *ibid.*, pp. 369, 378, 385.

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

[5] Schildknecht, " Vinyl and Related Polymers," J. Wiley and Sons, Inc., New York, 1952, p. 388.

[6] Furukawa, *J. Polymer Sci.*, 1959, **40**, 237.

[7] Desreux, *Rec. Trav. chim.*, 1949, **68**, 789.

[8] Cleland, *J. Polymer Sci.*, 1958, **27**, 349.

[9] Ciampa and Schwindt, *Makromol. Chem.*, 1956, **21**, 169.

[10] (*a*) Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953, chapter 2; Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405; (*b*) Le Fèvre and Le Fèvre, *J.*, 1953, 4041; 1954, 1577; (*c*) Le Fèvre and Le Fèvre, *Rev. Pure and Appl. Chem.*, 1955, **5**, 261; (*d*) Le Fèvre and Le Fèvre, chapter XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, London, 3rd edn., Vol. I, p. 2459.

TABLE 1.

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

Vinyl chloride in dioxan

10^5w_2	8428	10,477	11,978	13,078	16,286	19,122
ε_{12}	2·5020	2·5745	2·6390	2·6570	2·7713	2·8817
d_{12}	1·02118	1·01978	1·01871	1·01755	1·01512	1·01242
$-10^4\Delta n$	27	33	38	40	52	60

whence $\sum\Delta\varepsilon/\sum w_2 = 3{\cdot}492$, $\sum\Delta d/\sum w_2 = -0{\cdot}0797$, and $\sum\Delta n/\sum w_2 = -0{\cdot}031_5$.

10^5w_2	1943	3497	5384	7926	10,477	11,978
$10^7\Delta B$	$0{\cdot}073_7$	$0{\cdot}133_6$	$0{\cdot}205_2$	$0{\cdot}285_7$	$0{\cdot}390_7$	$0{\cdot}467_8$

whence $\sum\Delta B/\sum w_2 = 3{\cdot}77_8 \times 10^{-7}$.

Polymer I in dioxan

10^5w_2	2062	2614	3221	3873	4111	4477
ε_{12}	2·3142	2·3433	2·3829	2·4213	2·4375	2·4606
d_{12}	1·03337	1·03545	1·03665	1·03818	1·03905	1·04074
$10^7\Delta B$	0·0078	$0{\cdot}010_0$	$0{\cdot}012_1$	$0{\cdot}015_1$	$0{\cdot}016_1$	$0{\cdot}016_9$

whence $\sum\Delta\varepsilon/\sum w_2 = 5{\cdot}432$, $\sum\Delta d/\sum w_2 = 0{\cdot}272_3$, and $\sum\Delta B/\sum w_2 = 0{\cdot}382_6 \times 10^{-7}$.

10^5w_2	2437	3105	3442	3684
$10^4\Delta n$	25	35	38	41
$10^4\Delta n^2$	71	100	108	117

whence $\sum\Delta n/\sum w_2 = 0{\cdot}109_7$ and $\sum\Delta n^2/\sum w_2 = 0{\cdot}312_6$.

Polymer I in cyclohexanone

10^4C	3240	4356	4682	7760	10,010
d_{12}	0·94315	0·94350	0·94360	0·94442	0·94512
$10^5\eta_{sp}$	12,584	17,132	18,600	31,860	42,673

whence $[\eta_{sp}/C]_{C\rightarrow 0} = 0{\cdot}3702$.

Polymer II in dioxan

10^5w_2	501	862	1348	1788	2096	2503
ε_{12}	2·2361	2·2556	2·2821	2·3062	2·3238	2·3491
d_{12}	1·02935	1·03032	1·03165	1·03291	1·03377	1·03493
$10^7\Delta B$	$0{\cdot}005_8$	$0{\cdot}009_4$	$0{\cdot}013_8$	$0{\cdot}020_1$	$0{\cdot}021_3$	$0{\cdot}024_9$

whence $\sum\Delta\varepsilon/\sum w_2 = 5{\cdot}484$, $\sum\Delta d/\sum w_2 = 0{\cdot}274_0$, and $\sum\Delta B/\sum w_2 = 1{\cdot}047 \times 10^{-7}$.

10^5w_2	2001	2346	2728	3105
$10^4\Delta n$	22	26	31	35
$10^4\Delta n^2$	62	74	88	99

whence $\sum\Delta n/\sum w_2 = 0{\cdot}112_0$ and $\sum\Delta n^2/\sum w_2 = 0{\cdot}317_3$.

Polymer II in cyclohexanone

10^4C	2899	3590	4605	6211	8210
d_{12}	0·94322	0·94325	0·94356	0·94415	0·94480
$10^5\eta_{sp}$	14,200	17,761	23,242	31,822	43,060

whence $[\eta_{sp}/C]_{C\rightarrow 0} = 0{\cdot}4732$.

Polymer III in dioxan

10^5w_2	1248	1657	2063	2451	2805	3211
ε_{12}	2·2780	2·3008	2·3233	2·3449	2·3647	2·3874
d_{12}	1·03141	1·03248	1·03364	1·03482	1·03580	1·03671
$10^7\Delta B$	$0{\cdot}016_2$	$0{\cdot}022_1$	$0{\cdot}029_1$	$0{\cdot}034_0$	$0{\cdot}039_0$	$0{\cdot}046_6$

whence $\sum\Delta\varepsilon/\sum w_2 = 5{\cdot}547$, $\sum\Delta d/\sum w_2 = 0{\cdot}274_4$, and $\sum\Delta B/\sum w_2 = 1{\cdot}39_2 \times 10^{-7}$.

10^5w_2	1365	1823	2246	2939
$10^4\Delta n$	16	21	27	34
$10^4\Delta n^2$	46	60	77	97

whence $\sum\Delta n/\sum w_2 = 0{\cdot}117_1$ and $\sum\Delta n^2/\sum w_2 = 0{\cdot}334_5$.

TABLE 1. (*Continued*).

Polymer III in cyclohexanone

10^4C	8823	11,618	16,344	21,426	23,187
d_{12}	0·94460	0·94577	0·94726	0·94875	0·94986
$10^4\eta_{sp}$	6099	8504	13,005	17,714	21,918

whence $[\eta_{sp}/C]_{C\to 0} = 0{\cdot}5855$.

Polymer IV in dioxan

10^5w_2	1105	1519	1907	2361	2762	3105
ε_{12}	2·2703	2·2936	2·3158	2·3413	2·3644	2·3847
d_{12}	1·03108	1·03226	1·03333	1·03464	1·03582	1·03669

whence $\sum\Delta\varepsilon/\sum w_2 = 5{\cdot}612$ and $\sum\Delta d/\sum w_2 = 0{\cdot}280_7$.

10^5w_2	551	962	1548	2088	2496	2803
$10^7\Delta B$	$0{\cdot}009_5$	$0{\cdot}015_6$	$0{\cdot}026_2$	$0{\cdot}036_5$	$0{\cdot}044_2$	$0{\cdot}050_1$

whence $\sum\Delta B/\sum w_2 = 1{\cdot}74_3 \times 10^{-7}$.

10^5w_2	1864	2344	2581	2732
$10^4\Delta n$	23	29	32	35
$10^4\Delta n^2$	66	83	91	100

whence $\sum\Delta n/\sum w_2 = 0{\cdot}125_0$ and $\sum\Delta n^2/\sum w_2 = 0{\cdot}357_1$.

Polymer IV in cyclohexanone

10^4C	6980	11,891	16,113	20,173	25,382
d_{12}	0·94440	0·94610	0·94757	0·94907	0·95082
$10^4\eta_{sp}$	5279	9875	14,509	19,896	27,346

whence $[\eta_{sp}/C]_{C\to 0} = 0{\cdot}6637$.

Polymer V in dioxan

10^5w_2	1013	1498	1857	2012	2314	2587
ε_{12}	2·2664	2·2943	2·3077	2·3201	2·3346	2·3603
d_{12}	1·03078	1·03224	1·03331	1·03372	1·03446	1·03544
$10^7\Delta B$	$0{\cdot}030_7$	$0{\cdot}041_7$	$0{\cdot}052_4$	$0{\cdot}062_8$	$0{\cdot}067_6$	$0{\cdot}081_2$

whence $\sum\Delta\varepsilon/\sum w_2 = 5{\cdot}580$, $\sum\Delta d/\sum w_2 = 0{\cdot}283_2$, and $\sum\Delta B/\sum w_2 = 2{\cdot}98_2 \times 10^{-7}$.

10^5w_2	1248	1832	2134	2334
$10^4\Delta n$	17	24	28	32
$10^4\Delta n^2$	49	69	80	91

whence $\sum\Delta n/\sum w_2 = 0{\cdot}133_8$ and $\sum\Delta n^2/\sum w_2 = 0{\cdot}382_9$.

Polymer V in cyclohexanone

10^4C	5513	8511	12,070	15,695	19,473
d_{12}	0·94638	0·94759	0·94881	0·95014	0·95112
$10^4\eta_{sp}$	6944	11,449	17,774	25,553	35,075

whence $[\eta_{sp}/C]_{C\to 0} = 1{\cdot}0900$.

Polymer VI in dioxan

10^5w_2	1602	2045	2472	2902	3506	3969
ε_{12}	2·3001	2·3315	2·3524	2·3832	2·4201	2·4515
d_{12}	1·03274	1·03393	1·03537	1·03689	1·03834	1·03938

whence $\sum\Delta\varepsilon/\sum w_2 = 5{\cdot}970$ and $\sum\Delta d/\sum w_2 = 0{\cdot}294_9$.

10^5w_2	341	500	751	1105	1519
$10^7\Delta B$	$0{\cdot}012_8$	$0{\cdot}017_6$	$0{\cdot}025_6$	$0{\cdot}039_0$	$0{\cdot}052_2$

whence $\sum\Delta B/\sum w_2 = 3{\cdot}49_2 \times 10^{-7}$.

10^5w_2	1145	1364	1624	1954
$10^4\Delta n$	16	20	23	28
$10^4\Delta n^2$	46	57	66	80

whence $\sum\Delta n/\sum w_2 = 0{\cdot}142_9$ and $\sum\Delta n^2/\sum w_2 = 0{\cdot}409_1$.

Polymer VI in cyclohexanone

10^4C	2819	5090	9222	11,638	14,103
d_{12}	0·94290	0·94371	0·94515	0·94605	0·94690
$10^4\eta_{sp}$	4173	8075	15,505	20,963	26,839

whence $[\eta_{sp}/C]_{C\to 0} = 1{\cdot}3910$.

are written $_\infty({}_mK_2)$, $_\infty P_2$, etc. Calculations are through specific quantities, *e.g.*, $_SK_2$, p_2, r_2, which when $w_2 = 0$ are given by:

$$_\infty({}_SK_2) = {}_SK_1(1 - \beta + \gamma + \delta - Hr - J\alpha\varepsilon_1), \qquad (1)$$

where

$$_SK_1 = 6\lambda n_1B_1/(n_1^2 + 2)^2(\varepsilon_1 + 2)^2d_1,$$

$$H = 4n_1^2/(n_1^2 + 2),$$

and

$$J = 2/(\varepsilon_1 + 2);$$

$$_\infty p_2 = p_1(1 - \beta) + 3\alpha\varepsilon_1/d_1(\varepsilon_1 + 2)^2, \qquad (2)$$

where

$$p_1 = (\varepsilon_1 - 1)/d_1(\varepsilon_1 + 2);$$

$$_\infty r_2 = r_1(1 - \beta) + 3\gamma' n_1^2/d_1(n_1^2 + 2)^2, \qquad (3)$$

where

$$r_1 = (n_1^2 - 1)/d_1(n_1^2 + 2)$$

Derivations of these equations may be found in refs. 10(*c*) or (*d*) for (1), and in 10(*a*) for (2) and (3).

Solvents.—Dioxan, the only common non-polar medium in which polyvinyl chloride is sufficiently soluble, purified as described by Vogel,[11] has been used as far as possible. Since no equations connecting the viscosities of solutions in dioxan with the molecular weights of the solutes could be found in the literature, determinations of M_2 have been made in cyclohexanone,[9] a bulk supply of which, dehydrated by distillation, had d_4^{25} 0·94190, and an efflux time at 25° in the Ostwald viscometer used of 239·3 sec.; details for the individual solutions may be computed from Table 1.

Observations.—These are set out in Table 1. When $w_2 = 0$, the various properties of dioxan at 25° are: $n_1 = 1{\cdot}4202$, $\varepsilon_1 = 2{\cdot}2090$, $d_1 = 1{\cdot}02800$, and $B_1 = 0{\cdot}068 \times 10^{-7}$.

TABLE 2.

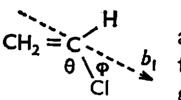
Calculation of results.

Solute	Monomer	I	II	III	IV	V	VI
$\alpha\varepsilon_1$	3·492	5·432	5·484	5·547	5·612	5·580	5·970
β	$-0{\cdot}077_5$	$0{\cdot}264_9$	$0{\cdot}266_6$	$0{\cdot}266_9$	$0{\cdot}273_1$	$0{\cdot}275_5$	$0{\cdot}286_9$
γ	$-0{\cdot}022_2$	$0{\cdot}077_3$	$0{\cdot}078_9$	$0{\cdot}082_4$	$0{\cdot}088_0$	$0{\cdot}094_2$	$0{\cdot}100_6$
$\gamma'n_1^2$	$-0{\cdot}098_6$	$0{\cdot}312_6$	$0{\cdot}317_3$	$0{\cdot}334_5$	$0{\cdot}357_1$	$0{\cdot}382_9$	$0{\cdot}409_1$
δ	55·56	$5{\cdot}62_7$	$15{\cdot}40_0$	$20{\cdot}47_1$	$25{\cdot}63_2$	$43{\cdot}85_3$	$51{\cdot}34_6$
$_\infty p_2$ (c.c.)	0·8957	1·1001	1·1084	1·1185	1·1276	1·1216	1·1827
$_\infty r_2$ (c.c.)	$0{\cdot}249_1$	$0{\cdot}237_6$	$0{\cdot}238_0$	$0{\cdot}241_0$	$0{\cdot}243_6$	$0{\cdot}247_7$	$0{\cdot}249_6$
$_\infty({}_sK_2)10^{14}$ ...	63·91	4·26	15·63	21·48	27·43	48·61	57·08
$[\eta_{sp}/C]_{C\rightarrow 0}$ ...	—	0·3702	0·4732	0·5855	0·6637	1·0900	1·3910
M_2	62·48	33,650	43,020	53,230	60,340	99,100	126,400
$_\infty({}_mK_2)10^{12}$ ...	39·93	1433	6722	11,434	16,549	48,170	72,147
$_\infty P_2$ (c.c.)	$55{\cdot}9_6$	37,018	47,682	59,538	68,040	111,152	149,493
R_D (c.c.)	15·57	7994	10,239	12,831	14,699	24,544	31,549
μ * (D)	$1{\cdot}3_9$	37·4	42·5	47·4	50·7	64·6	75·4

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

DISCUSSION

Polarity and Anisotropy of Vinyl Chloride.—The dipole moment ($1{\cdot}3_9$ D) now found for vinyl chloride dissolved in dioxan compares satisfactorily with that (1·44 D) reported by Hugill, Coop, and Sutton[2] for the gas between 14° and 140°, the " solvent effect " (shown[12] by $\mu^2_{\text{soln}}/\mu^2_{\text{gas}} = 0{\cdot}93_2$) being of the expected order; evidently therefore the medium does not combine with, or otherwise markedly affect, this mesomeric[2,13] solute.



The lowering of moment from ethyl chloride to vinyl chloride has been attributed[2,13] to the contribution of the polar structure $^-CH_2{\cdot}CH^+Cl$ to the real state of the molecule; thus the observed moment may be regarded as the resultant of $\mu_{C\rightarrow Cl} = ca.$ 2 D and a component of unknown magnitude acting along the Cl—CH$_2$ line; such a resultant should be located by clockwise rotation from the C–Cl axis in the adjoining formula.

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[11] Vogel, " Practical Organic Chemistry," Longmans, London, 3rd edn., 1956.

[12] Buckingham and Le Fèvre, *J.*, 1952, 1932.

[13] Smyth, " Dielectric Behaviour and Structure," McGraw-Hill, New York, 1955, p. 276.

That μ for vinyl chloride deviates from the C–Cl direction is indicated by the following calculations. According to ref. 14 the C=C–Cl angle θ is 122° ± 2°. The longitudinal, transverse, and " vertical " polarisabilities * of the three bonds involved are:

Bond	C–H	C=C	C–Cl
b_L	0·064	0·280	0·399
b_T	0·064	0·073	0·185
b_V	0·064	0·077	0·185
Ref.	10*c*	15	15

(The set for C–Cl, having been found[15] suitable with vinylidene chloride, appear appropriate here.) Computations carried out as described on p. 2486 of ref. 10(*d*) show $b_{\max}$ (*i.e.*, b_1 by definition[10c]) not to be collinear with any one bond axis, but at ϕ° anticlockwise to C–Cl in the C=C–Cl plane. Results for the cases when θ = 120°, 122°, or 124° are:

θ°	b_1	b_2	b_3	ϕ°
120	0·767	0·556	0·454	29·0
122	0·772	0·549	0·454	28·2
124	0·778	0·543	0·454	27·35

The corresponding molar Kerr constants depend upon the angle which $\mu_{\text{resultant}}$ makes with b_1; if $\mu_{\text{resultant}}$ is at ψ° clockwise from the C–Cl bond, the following ${}_mK$'s are forecast:

θ°	120	120	122	122	124	124
ψ	0°	3° 48′	0°	5° 22′	0°	7° 2′
$10^{12}{}_mK$ (calc.)	43·9	39·9	45·8	39·9	48·0	39·9

Thus *a priori* calculations yield the observed ${}_mK$ of $39{\cdot}9_3 \times 10^{-12}$ provided the direction of action of $\mu_{\text{resultant}}$ is situated, relatively to C–Cl, in the sense predicted.

Physical Properties and Molecular Weights of Polyvinyl Chlorides.—As previously with polystyrenes[1] and polyethylene glycols,[16] a tendency can be seen for most of the measured quantities to change smoothly with increasing molecular weight. Empirical equations may be fitted to the dielectric constant, density, refractive index, 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:

$$\alpha\varepsilon_1 = 4{\cdot}651 - 0{\cdot}094L + 0{\cdot}140L^2;\ \beta d_1 = 0{\cdot}2510 - 0{\cdot}0174L + 0{\cdot}0090L^2;$$
$$\gamma n_1 = 0{\cdot}0575 - 0{\cdot}0141L + 0{\cdot}0120L^2;\ \delta B_1 = 5{\cdot}315L - 14{\cdot}10;$$
$${}_\infty p_2 = 1{\cdot}03 - 0{\cdot}051L + 0{\cdot}028L^2;\ {}_\infty r_2 = 0{\cdot}2170 - 0{\cdot}0056L + 0{\cdot}0047L^2;$$
$${}_\infty({}_{\mathrm{S}}K_2) = 91{\cdot}67L - 245{\cdot}76;\ \mu = -48{\cdot}5 + 1{\cdot}242L + 10{\cdot}78L^2.$$

A comparison of calculated and observed values is given in Table 3. In reverse, these equations make estimates of " Cyclohexanone-viscosity molecular weights " accessible from observations on solutions in dioxan; *e.g.*, from the simply measured factor γn_1 = 0·143 for polymer VI, the calculated M is $130{\cdot}8 \times 10^3$ (cf. $126{\cdot}4 \times 10^3$ from viscosity determinations).

Apparent Dipole Moments of Polyvinyl Chlorides.—As the last two lines of Table 3 show, the apparent polarities increase over the range of molecular complexity of polymers I—VI. For *complete* flexibility the moments would be $\mu_0 x^{0{\cdot}5}$, where x is the degree of polymerisation and μ_0 is the component appropriate for the smallest repeating unit, in this case $-\mathrm{CH_2{\cdot}CHCl}-$, the polarity of which should resemble that of ethyl chloride, *i.e.*,

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* Polarisabilities b_i (i = L, T, or V, for bonds, or 1, 2, or 3 for molecules) are given throughout this paper in 10^{-23} c.c. units.

[14] Sutton *et al.*, " Interatomic Distances," *Chem. Soc. Spec. Publ.*, No. 11, 1958, M 126.

[15] Bramley, Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 1183.

[16] (*a*) Aroney, Le Fèvre, and Parkins, *J.*, 1960, 2890; (*b*) Le Fèvre, Parkins, and Roper, *Austral. J. Chem.*, 1960, **13**, 169.

$1{\cdot}9_8$ D (measured in carbon tetrachloride solution,[17] cf. refs. 4 and 18); $\mu_0 x^{0\cdot5}$ values for preparations I—VI accordingly appear as 45·9, 52·0, 57·8, 61·5, 78·9, and 89·0 D, respectively, and thus are higher than those from experiment. Debye and Bueche [19] have given an *a priori* treatment of a polymer chain in which rotations around valency directions are " free " except for restrictions imposed by interatomic distances and angles, and from every second carbon atom of which a dipole moment μ_0 acts at angles β and γ to the preceding and succeeding C–C bonds; by this, in the present instance, with $\beta = 70°$ and $\gamma = 110°$, $\mu^2_{\text{apparent}}/x\mu_0^2$ should be 0·92, but in fact it lies between 0·66 and 0·72:

TABLE 3.

Calculated * and observed values of $\alpha\varepsilon_1$, βd_1, etc.

Polymer	I	II	III	IV	V	VI
$\alpha\varepsilon_1$ calc.	5·44	5·51	5·58	5·61	5·78	5·87
expt.	5·43	5·48	5·55	5·61	5·58	5·97
βd_1 calc.	0·270	0·274	0·277	0·279	$0{\cdot}287_5$	0·292
expt.	0·272	0·274	0·274	0·281	0·283	0·295
γn_1 calc.	0·108	0·114	0·117	0·122	0·135	0·142
expt.	0·110	0·112	0·117	0·125	0·134	0·143
δB_1 calc.	0·410	0·995	1·47	1·74	2·91	3·49
expt.	0·383	1·05	1·40	1·74	2·98	3·49
$_\infty p_2$ calc.	1·10	1·11	1·12	1·13	1·15	1·17
expt.	1·10	1·11	1·12	1·13	1·12	1·18
$_\infty r_2$ calc.	0·237	0·239	0·241	0·242	0·247	0·250
expt.	0·238	0·238	0·241	0·244	0·248	0·250
$_\infty({}_{\mathrm{S}}K_2)$ calc.	4·50	14·6	22·8	27·4	47·6	57·7
expt.	4·26	15·6	21·5	27·4	48·6	57·1
μ calc.	35·2	42·0	47·6	50·9	65·9	73·8
expt.	37·4	42·5	47·4	50·7	64·6	75·4

* The heading to Table 4 of ref. 16*a* incorrectly contains log *L* instead of *L*.

Polymer	I	II	III	IV	V	VI
$\mu^2_{\text{apparent}}/x\mu_0^2$	0·662	0·669	0·674	0·679	0·671	0·717

Internal rotations are therefore more limited than supposed. Thus polarity evidence indicates little more than that the average (or effective) configuration of this macromolecule is one in which the C–Cl dipoles are sufficiently opposed to bring $\mu^2_{\text{apparent}}/x\mu_0^2$ down from 0·92 to the 0·6—0·7 observed. Debye and Bueche suggest (actually for poly-4-chlorostyrene, but the argument is applicable also to polyvinyl chloride) a non-planar four-carbon-link unit as the simplest—though not the only—repeating chain-segment capable of satisfying the experimental facts.

It seems reasonable to expect the conformations of polyvinyl chloride as a solute to be flexed versions of those occurring in the solid state. The material in bulk is substantially amorphous until drawn into fibres; these then show diffuse *X*-ray diffractions reconcilable with chlorine atoms alternating from side to side of a zig-zag carbon backbone. In general literature (*e.g.*, refs. 19 and 20), this zig-zag is often said to be flat, but Natta and Corradini [21] envisage deviations from planarity produced by rotations of each chain-bond a few degrees from the strictly *trans*-position relatively to the next but one preceding bond. Repulsions between C–H links [22] (which are sufficient to stabilise the " chair " form of cyclohexane) could cause such rotations and thus confer on portions of the linear polymer a regularity of structure, the most obvious form of which is helical.[23] Natta and

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[17] Le Fèvre, unpublished work.

[18] Nickerson and McIntosh, *Canad. J. Chem.*, 1957, **35**, 1325.

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

[20] Roff, " Fibres, Plastics, and Rubbers," Butterworth's Scientific Publns., London, 1956, p. 173; Bawn, " The Chemistry of High Polymers," Butterworth's Scientific Publns., London, 1948, p. 192.

[21] Natta and Corradini, *J. Polymer Sci.*, 1956, **20**, 251.

[22] McCoubrey and Ubbelohde, *Quart. Rev.*, 1951, **5**, 364; Barton and Cookson, *ibid.*, 1956, **10**, 44.

[23] Bernal, *Discuss. Faraday Soc.*, 1958, **25**, 7; Bunn and Holmes, *ibid.*, p. 95.

Corradini recognised polyvinyl chloride as syndiotactic; Bunn and Howells [24] considered any repeated alternation as confined to short sequences. In solution, chains of such segments would tend to fold and coil [23] about themselves, and also to associate mutually, owing to intra- and inter-molecular energy-diminishing interactions (such as van der Waals forces). In fact, Doty, Wagner, and Singer,[25] from light-scattering measurements, reported that polyvinyl chloride in dioxan formed clusters in varying degrees and that these clusters were less anisotropic than the individual molecules composing them, while Arlman, Boog, and Coumou [26] found the streaming birefringence of solutions in cyclohexanone to decrease with increasing concentration.

Apparent Anisotropic Polarisabilities of Polyvinyl Chlorides.—In the light of the above, the simplifying assumption is made that the dissolved polyvinyl chlorides possess polarisability ellipsoids of revolution, *i.e.*, $b_1 \neq b_2 = b_3$. If $\mu_{\text{resultant}}$ acts parallel to a major axis then, from the data of Table 2, semi-axes of polarisability can be deduced (cf. ref. 10*d*, p. 2491) as in Table 4. The differences $(b_1 - b_2)$ are obtained from the measured $_\infty({}_mK_2)$'s *via* quadratic equations; hence arise the alternative signs. Separate values of b_1 and $b_2 = b_3$ then follow from the totals $b_1 + 2b_2$, which for polymers I—VI correspond to 0·93—0·89 of the R_D's observed.

TABLE 4.

Apparent semi-axes of polarisability.*

Polymer	$\pm(b_1 - b_2)$	$b_1 + 2b_2$	b_1	b_2	Polymer	$\pm(b_1 - b_2)$	$b_1 + 2b_2$	b_1	b_2
I	0·01	886·68	295·57	295·56	IV	0·06	1582·89	527·67	527·61
II	0·03	1129·70	376·59	376·56	V	$0{\cdot}10_5$	2607·50	$869{\cdot}23_5$	869·13
III	0·05	1398·98	466·36	466·31	VI	0·11	3323·40	1107·87	1107·76

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

The anisotropy thus revealed is low, consistently with other evidence: polyvinyl chloride in cyclohexanone causes less birefringence under flow [26] than does polystyrene; the birefringence of stretched fibres of polyvinyl chloride is *ca.* 0 (cf. —0·03 for polystyrene [20]); polystyrene itself, by methods involving the Kerr effect, shows only a small anisotropy in carbon tetrachloride.[1]

By considering Table 4 in relation to bond polarisabilities a few negative deductions may be made. For example, the solute molecules cannot have flat, all-*trans*, zig-zag carbon backbones carrying the chlorines alternately above and below the $[C-C]_n$ plane, because for such conformations the calculated moments and molar Kerr constants should range from 613 to 2300 D and from -359×10^{-7} to $-18{,}880 \times 10^{-7}$ for polymers I—VI; nor is the situation improved by twisting the C–Cl links so that the angles between them become 176—178°, which reconciles the observed and the predicted moments but leaves the ${}_mK$'s (calc.) still large and algebraically incorrect in sign (-61×10^{-7} to -920×10^{-7}). In general, it is evident that the results of Tables 2 and 4 *could* arise were the various segments composing the macromolecules to be so arranged that the b_1, b_2, and b_3 of one lie respectively nearly parallel to the b_2, b_3, and b_1 of another, and to the b_3, b_1, and b_2 of a third; within an almost random polymer coil many such relative orientations should occur and cause the solute particle *in toto* to exhibit a low anisotropy.

Since segment sequences arrayed helically would, depending on the pitch chosen, conform qualitatively to the description just given, Barton models for polyvinyl chloride have been constructed with $[C-C]_n$ chains resembling Mumford's β-forms of n-alkanes.[27] The eight-link helix thus generated carries its C–Cl bonds nearly perpendicular to the helical axis. Measurement by hand of necessary angles gives for one repeating unit (containing four monomer molecules) expected polarisabilities of $b_1 = 2{\cdot}17$ (along the

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[24] Bunn and Howells, *J. Polymer Sci.*, 1955, **18**, 307.

[25] Doty, Wagner, and Singer, *J. Phys. Colloid Chem.*, 1947, **51**, 32.

[26] Arlman, Boog, and Coumou, *J. Polymer Sci.*, 1953, **10**, 543.

[27] Mumford, *J.*, 1952, 4897.

helical axis) and a mean b at right angles of 2·20. These magnitudes are roughly that (2·19) obtained by dividing b_1 or b_2 (in Table 4) by the number of repeating units (*viz.*, for polymers I—VI, 135, 172, 213, 241, 397, and 506, respectively). Moreover, by assuming that every monomer unit carries a moment of 1·98 D, and that these moments are disposed (as appears possible on the model) uniformly at 88—89° around a helical axis, correct predictions of the observed μ's can be made. These facts are mentioned to illustrate that in the case of polyvinyl chloride in dioxan it is impossible to distinguish experimentally between conformations as different as almost random coils on one hand and helices on the other.

The authors gratefully acknowledge the award of an H.B. and F.M. Gritton Research Scholarship to K. M. S., and help from Mrs. A. Sundaram with many of the calculations.

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA. [*Received, September* 11*th*, 1961.]