786. *Molecular Polarisability: Molar Kerr Constants and Dipole Moments of Vinyl Bromide and Six Polyvinyl Bromides as Solutes in Dioxan.*

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

Apparent dipole moments and molar Kerr constants are reported for vinyl bromide and six polyvinyl bromides (molecular weights between 10,000 and 38,000) as solutes in dioxan. Values for the monomer are $1{\cdot}3_8$ D and $58{\cdot}4 \times 10^{-12}$; for the polymers μ's and $_\infty({}_mK_2)$'s range from 14·1 to 33·5 D. and 228×10^{-12} to 3489×10^{-12}, respectively. As solutes, these macromolecules display small anisotropies of polarisability consistent with conformations as near-random coils or as helices. No notable differences between polyvinyl chlorides or bromides are found. Empirical relations are given for the polyvinyl bromide series whereby certain easily observable physical quantities may be connected with degrees of polymerisation.

THE work here reported parallels that recently [1] described on vinyl chloride and a number of polyvinyl chlorides. Its purpose was to find whether the greater effective radius of bromine than of chlorine [2] affects the relative flexibilities of polyvinyl bromides and chlorides in ways detectable by polarity and polarisability measurements.

Experimental

Vinyl Bromide.—This was prepared [3] by dropping 1,2-dibromoethane into an excess of a warm 20% solution of potassium hydroxide in 95% ethanol. The vapours were led consecutively through water, potassium hydroxide pellets, and anhydrous calcium chloride, then collected in a trap cooled in solid carbon dioxide–acetone. The liquid monomer was kept in the dark over anhydrous magnesium sulphate in sealed tubes at about 0°. Shortly before use it was distilled directly from the drying agent (b. p. 15·8°).

[1] Le Fèvre and Sundaram, *J.*, 1962, 1494.
[2] Stuart, *Z. phys. Chem.*, 1935, *B*, **27**, 350.
[3] Kharasch, McNab, and Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 2521.

TABLE 1.

Dielectric constants, birefringences, etc., observed for solutions of vinyl bromide and six polymers.

Vinyl bromide in dioxan

$10^5 w_2$	1158	2648	4203	5811	8003	9391
$10^4 \Delta n$	1	3	5	7	9	11
ε_{12}	2·2338	2·2654	2·3038	2·3425	2·3770	2·4057
d_{12}	1·03187	1·03674	1·04223	1·04788	1·05526	1·05929
$10^7 \Delta B$	$0{\cdot}037_0$	$0{\cdot}087_1$	$0{\cdot}136_8$	$0{\cdot}187_2$	$0{\cdot}258_2$	$0{\cdot}298_9$

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}011_5$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}160$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}3373$; $\Sigma\Delta B/\Sigma w_2 = 3{\cdot}22_0 \times 10^{-7}$

Polyvinyl bromide I in dioxan

$10^5 w_2$	1771	1929	2341	2693	2944	3205
$10^4 \Delta n$	15	18	20	22	24	27
$10^4 \Delta n^2$	42	51	57	62	68	77
ε_{12}	2·2527	2·2579	2·2649	2·2811	2·2846	2·2878
d_{12}	1·03708	1·03777	1·03993	1·04150	1·04324	1·04444

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}084_6$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}239_9$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}519$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}5104$

$10^5 w_2$	2693	2944	3205	3861	4123	4462
$10^7 \Delta B$	$0{\cdot}004_4$	$0{\cdot}005_5$	$0{\cdot}006_0$	$0{\cdot}006_7$	$0{\cdot}007_4$	$0{\cdot}007_9$

whence $\Sigma\Delta B/\Sigma w_2 = 0{\cdot}175_8 \times 10^{-7}$

Polyvinyl bromide I in cyclohexanone

$10^4 c$	7611	10,801	14,002	16,400	18,821
d_{12}	0·94753	0·94891	0·94999	0·95091	0·95187
$10^4 \eta_{sp}$	415	591	772	910	1046

whence $[\eta_{sp}/c]_{c\rightarrow 0} = 0{\cdot}0540$

Polyvinyl bromide II in dioxan

$10^5 w_2$	1244	1489	1751	1984	2344	2684
$10^4 \Delta n$	11	12	15	17	20	22
$10^4 \Delta n^2$	32	34	43	49	57	63
ε_{12}	2·2434	2·2490	2·2564	2·2612	2·2708	2·2797
d_{12}	1·03434	1·03564	1·03691	1·03838	1·04011	1·04178

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}084_4$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}241_8$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}667$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}5146$

$10^5 w_2$	1366	1741	2091	2322	2641	2902
$10^7 \Delta B$	$0{\cdot}002_9$	$0{\cdot}004_5$	$0{\cdot}004_8$	$0{\cdot}005_7$	$0{\cdot}006_8$	$0{\cdot}007_3$

whence $\Sigma\Delta B/\Sigma w_2 = 0{\cdot}245_0 \times 10^{-7}$

Polyvinyl bromide II in cyclohexanone

$10^4 c$	6212	9703	13,192	15,824	18,233
d_{12}	0·94660	0·94688	0·94756	0·94982	0·95078
$10^4 \eta_{sp}$	383	601	821	988	1143

whence $[\eta_{sp}/c]_{c\rightarrow 0} = 0{\cdot}0617$

Polyvinyl bromide III in dioxan

$10^5 w_2$	1346	1624	1928	2212	2416	2815
$10^4 \Delta n$	11	14	16	18	20	23
$10^4 \Delta n^2$	31	40	46	51	55	66
ε_{12}	2·2496	2·2571	2·2644	2·2785	2·2831	2·2905
d_{12}	1·03477	1·03632	1·03783	1·03927	1·04040	1·04246
$10^7 \Delta B$	$0{\cdot}005_4$	$0{\cdot}006_7$	$0{\cdot}007_9$	$0{\cdot}009_0$	$0{\cdot}009_7$	$0{\cdot}011_6$

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}082_6$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}234_2$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}992$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}5110$; $\Sigma\Delta B/\Sigma w_2 = 0{\cdot}407_6 \times 10^{-7}$

Polyvinyl bromide III in cyclohexanone

$10^4 c$	6989	11,043	13,004	16,400	18,410
d_{12}	0·94664	0·94727	0·94987	0·95126	0·95321
$10^4 \eta_{sp}$	537	857	1012	1280	1443

whence $[\eta_{sp}/c]_{c\rightarrow 0} = 0{\cdot}0761$

TABLE 1. (*Continued.*)

Polyvinyl bromide IV in dioxan

$10^5 w_2$	1548	2133	2683	3449	3921	4275
$10^4 \Delta n$	13	18	22	30	32	33
$10^4 \Delta n^2$	37	51	63	86	91	94
ε_{12}	2·2553	2·2744	2·2888	2·3215	2·3340	2·3462
d_{12}	1·03631	1·03881	1·04307	1·04593	1·04855	1·05144

whence $\sum\Delta n/\sum w_2 = 0{\cdot}082_2$; $\sum\Delta n^2/\sum w_2 = 0{\cdot}234_3$; $\sum\Delta\varepsilon/\sum w_2 = 3{\cdot}144$; $\sum\Delta d/\sum w_2 = 0{\cdot}5337$

$10^5 w_2$	1952	2382	2788	3245	3803	4314	4892
$10^7 \Delta B$	$0{\cdot}008_6$	$0{\cdot}010_1$	$0{\cdot}012_8$	$0{\cdot}014_3$	$0{\cdot}016_7$	$0{\cdot}019_5$	$0{\cdot}021_8$

whence $\sum\Delta B/\sum w_2 = 0{\cdot}444_1 \times 10^{-7}$

Polyvinyl bromide IV in cyclohexanone

$10^4 c$	8005	11,541	14,512	19,473	25,308
d_{12}	0·94964	0·95168	0·95318	0·95554	0·95831
$10^4 \eta_{sp}$	673	978	1237	1688	2209

whence $[\eta_{sp}/c]_{c\to 0} = 0{\cdot}0825$

Polyvinyl bromide V in dioxan

$10^5 w_2$	1467	1782	1926	2234	2532	3064	3344
$10^4 \Delta n$	12	14	15	18	21	25	28
$10^4 \Delta n^2$	34	39	42	51	59	71	79
ε_{12}	2·2598	2·2716	2·2761	2·2854	2·2970	2·3165	2·3220
d_{12}	1·03582	1·03769	1·03807	1·04006	1·04185	1·04414	1·04644

whence $\sum\Delta n/\sum w_2 = 0{\cdot}081_3$; $\sum\Delta n^2/\sum w_2 = 0{\cdot}229_4$; $\sum\Delta\varepsilon/\sum w_2 = 3{\cdot}458$; $\sum\Delta d/\sum w_2 = 0{\cdot}5387$

$10^5 w_2$	1728	1994	2334	2648	2905	3304
$10^7 \Delta B$	$0{\cdot}009_2$	$0{\cdot}010_9$	$0{\cdot}012_5$	$0{\cdot}014_0$	$0{\cdot}015_5$	$0{\cdot}017_2$

whence $\sum\Delta B/\sum w_2 = 0{\cdot}531_7 \times 10^{-7}$

Polyvinyl bromide V in cyclohexanone

$10^4 c$	6200	9001	12,806	15,399	17,741
d_{12}	0·94786	0·95147	0·95392	0·95527	0·95674
$10^4 \eta_{sp}$	591	865	1250	1516	1762

whence $[\eta_{sp}/c]_{c\to 0} = 0{\cdot}0927$

Polyvinyl bromide VI in dioxan

$10^5 w_2$	2033	2645	3126	3508	3751	4104	4672
$10^4 \Delta n$	16	20	23	27	29	31	36
$10^4 \Delta n^2$	45	57	65	77	82	88	102
ε_{12}	2·2856	2·3109	2·3309	2·3457	2·3540	2·3682	2·4008
d_{12}	1·03879	1·04167	1·04460	1·04675	1·04828	1·04984	1·05281

whence $\sum\Delta n/\sum w_2 = 0{\cdot}076_3$; $\sum\Delta n^2/\sum w_2 = 0{\cdot}216_4$; $\sum\Delta\varepsilon/\sum w_2 = 3{\cdot}914$; $\sum\Delta d/\sum w_2 = 0{\cdot}5316$

$10^5 w_2$	987	1099	1186	1354	1725	1916	2105
$10^7 \Delta B$	$0{\cdot}006_3$	$0{\cdot}006_9$	$0{\cdot}007_7$	$0{\cdot}008_7$	$0{\cdot}010_9$	$0{\cdot}012_4$	$0{\cdot}013_7$

whence $\sum\Delta B/\sum w_2 = 0{\cdot}642_1 \times 10^{-7}$

Polyvinyl bromide VI in cyclohexanone

$10^4 c$	4003	6605	8001	10,211	12,011
d_{12}	0·94911	0·95172	0·95432	0·95653	0·95701
$10^4 \eta_{sp}$	535	923	1177	1549	1909

whence $[\eta_{sp}/c]_{c\to 0} = 0{\cdot}1212$

Polymerisation.—The pure monomer (64 ml.) was collected under nitrogen in an ampoule containing 0·10 g. of benzoyl peroxide. The ampoule was then sealed and irradiated at room temperature for 12 hr. by a 300-w Hanovia-Slough mercury lamp, from a distance of 10 cm. The liquid monomer was transformed gradually into a cream-coloured powder, which was purified [4] by extraction with warm dioxan and reprecipitation by an excess of methanol. The separated white polymer (32 g.) was washed several times with methanol and dried *in vacuo*.

[4] Blauer, Shenblat, and Katchalsky, *J. Polymer Sci.*, 1959, **38**, 189.

Fractionation.—The total polymer was dissolved in dioxan (2 l.) at 25°. This 1·6% solution was diluted by methanol until the appearance of cloudiness which, on stirring and cooling, became a precipitate removable by filtration. The procedure was recommenced on the filtrate,

TABLE 4.

Empirical connections between physical properties and logarithms of the degrees of polymerisation of polyvinyl bromide preparations.

			$\alpha\varepsilon_1 = 1{\cdot}22 - 0{\cdot}910L + 0{\cdot}758L^2$			
$\alpha\varepsilon_1$ (obs.)	2·519	2·667	2·992	3·144	3·458	3·914
$\alpha\varepsilon_1$ (calc.)	2·432	2·675	3·060	3·242	3·485	3·900
			$\beta d_1 = 0{\cdot}3850 + 0{\cdot}063L$			
βd_1 (obs.)	0·5104	0·5146	0·5110	0·5337	0·5387	0·5316
βd_1 (calc.)	0·5110	0·5177	0·5281	0·5321	0·5379	0·5453
			$\gamma n_1 = 0{\cdot}0900 + 0{\cdot}0080L - 0{\cdot}0051L^2$			
γn_1 (obs.)	0·085	0·084	0·083	0·082	0·081	0·076
γn_1 (calc.)	0·086	0·084	0·082	0·081	0·080	0·077
			$\delta B_1 = -1{\cdot}51 + 0{\cdot}843L$			
δB_1 (obs.)	0·176	0·245	0·408	0·444	0·532	0·642
δB_1 (calc.)	0·176	0·265	0·405	0·459	0·536	0·636
			$_\infty p_2 = 0{\cdot}4200 - 0{\cdot}221L + 0{\cdot}141L^2$			
$_\infty p_2$ (obs.)	0·5557	0·5789	0·6335	0·6523	0·7027	0·7797
$_\infty p_2$ (calc.)	0·5440	0·5817	0·6456	0·6731	0·7144	0·7706
			$_\infty r_2 = 0{\cdot}2200 - 0{\cdot}0253L$			
$_\infty r_2$ (obs.)	0·1674	0·1667	0·1662	0·1608	0·1587	0·1581
$_\infty r_2$ (calc.)	0·1700	0·1667	0·1625	0·1609	0·1586	0·1556
			$_\infty({}_sK_2) = -24{\cdot}00 + 13{\cdot}05L$			
$10^{14}{}_\infty({}_sK_2)$ (obs.)	2·128	3·224	5·829	6·343	7·663	9·309
$10^{14}{}_\infty({}_sK_2)$ (calc.)	2·110	3·486	5·644	6·478	7·680	9·207
			$\mu = 1{\cdot}60 - 17{\cdot}48L + 11{\cdot}64L^2$			
μ (obs.)	14·11	16·41	21·17	23·38	27·38	33·52
μ (calc.)	13·20	16·54	21·90	24·44	27·85	32·60

TABLE 5.

Apparent semi-axes of polarisability of polyvinyl bromides.

Polymer	M_2	$(b_1 - b_2)$	$b_1 + 2b_2$	b_1	b_2
I	10,720	0·01	202·62	67·55	67·54
II	13,660	0·02	257·33	85·79	85·77
III	19,990	0·02	375·28	125·11	125·09
IV	23,160	$0{\cdot}02_5$	420·68	140·24	140·22
V	28,630	0·03	513·42	171·16	171·13
VI	37,480	0·03	669·20	223·09	223·06

for the two C–C, three C–H, and C–Br bonds [16] in the $-CH_2-CHBr$ repeating unit, when multiplied by x, gives $(b_1 + 2b_2)$, for polymers I—IV, respectively, as follow: 197·09, 251·19, 367·63, 425·86, 526·57, and 689·24).

A low anisotropy is thus revealed. These polymers therefore behave as would be expected if, in solution, they exist as almost random coils. Remarks in ref. 1 regarding the polyvinyl chlorides apply *mutatis mutandis* to the bromides; in particular, it is again the case that helical conformations can be proposed which are equivalent from polarity and polarisability viewpoints to near-random coils. By experiment these two types cannot be distinguished, nor can any notable differences in flexibility between the chlorides and bromides be convincingly detected.

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UNIVERSITY OF SYDNEY, SYDNEY, AUSTRALIA. [*Received, December 27th*, 1961.]

For the calculation *a priori* of the polarisability semi-axes of vinyl chloride Le Fèvre and Sundaram[1] used b_L^{C-Cl} and $b_T^{C-Cl} = b_V^{C-Cl}$ values * as drawn from carbon tetrachloride and chloroform. Unpublished measurements[12] on bromoform give analogous longitudinal and transverse polarisabilities for C–Br as $b_L^{C-Br} = 0{\cdot}56$ and $b_T^{C-Br} = b_V^{C-Br} = 0{\cdot}26$. Taking the C–C–Br angle in vinyl bromide as 122° (ref. 13 quotes 121·7° ± 1° or 121° ± 3°), and the bond polarisabilities of C–H and C=C as in Le Fèvre and Sundaram,[1] then leads to molecular semi-axes having the magnitudes and locations shown in Table 3.

TABLE 3.

Polarisability semi-axes calculated for vinyl bromide.

	Direction cosines with *			
	X	Y	Z	
$b_1 = 0{\cdot}918_5$	0·7986	−0·6018	0	$\mu_1 = 1{\cdot}23_1$
$b_2 = 0{\cdot}638_4$	0·6018	0·7986	0	$\mu_2 = 0{\cdot}62_3$
$b_3 = 0{\cdot}529$	0	0	1	$\mu_3 = 0$

* Axes X, Y, Z taken with X collinear with C=C and Z perpendicular to molecular plane.

Thus b_1 is at $\phi = 21°$ anti-clockwise to C–Br in the C=C–Br plane, and when $\mu_{\text{resultant}}$ acts $\psi = 5° 52'$ clockwise from C–Br the calculated molar Kerr constant equals that found; these results resemble those for vinyl chloride[1] (for which $\phi = ca.\ 28°$ and $\psi = 5° 22'$) and the remarks of ref. 1 concerning mesomerism in the chloride apply also to the bromide.

Physical Properties and Molecular Weights of Polyvinyl Bromides.—As with the polyvinyl chlorides, empirical equations may be fitted fairly satisfactorily to most of the measured quantities. Table 4 summarises the relations between dielectric constant, density factors, etc., and $L = \log (M_{\text{polymer}}/M_{\text{monomer}})$.

Apparent Dipole Moments of Polyvinyl Bromides.—As with the polyvinyl chlorides reported in ref. 1, the apparent polarities increase with molecular weight. If the moment μ_0 of the repeating unit be taken as that[14] of ethyl bromide ($1{\cdot}9_3$ D), x is the degree of polymerisation, and all inter-bond angles are assumed to be tetrahedral, then the Debye–Bueche[15] quotients rise from $0{\cdot}5_3$ to $0{\cdot}8_6$:

Polymer	I	II	III	IV	V	VI
$\mu^2_{\text{apparent}}/x\mu_0^2$	0·53	0·57	0·64	0·68	0·75	0·86

The quotient would[15] be 0·92 were internal rotations " free " except for steric restrictions imposed by bond angles and lengths. The observed quotients therefore suggest that flexibility becomes greater with the size of the polymer, but this of course is to be expected from elementary principles. Comparison with our results[1] for polyvinyl chlorides is handicapped by the fact that, through preparative causes, the x ranges for the chlorides and bromides are different (539—2023 and 100—350, respectively); nevertheless the emergence of similar quotients (*e.g.*, ~0·7) for the two polymers at degrees of polymerisation related roughly as 8 : 1 may be interpreted as indicating a somewhat greater rigidity among the chain segments assembled in the macromolecules of the chloride than among those of the bromide.

Apparent Anisotropic Polarisabilities of Polyvinyl Bromides.—Table 5 summarises calculations made by assuming that the dissolved polyvinyl bromides have polarisability ellipsoids of revolution, that b_1 is greater than $b_2 = b_3$, that $\mu_{\text{resultant}}$ acts parallel to the axis b_1, and that ${}_EP = 0{\cdot}95R_D$ (the factor 0·95 is a mean value; the sum $b_L + 2b_T = 1{\cdot}967$,

* Polarisabilities quoted throughout in units 10^{-23} c.c.

12 Le Fèvre and Ritchie, unpublished work.
13 " Tables of Interatomic Distances and Configuration in Molecules and Ions," ed. Sutton, *Chem. Soc. Spec. Publ.* No. 11, 1958.
14 Le Fèvre and Williams, unpublished work.
15 Debye and Bueche, *J. Chem. Phys.*, 1951, **19**, 589

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$\alpha\varepsilon_1$ (calc.)	2·432	2·675	3·060	3·242	3·485	3·900
		$\beta d_1 = 0{\cdot}3850 + 0{\cdot}063L$				
βd_1 (obs.)	0·5104	0·5146	0·5110	0·5337	0·5387	0·5316
βd_1 (calc.)	0·5110	0·5177	0·5281	0·5321	0·5379	0·5453
		$\gamma n_1 = 0{\cdot}0900 + 0{\cdot}0080L - 0{\cdot}0051L^2$				
γn_1 (obs.)	0·085	0·084	0·083	0·082	0·081	0·076
γn_1 (calc.)	0·086	0·084	0·082	0·081	0·080	0·077
		$\delta B_1 = -1{\cdot}51 + 0{\cdot}843L$				
δB_1 (obs.)	0·176	0·245	0·408	0·444	0·532	0·642
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		$_\infty p_2 = 0{\cdot}4200 - 0{\cdot}221L + 0{\cdot}141L^2$				
$_\infty p_2$ (obs.)	0·5557	0·5789	0·6335	0·6523	0·7027	0·7797
$_\infty p_2$ (calc.)	0·5440	0·5817	0·6456	0·6731	0·7144	0·7706
		$_\infty r_2 = 0{\cdot}2200 - 0{\cdot}0253L$				
$_\infty r_2$ (obs.)	0·1674	0·1667	0·1662	0·1608	0·1587	0·1581
$_\infty r_2$ (calc.)	0·1700	0·1667	0·1625	0·1609	0·1586	0·1556
		$_\infty({}_sK_2) = -24{\cdot}00 + 13{\cdot}05L$				
$10^{14}{}_\infty({}_sK_2)$ (obs.)	2·128	3·224	5·829	6·343	7·663	9·309
$10^{14}{}_\infty({}_sK_2)$ (calc.)	2·110	3·486	5·644	6·478	7·680	9·207
		$\mu = 1{\cdot}60 - 17{\cdot}48L + 11{\cdot}64L^2$				
μ (obs.)	14·11	16·41	21·17	23·38	27·38	33·52
μ (calc.)	13·20	16·54	21·90	24·44	27·85	32·60

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[16] Le Fèvre, Liversidge Lecture, *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1.