

**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  $1.3_d$  D and  $58.4 \times 10^{-12}$ ; for the polymers  $\mu$ 's and  $\infty(mK_2)$ 's range from  $14.1$  to  $33.5$  D. and  $228 \times 10^{-12}$  to  $3489 \times 10^{-12}$ , 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<sup>1</sup> 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<sup>2</sup> affects the relative flexibilities of polyvinyl bromides and chlorides in ways detectable by polarity and polarisability measurements.

#### EXPERIMENTAL

*Vinyl Bromide.*—This was prepared<sup>3</sup> 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.  $15.8^\circ$ ).

<sup>1</sup> Le Fèvre and Sundaram, *J.*, 1962, 1494.

<sup>2</sup> Stuart, *Z. phys. Chem.*, 1935, B, 27, 350.

<sup>3</sup> Kharasch, McNab, and Mayo, *J. Amer. Chem. Soc.*, 1933, 55, 2521.

TABLE I.

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

<i>Vinyl bromide in dioxan</i>						
$10^5 w_2$ .....	1158	2648	4203	5811	8003	9391
$10^4 \Delta n$ .....	1	3	5	7	9	11
$\epsilon_{12}$ .....	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
$10^7 \Delta B$ .....	0.037 <sub>0</sub>	0.087 <sub>1</sub>	0.136 <sub>8</sub>	0.187 <sub>2</sub>	0.258 <sub>2</sub>	0.298 <sub>9</sub>
whence $\Sigma \Delta n / \Sigma w_2 = 0.011_8$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 2.160$ ; $\Sigma \Delta d / \Sigma w_2 = 0.3373$ ; $\Sigma \Delta B / \Sigma w_2 = 3.22_0 \times 10^{-7}$						
<i>Polyvinyl bromide I in dioxan</i>						
$10^5 w_2$ .....	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
$\epsilon_{12}$ .....	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 $\Sigma \Delta n / \Sigma w_2 = 0.084_8$ ; $\Sigma \Delta n^2 / \Sigma w_2 = 0.239_9$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 2.519$ ; $\Sigma \Delta d / \Sigma w_2 = 0.5104$						
$10^5 w_2$ .....	2693	2944	3205	3861	4123	4462
$10^7 \Delta B$ .....	0.004 <sub>4</sub>	0.005 <sub>5</sub>	0.006 <sub>0</sub>	0.006 <sub>7</sub>	0.007 <sub>4</sub>	0.007 <sub>9</sub>
whence $\Sigma \Delta B / \Sigma w_2 = 0.175_8 \times 10^{-7}$						
<i>Polyvinyl bromide I in cyclohexanone</i>						
$10^4 c$ .....	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 $[\eta_{sp}/c]_{c \rightarrow 0} = 0.0540$						
<i>Polyvinyl bromide II in dioxan</i>						
$10^5 w_2$ .....	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
$\epsilon_{12}$ .....	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 $\Sigma \Delta n / \Sigma w_2 = 0.084_4$ ; $\Sigma \Delta n^2 / \Sigma w_2 = 0.241_8$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 2.667$ ; $\Sigma \Delta d / \Sigma w_2 = 0.5146$						
$10^5 w_2$ .....	1366	1741	2091	2322	2641	2902
$10^7 \Delta B$ .....	0.002 <sub>9</sub>	0.004 <sub>5</sub>	0.004 <sub>8</sub>	0.005 <sub>7</sub>	0.006 <sub>8</sub>	0.007 <sub>3</sub>
whence $\Sigma \Delta B / \Sigma w_2 = 0.245_0 \times 10^{-7}$						
<i>Polyvinyl bromide II in cyclohexanone</i>						
$10^4 c$ .....	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 $[\eta_{sp}/c]_{c \rightarrow 0} = 0.0617$						
<i>Polyvinyl bromide III in dioxan</i>						
$10^5 w_2$ .....	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
$\epsilon_{12}$ .....	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
$10^7 \Delta B$ .....	0.005 <sub>4</sub>	0.006 <sub>7</sub>	0.007 <sub>9</sub>	0.009 <sub>0</sub>	0.009 <sub>7</sub>	0.011 <sub>6</sub>
whence $\Sigma \Delta n / \Sigma w_2 = 0.082_6$ ; $\Sigma \Delta n^2 / \Sigma w_2 = 0.234_2$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 2.992$ ; $\Sigma \Delta d / \Sigma w_2 = 0.5110$ ; $\Sigma \Delta B / \Sigma w_2 = 0.407_6 \times 10^{-7}$						
<i>Polyvinyl bromide III in cyclohexanone</i>						
$10^4 c$ .....	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 $[\eta_{sp}/c]_{c \rightarrow 0} = 0.0761$						

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	
$\epsilon_{12}$ .....	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 $\Sigma \Delta n / \Sigma w_2 = 0.082_2$ ; $\Sigma \Delta n^2 / \Sigma w_2 = 0.234_3$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 3.144$ ; $\Sigma \Delta d / \Sigma w_2 = 0.5337$							
$10^5 w_2$ .....	1952	2382	2788	3245	3803	4314	4892
$10^7 \Delta B$ .....	0.008 <sub>6</sub>	0.010 <sub>1</sub>	0.012 <sub>8</sub>	0.014 <sub>3</sub>	0.016 <sub>7</sub>	0.019 <sub>6</sub>	0.021 <sub>8</sub>
whence $\Sigma \Delta B / \Sigma w_2 = 0.444_1 \times 10^{-7}$							
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 $[\eta_{sp}/c]_{c \rightarrow 0} = 0.0825$							
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
$\epsilon_{12}$ .....	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 $\Sigma \Delta n / \Sigma w_2 = 0.081_3$ ; $\Sigma \Delta n^2 / \Sigma w_2 = 0.229_4$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 3.458$ ; $\Sigma \Delta d / \Sigma w_2 = 0.5387$							
$10^5 w_2$ .....	1728	1994	2334	2648	2905	3304	
$10^7 \Delta B$ .....	0.009 <sub>2</sub>	0.010 <sub>9</sub>	0.012 <sub>5</sub>	0.014 <sub>0</sub>	0.015 <sub>5</sub>	0.017 <sub>2</sub>	
whence $\Sigma \Delta B / \Sigma w_2 = 0.531_7 \times 10^{-7}$							
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 $[\eta_{sp}/c]_{c \rightarrow 0} = 0.0927$							
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
$\epsilon_{12}$ .....	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 $\Sigma \Delta n / \Sigma w_2 = 0.076_3$ ; $\Sigma \Delta n^2 / \Sigma w_2 = 0.216_4$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 3.914$ ; $\Sigma \Delta d / \Sigma w_2 = 0.5316$							
$10^5 w_2$ .....	987	1099	1186	1354	1725	1916	2105
$10^7 \Delta B$ .....	0.006 <sub>3</sub>	0.006 <sub>9</sub>	0.007 <sub>7</sub>	0.008 <sub>7</sub>	0.010 <sub>9</sub>	0.012 <sub>4</sub>	0.013 <sub>7</sub>
whence $\Sigma \Delta B / \Sigma w_2 = 0.642_1 \times 10^{-7}$							
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 $[\eta_{sp}/c]_{c \rightarrow 0} = 0.1212$							

**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 <sup>4</sup> 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*.

<sup>4</sup> 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.

$\alpha\epsilon_1 = 1.22 - 0.910L + 0.758L^2$						
$\alpha\epsilon_1$ (obs.) .....	2.519	2.667	2.992	3.144	3.458	3.914
$\alpha\epsilon_1$ (calc.) .....	2.432	2.675	3.060	3.242	3.485	3.900
$\beta d_1 = 0.3850 + 0.063L$						
$\beta d_1$ (obs.) .....	0.5104	0.5146	0.5110	0.5337	0.5387	0.5316
$\beta d_1$ (calc.) .....	0.5110	0.5177	0.5281	0.5321	0.5379	0.5453
$\gamma n_1 = 0.0900 + 0.0080L - 0.0051L^2$						
$\gamma n_1$ (obs.) .....	0.085	0.084	0.083	0.082	0.081	0.076
$\gamma n_1$ (calc.) .....	0.086	0.084	0.082	0.081	0.080	0.077
$\delta B_1 = -1.51 + 0.843L$						
$\delta B_1$ (obs.) .....	0.176	0.245	0.408	0.444	0.532	0.642
$\delta B_1$ (calc.) .....	0.176	0.265	0.405	0.459	0.536	0.636
$\infty p_2 = 0.4200 - 0.221L + 0.141L^2$						
$\infty p_2$ (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
$\infty r_2 = 0.2200 - 0.0253L$						
$\infty r_2$ (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
$\infty ({}_sK_2) = -24.00 + 13.05L$						
$10^{14}\infty ({}_sK_2)$ (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
$\mu = 1.60 - 17.48L + 11.64L^2$						
$\mu$ (obs.) .....	14.11	16.41	21.17	23.38	27.38	33.52
$\mu$ (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	0.02 <sub>s</sub>	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<sup>16</sup> in the  $-\text{CH}_2-\text{CHBr}$  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.

The award of an H. B. and F. M. Gritton Research Scholarship to K. M. S. S. is gratefully acknowledged.

For the calculation *a priori* of the polarisability semi-axes of vinyl chloride Le Fèvre and Sundaram<sup>1</sup> used  $b_L^{C-Cl}$  and  $b_T^{C-Cl} = b_V^{C-Cl}$  values\* as drawn from carbon tetrachloride and chloroform. Unpublished measurements<sup>12</sup> on bromoform give analogous longitudinal and transverse polarisabilities for C-Br as  $b_L^{C-Br} = 0.56$  and  $b_T^{C-Br} = b_V^{C-Br} = 0.26$ . Taking the C-C-Br angle in vinyl bromide as  $122^\circ$  (ref. 13 quotes  $121.7^\circ \pm 1^\circ$  or  $121^\circ \pm 3^\circ$ ), and the bond polarisabilities of C-H and C=C as in Le Fèvre and Sundaram,<sup>1</sup> 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	
$b_1 = 0.918_3$	0.7986	-0.6018	0	$\mu_1 = 1.23_1$
$b_2 = 0.638_4$	0.6018	0.7986	0	$\mu_2 = 0.62_3$
$b_3 = 0.529$	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  $\phi = 21^\circ$  anti-clockwise to C-Br in the C=C-Br plane, and when  $\mu_{\text{resultant}}$  acts  $\psi = 5^\circ 52'$  clockwise from C-Br the calculated molar Kerr constant equals that found; these results resemble those for vinyl chloride<sup>1</sup> (for which  $\phi = ca. 28^\circ$  and  $\psi = 5^\circ 22'$ ) 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  $\mu_0$  of the repeating unit be taken as that<sup>14</sup> of ethyl bromide ( $1.9_3$  D),  $x$  is the degree of polymerisation, and all inter-bond angles are assumed to be tetrahedral, then the Debye-Bueche<sup>15</sup> quotients rise from 0.53 to 0.86:

Polymer	I	II	III	IV	V	VI
$\mu^2_{\text{apparent}}/x\mu_0^2 \dots\dots\dots$	0.53	0.57	0.64	0.68	0.75	0.86

The quotient would<sup>15</sup> 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<sup>1</sup> 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.*,  $\sim 0.7$ ) 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  ${}_xP = 0.95R_D$  (the factor 0.95 is a mean value; the sum  $b_L + 2b_T = 1.967$ ,

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

<sup>12</sup> Le Fèvre and Ritchie, unpublished work.

<sup>13</sup> "Tables of Interatomic Distances and Configuration in Molecules and Ions," ed. Sutton, *Chem. Soc. Spec. Publ.* No. 11, 1958.

<sup>14</sup> Le Fèvre and Williams, unpublished work.

<sup>15</sup> Debye and Bueche, *J. Chem. Phys.*, 1951, **19**, 589

TABLE 4.

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

$\alpha\epsilon_1 = 1.22 - 0.910L + 0.758L^2$						
$\alpha\epsilon_1$ (obs.) .....	2.519	2.667	2.992	3.144	3.458	3.914
$\alpha\epsilon_1$ (calc.) .....	2.432	2.675	3.060	3.242	3.485	3.900
$\beta d_1 = 0.3850 + 0.063L$						
$\beta d_1$ (obs.) .....	0.5104	0.5146	0.5110	0.5337	0.5387	0.5316
$\beta d_1$ (calc.) .....	0.5110	0.5177	0.5281	0.5321	0.5379	0.5453
$\gamma n_1 = 0.0900 + 0.0080L - 0.0051L^2$						
$\gamma n_1$ (obs.) .....	0.085	0.084	0.083	0.082	0.081	0.076
$\gamma n_1$ (calc.) .....	0.086	0.084	0.082	0.081	0.080	0.077
$\delta B_1 = -1.51 + 0.843L$						
$\delta B_1$ (obs.) .....	0.176	0.245	0.408	0.444	0.532	0.642
$\delta B_1$ (calc.) .....	0.176	0.265	0.405	0.459	0.536	0.636
$\infty p_2 = 0.4200 - 0.221L + 0.141L^2$						
$\infty p_2$ (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
$\infty r_2 = 0.2200 - 0.0253L$						
$\infty r_2$ (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
$\infty ({}_s K_2) = -24.00 + 13.05L$						
$10^{14} \infty ({}_s K_2)$ (obs.) ...	2.128	3.224	5.829	6.343	7.663	9.309
$10^{14} \infty ({}_s K_2)$ (calc.) ...	2.110	3.486	5.644	6.478	7.680	9.207
$\mu = 1.60 - 17.48L + 11.64L^2$						
$\mu$ (obs.) .....	14.11	16.41	21.17	23.38	27.38	33.52
$\mu$ (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	0.02 <sub>5</sub>	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<sup>16</sup> in the  $-\text{CH}_2-\text{CHBr}$  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.

The award of an H. B. and F. M. Gritton Research Scholarship to K. M. S. S. is gratefully acknowledged.

UNIVERSITY OF SYDNEY, SYDNEY, AUSTRALIA.

[Received, December 27th, 1961.]

<sup>16</sup> Le Fèvre, Liversidge Lecture, *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1.