583. *Molecular Polarisability. The Molar Kerr Constants and Dipole Moments of Six Polyethylene Glycols as Solutes in Benzene.*

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Dipole moments and molar Kerr constants have been measured for the cases of $HO{\cdot}[CH_2{\cdot}CH_2{\cdot}O]_x{\cdot}H$ in which $x = 4{\cdot}1$, $6{\cdot}4$, 18, 34, 78, and 153. Both properties can be reconciled with the supposition that *gauche-* and *trans-*conformations of the group $\cdot O{\cdot}CH_2{\cdot}CH_2{\cdot}O\cdot$ are equally probable for x up to about 5, but that thereafter *gauche-* or *cis-*arrangements occur more frequently than *trans*. A tendency for the larger macromolecular chains to contain helically coiled portions (a possibility already indicated by infrared studies) is therefore explicable.

The polyethylene glycols (I) differ from the polyvinyls (II) previously [1] examined here in that their polarities must be the vector sums of component " ether " moments residing in the main chain itself rather than in the attached side groups R or R′. At the outset therefore it seemed likely that information on the conformations adopted by macromolecules of type (I) as solutes might be provided by measurements of polarity and electric

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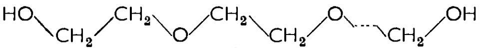
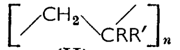
[1] Le Fèvre, Le Fèvre, and Parkins, *J.*, 1958, 1468; Le Fèvre, Le Fèvre, and Parkins, *J.*, 1960, 1814; Le Fèvre and Somasundaram (polyacrylates, methacrylates, etc.), unpublished work.

birefringence. The possibility that polyethylene glycols have highly crumpled helical structures had already been demonstrated by X-ray studies [2] of the solid phases, and by infrared work [3] on both crystals and melt from a specimen having a molecular weight of 6000. However, dipole-moment measurements in dioxan by Uchida *et al.*[4] on a series in which x in $HO\cdot[C_2H_4O]_x\cdot H$ progressed from 1 to 7, were, for $x = 1—5$, reconcilable with



(I)



(II)

structures involving free rotation (in the sense that *trans*- and *gauche*-conformations, wherever there is a choice, are equally probable). Apart from work described now and elsewhere,[4] the only relevant dipole-moment determination is one by Svirbely and Lander,[5] who reported $\mu = 9{\cdot}91$ D for a specimen of $M = 3750$ in benzene at 44°, and noted that this result disagreed with either of the two simplest linear structures. Moreover it is *ca.* 2 D lower than the moment required for a free-rotation model. Examination of members having x greater than 7 thus seemed desirable.

EXPERIMENTAL

Solutes.—Six polyethylene glycols (commercially termed PEG followed by a number denoting the approximate molecular weight) were presented to us by Shell Chemicals (Australia) Pty. Ltd.; of these PEG 200 and 300 were viscous oils, 800 and 1500 were waxes, and 4000 and 6000 were apparently crystalline. Their molecular-weight distributions (determined by end-group analysis) were 190—210, 285—315, 760—840, 1430—1570, 3300—3600, and 6000—7500. For purposes of calculation, the mid-point of each range has been taken as M. The PEG's were used without additional treatment.

Procedures.—Dielectric constants, ε, densities, d, refractive indexes, n, and Kerr constants, B, of solutions in sodium-dried benzene were measured as described before.[6] Concentrations were recorded as weight fractions, w, of solute. In the Tables and elsewhere below, suffixes 1, 2, and 12 indicate respectively solvent, solute, and solution; the prefix Δ denotes a difference between the property of a solution and that of the solvent, *e.g.*, $\Delta B = B_{12} - B_1$, $\Delta\varepsilon = \varepsilon_{12} - \varepsilon_1$, etc. The symbols α, β, γ, and δ are drawn [6a] from equations, assumed to apply at higher dilutions, of the following forms: $\varepsilon_{12} = \varepsilon_1(1 + \alpha w_2)$, $d_{12} = d_1(1 + \beta w_2)$, $n_{12} = n_1(1 + \gamma w_2)$, and $B_{12} = B_1(1 + \delta w_2)$. Total polarisations, or molar Kerr constants, extrapolated to infinite dilution are shown thus: ${}_{\infty}P_2$ or ${}_{\infty}({}_{\mathrm{m}}K_2)$; calculations are actually performed on specific quantities, p_2 or ${}_{\mathrm{S}}K_2$, which when $w_2 = 0$ are given by:

$${}_{\infty}p_2 = p_1(1 - \beta) + 3\alpha\varepsilon_1/d_1(\varepsilon_1 + 2)^2 \text{ or } {}_{\infty}({}_{\mathrm{S}}K_2) = {}_{\mathrm{S}}K_1(1 - \beta + \gamma + \delta - H\gamma - J\alpha\varepsilon_1)$$

where $p_1 = (\varepsilon_1 - 1)/d_1(\varepsilon_1 + 2)$, ${}_{\mathrm{S}}K_1 = 6\lambda n_1 B_1/(n_1^2 + 2)^2(\varepsilon_1 + 2)^2 d_1$,

$$H = 4n_1^2/(n_1^2 + 2), \text{ and } J = 2/(\varepsilon_1 + 2).$$

All measurements have been at 25° for light of $\lambda = 5893$ Å. Fuller details of our methods are given on p. 283 of ref. 6(*b*). For benzene, values are: $\varepsilon_1 = 2{\cdot}2725$, $d_1 = 0{\cdot}87378$, $n_1 = 1{\cdot}4973$, $p_1 = 0{\cdot}34086$ c.c., $H = 2{\cdot}114$, $J = 0{\cdot}4681$, $B_1 = 0{\cdot}410 \times 10^{-7}$, and ${}_{\mathrm{S}}K_1 = 7{\cdot}56 \times 10^{-14}$.

Results.—These are set out in Table 1. In certain instances the relations between $\Delta\varepsilon$ or ΔB and w_2 are not rectilinear; data have therefore been fitted by the method of least squares to equations such as $\Delta\varepsilon = aw_2 + bw_2^2$ or $\Delta B = a'w_2 + b'w_2^2$; then $a = (\alpha\varepsilon_1)_{w_2=0}$ or $a' = (B_1\delta)_{w_2=0}$.

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[2] Sauter, *Z. phys. Chem.*, 1933, *B*, **21**, 161; Barnes and Ross, *J. Amer. Chem. Soc.*, 1936, **58**, 1129; Fuller, *Rubber Chem. Tech.*, 1941, **14**, 323.

[3] Davison, *J.*, 1955, 3270.

[4] Uchida, Kurita, Koizumi, and Kubo, *J. Polymer Sci.*, 1956, **21**, 313.

[5] Svirbely and Lander, *J. Amer. Chem. Soc.*, 1945, **67**, 2189.

[6] (*a*) Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953, chap. 2; Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405; Le Fèvre and Le Fèvre, *J.*, 1953, 4041; **1954**, 1577; (*b*) *Rev. Pure and Appl. Chem.*, 1955, **5**, 261.

TABLE 1. *Dielectric constants, densities, refractive indexes, and Kerr effects for solutions of* PEG's *in benzene at* 25° *and* $\lambda = 5893$ Å.

PEG 200

10^5w_2	698	1082	1557	1589	1822	1856	2042	2226
ε_{12}	2·3209	2·3502	2·3816	2·3852	2·4015	2·4036	2·4200	2·4294
d_{12}	0·87524	0·87594	0·87687	0·87694	0·87737	—	0·87782	0·87811
10^5w_2	1200	1589	1600	1822	2085	2803	3529	4170
$10^7\Delta B$	0·035	0·047	0·046	0·055	0·060	0·076	0·084	—
$-10^4\Delta n$ ...	—	—	6	—	9	10	—	12·5

whence $\sum\Delta\varepsilon/\sum w_2 = 7{\cdot}08_8$; $\sum\Delta d/\sum w_2 = 0{\cdot}1969$; $10^7\Delta B = 3{\cdot}444w_2 - 28{\cdot}95w_2^2$; $\sum\Delta n/\sum w_2 = -0{\cdot}035_2$.

PEG 300

10^5w_2	1196	1756	2223		
ε_{12}	2·3442	2·3790	2·4051		
d_{12}	0·87618	0·87715	0·87817		
10^5w_2	1196	1572	1756	1913	2223
$10^7\Delta B$	0·022	0·031	0·034	0·037	0·041
$-10^4\Delta n$ ...	—	4	—	5	6

whence $\sum\Delta\varepsilon/\sum w_2 = 6{\cdot}00_6$; $\sum\Delta d/\sum w_2 = 0{\cdot}1952$; $10^7\Delta B = 2{\cdot}018w_2 - 6{\cdot}17w_2^2$; $\sum\Delta n/\sum w_2 = -0{\cdot}026_3$.

PEG 800

10^5w_2	1065	1295	1672	1849	1956	2558
ε_{12}	2·3129	2·3243	2·3369	2·3405	2·3463	2·3685
d_{12}	0·87598	0·87647	0·87726	0·87759	—	0·87907
$10^7\Delta B$	0·013	0·016	0·021	0·025	0·025	0·029
$-10^4\Delta n$ ...	3	5	8	—	—	—

whence $\Delta\varepsilon = 3{\cdot}963w_2 - 9{\cdot}31w_2^2$; $\sum\Delta d/\sum w_2 = 0{\cdot}2058$; $10^7\Delta B = 1{\cdot}439w_2 - 1{\cdot}04w_2^2$; $\sum\Delta n/\sum w_2 = -0{\cdot}024_1$.

PEG 1500

10^5w_2	993	1297	1431	1576	1807	2041	2416	2418	2559
ε_{12}	2·3076	2·3178	2·3204	—	2·3326	—	—	2·3557	2·3620
d_{12}	0·87603	0·87655	0·87683	—	0·87771	—	—	0·87893	0·87913
$10^7\Delta B$	—	—	—	0·013	—	0·020	0·024	0·023	0·027
$-10^4\Delta n$ ...	2	—	—	—	—	—	4	4	5

whence $\sum\Delta\varepsilon/\sum w_2 = 3{\cdot}43_7$; $\sum\Delta d/\sum w_2 = 0{\cdot}2130$; $10^7\Delta B = 0{\cdot}5585w_2 + 18{\cdot}3w_2^2$; $\sum\Delta n/\sum w_2 = -0{\cdot}018_4$.

PEG 4000

10^5w_2	772	1172	1374	1761	1767
ε_{12}	2·2964	2·3096	2·3151	2·3272	2·3284
d_{12}	0·87543	0·87630	0·87673	0·87750	0·87761
$10^7\Delta B$	0·000	−0·001	0·000	−0·002	0·001
$-10^4\Delta n$ ...	—	2	—	2	3

whence $\sum\Delta\varepsilon/\sum w_2 = 3{\cdot}141$; $\sum\Delta d/\sum w_2 = 0{\cdot}2128$; $\sum\Delta B/\sum w_2 = -0{\cdot}03$; $\sum\Delta n/\sum w_2 = -0{\cdot}0149$.

PEG 6000

10^5w_2	871	1249	1558	1595	1632	1725
ε_{12}	2·3001	2·3117	2·3207	—	2·3235	—
d_{12}	0·87557	0·87639	0·87703	—	0·87716	—
$10^7\Delta B$	−0·004	−0·006	−0·008	−0·008	−0·009	−0·010
$-10^4\Delta n$ ...	—	—	—	1	1	2

whence $\sum\Delta\varepsilon/\sum w_2 = 3{\cdot}126$; $\sum\Delta d/\sum \mathrm{w}_2 = 0{\cdot}2062$; $10^7\Delta B = -0{\cdot}303w_2 - 1{\cdot}45w_2^2$; $\sum\Delta n/\sum w_2 = -0{\cdot}008$.

DISCUSSION

Dipole Moments.—PEG's 200—300 correspond roughly to the "tetramer" and "hexamer" included among the seven compounds examined by Uchida *et al.*,[4] for which moments (in dioxan) were recorded as:

x	1	2	3	4	5	6	7
μ (D)	2·38	2·69	2·99	3·25	3·42	3·46	3·65

Thus our results (in benzene) appear to be 0·4 and 0·6 D, respectively, higher than those of the Japanese workers. The moment of 9·91 D reported by Svirbely and Lander[5] for a PEG of $M = 3750$ in benzene is in reasonable accord with 10·1 D now found for PEG 4000.

The literature[7] shows the moment of ethylene glycol in either ethyl ether or dioxan

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

to be temperature variant, but between 2·2 and 2·4 D at 25°, in agreement with 2·38 D quoted by Uchida *et al.*[4] As a gas, observed by Zahn (quoted by Wesson [7]) from 417° to 506° K, $\mu = 2{\cdot}2_5$ D. Higher glycols have only slightly greater moments, *e.g.*, $HO{\cdot}[CH_2]_{10}{\cdot}OH$ has [7] $\mu = 2{\cdot}52$ D in dioxan at 25°. It is clear therefore, from both ref. 4 and Table 2,

TABLE 2. *Specific polarisations, refractions, Kerr constants, and dipole moments of six polyethylene glycols in benzene at 25°.*

Solute	PEG 200	PEG 300	PEG 800	PEG 1500	PEG 4000	PEG 6000
M_2	200	300	800	1500	3450	6750
x *	4·1	6·4	18	34	78	153
$\alpha\varepsilon_1$	7·088	6·006	3·963	3·437	3·141	3·126
β	0·224	0·223	0·206	0·244	0·244	0·236
$-\gamma$	0·024	0·018	0·016	0·012	0·010	0·005
δ	8·400	4·922	3·510	1·362	−0·076	−0·739
$_\infty p_2$ (c.c.)	1·598	1·394	1·006	0·904	0·849	0·848
$_\infty r_2$ (c.c.) †	0·240	0·245	0·242	0·241	0·244	0·251
$10^{12}{}_\infty({}_SK_2)$	0·445	0·220	0·187	0·040	−0·059	−0·108
μ (D)	3·64	4·10	5·46	6·97	10·1	14·0

* In $HO{\cdot}[C_2H_4O]_x{\cdot}H$. † Specific refraction of solute.

that in the PEG series the polarities increase progressively with molecular weight. This fact invalidates a configuration which is *trans* throughout, since for such forms the observed moments should be zero or a constant according as the number of repeat units is even or odd; it also rules out Staudinger's " meandered " form,[8] in which *cis-* and *trans*-arrangements occur alternately along the chain, because each of the successive ether moments would be directed anti-parallel to the preceding one, as in the simple zig-zag configuration.

Uchida, Kurita, Koizumi, and Kubo [4] developed an equation to give $\mu^2_{\text{obs.}}$ on the assumption that *trans* and *gauche* potential minima are equally important; when—following them—μ_{C-O} is inserted as 1·20 D, μ_{H-O} as 1·53 D, and $(\frac{1}{3})^x$ is neglected when x exceeds 3, we find that $\mu_x^2 = 3{\cdot}2399 + 1{\cdot}772x$. Calculated and observed moments for eleven examples of $HO{\cdot}[C_2H_4O]_x{\cdot}H$ are compared in Table 3; both are seen to increase with increasing molecular weight. From graphs we find that $\mu_{\text{calc.}} = \mu_{\text{obs.}}$ at $x =$ *ca.* 4 or *ca.* 10 for solvents dioxan or benzene respectively; above these values of x the calculated moments begin more and more to surpass those measured. Uchida *et al.*[4] attribute this deviation to " disregard of the volume effect favouring extended structures. These would simulate the zig-zag form having a number of pairs of bond moments directed antiparallel to each other." A tendency of larger molecules to adopt helical conformations would, of course, produce the same result.

TABLE 3. *Calculated and observed moments for the series* $HO{\cdot}[C_2H_4O]_x{\cdot}H$.

x	$\mu_{\text{calc.}}$	$\mu_{\text{obs.}}$ (ref. 8)	$\mu_{\text{obs.}}$ (this paper)	x	$\mu_{\text{calc.}}$	$\mu_{\text{obs.}}$ (ref. 8)	$\mu_{\text{obs.}}$ (this paper)
1	2·24	2·38	—	7	3·96	3·65	—
2	2·61	2·69	—	18	5·93	—	5·46
3	2·93	2·99	—	34	7·97	—	6·97
4	3·21	3·25	3·64	78	11·9	—	10·1
5	3·48	3·42	—	153	16·6	—	14·0
6	3·73	3·46	4·10				

In dioxan it is probable that all the hydroxyl groups form hydrogen bonds with the solvent, whereas in benzene no such solvent–solute interaction can occur. Presumably the over-all higher moments in dioxan compared with those in benzene may be explained by this interaction, the absence of which in benzene suggests that the μ's measured in this solvent are nearer the true values for the series.

Kerr Constants.—From the values of $_\infty({}_SK_2)$ and M in Table 2, molar Kerr constants $_\infty({}_mK_2) \times 10^{12}$ are, for the six PEG's respectively: +89, +66, +150, +60, −204, and

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[8] Staudinger, " Die Hochmolekulare organische Verbindungen, " Springer, Berlin, 1932, pp. 293, 301.

-729. The inversion of algebraic sign as M becomes fairly large is notable and has not hitherto been found with other polymers.[1]

Extraction of semi-axes of polarisability by usual [6] routes is not possible since neither depolarisation data nor information on the directions of action of the resultant moments is available. The quotients $10^{12}{}_{\mathrm{m}}K_2/x$ diminish from $+22$ through $10{\cdot}3$, $8{\cdot}3$, $1{\cdot}8$, $-2{\cdot}6$, to $-4{\cdot}8$ for PEG's 200 to 6000; thus the anistropy per monomer unit appears to be at a minimum between $M = 1500$ and 3450. The same behaviour is shown by δ or $10^{12}{}_{\infty}({}_{\mathrm{S}}K_2)$ in Table 2. Qualitatively, the incomplete flexibility indicated by the dipole moments of the higher numbers could be harmonised with the Kerr constants in two ways: Suppose b_1, b_2, and b_3 are the semi-axes of the molecular polarisability ellipsoid, and $b_1 \neq b_2 = b_3$; let $\mu_{\mathrm{resultant}}$ make an angle β with the b_1 axis; then the dipole term θ_2 (the subscript does not here denote solute, cf. p. 270 of ref. 6*b*) reduces to:

$$\theta_2 = (\text{constant})\ \mu^2[(3\cos^2\beta - 1)(b_1 - b_2)]$$

If $(b_1 - b_2)$ remains positive, then the algebraic sign of θ_2, and hence of ${}_{\infty}({}_{\mathrm{m}}K_2)$, will change from positive through zero to negative if, as the molecular weight rises, β increases and passes through the critical value of $54{\cdot}7°$. Alternatively, if β remains constant, a negative θ_2 may be produced when b_2 becomes greater than b_1. The actual state of affairs quite possibly involves both explanations.

Other evidence on the structures of polyethylene glycols is of interest. As mentioned earlier, *X*-ray methods [2] revealed that crystalline PEG had a very crumpled chain in which nine repeated units occurred in a fibre period of 19·5 Å. Infrared studies [3] on a PEG of $M = 6000$ indicated that the group $\mathrm{O{\cdot}[CH_2]_2{\cdot}O}$ substantially retained a *gauche*-configuration from the solid material into its melts. Davison,[3] after noting that the mean dichroic ratio of the symmetrical (A) wagging, twisting, and rocking $\mathrm{CH_2}$ modes is about 1·6, remarks " this means that the two-fold symmetry axis of the $\mathrm{O{\cdot}[CH_2]_2{\cdot}O}$ group is inclined at about 48° to the fibre axis. From the dichroic ratios of the B rocking mode (about 0·4) and of the B wagging mode (about 0·5) the X and Y axes of this group must be inclined at about 65° to the fibre axis. . . . The oblique orientation of the methylene and COC groups is consistent with a helical configuration." Davison adds that the best model he could construct by using Stuart-type atomic models, and incorporating the configurations and orientations deduced in his work, was a helix with a three-fold screw axis; nine repeating units of this model occupy the fibre period of 19·5 Å already found by *X*-ray diffraction. While our measurements were in progress a more recent paper by Kurodo and Kubo [9] appeared in which, from the $\mathrm{CH_2}$ rocking vibrations, the authors deduce that the polymers of higher molecular weight assume a crumpled helical structure resulting from *cis*-minima, and that those of lower molecular weight are not restricted to the same configuration but take somewhat irregular forms involving both the *cis*- and the *trans*-minima of the internal rotations about single bonds.

Reviewing all the evidence therefore, we conclude (*a*) that the lower numbers with x from 1 to about 5 have the random conformations to be expected from " free rotation," but (*b*) that above $x = 7$ the solute molecules tend to become extended and adopt less disordered arrangements in which *gauche*- or *cis*-minima are more frequent than *trans*; the use of such minima must lead to helical coiling of portions of the macromolecular chains, and in turn to the observed excess of $\mu_{\mathrm{calc.}}$ over $\mu_{\mathrm{obs.}}$, and the inversion from positivity to negativity of ${}_{\infty}({}_{\mathrm{S}}K_2)$ with increasing molecular weight.

Empirical Connections between Properties and Molecular Weights.—Inspection of Table 2 shows that the dielectric constant factors $\alpha\varepsilon_1$, the specific polarisations at infinite dilution ${}_{\infty}p_2$, the dipole moments μ, and the specific Kerr constants ${}_{\infty}({}_{\mathrm{S}}K_2)$ change fairly smoothly with increasing molecular weight. Equations for these four relationships have been extracted; results are given in Table 4, together with comparisons of observed and

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[9] Kurodo and Kubo, *J. Polymer Sci.*, 1957, **26**, 323.

calculated results. A similar correlation, useful for M determinations, between specific extinction coefficients at 7140 cm.$^{-1}$ of the PEG's in benzene and their molecular weights has already been reported.[10]

TABLE 4. *Relations between properties and log* $(M_x/200)$ = *log* L.

Dielectric constant factor .... $\alpha\varepsilon_1 = 7{\cdot}088 - 6{\cdot}526L + 2{\cdot}610L^2$
Specific polarisation, $_\infty p_2$ .... $_\infty p_2 = 1{\cdot}598 - 1{\cdot}239L + 0{\cdot}496L^2$
Dipole moment .... $\mu = 3{\cdot}64 + 0{\cdot}018L + 4{\cdot}39L^2$
Specific Kerr constant .... $_\infty({}_sK_2) = 0{\cdot}445 - 0{\cdot}614L + 0{\cdot}168L^2$

PEG	300	800	1500	4000	6000
$\alpha\varepsilon_1$ (calc.)...	5·95	4·10	3·38	3·01	3·21
(obs.) ...	6·01	3·96	3·44	3·14	3·13
$_\infty p_2$ (calc.)	1·395	1·032	0·894	0·825	0·863
(obs.)	1·394	1·006	0·904	0·849	0·849

PEG	300	800	1500	4000	6000
μ (calc.)	3·88	5·24	7·00	10·4	13·9
(obs.)	4·10	5·46	6·97	10·1	14·0
$_\infty({}_sK_2)$ (calc.)	0·34	0·14	0·04	−0·06	−0·10
(obs.)	0·22	0·19	0·04	−0·06	−0·10

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UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA. [*Received, December* 29*th*, 1959.]

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[10] Le Fèvre, Parkins, and Roper, *Austral. J. Chem.*, *J.*, 1960, **13**, 169.