Molecular Polarisability. The Apparent Dipole Moments and Molar Kerr Constants of Six Polypropylene Glycols as Solutes in Benzene

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Empirical relations between x in $HO[-CH_2\cdot CHMe\cdot O-]_xH$ and various physical properties needed for the evaluation of molar refractions, polarisations, Kerr constants, and dipole moments are deduced for polypropylene glycols (PPGs) having molecular weights from *ca.* 400 to *ca.* 4000. The inversions in algebraic sign, noted previously with polyethylene glycols, and now recorded for PPGs, are easily explained if slight angular distortions occur in the C·C·O·C backbones of the two polymers as the segment numbers x are increased.

THE polarisations and polarisabilities of six polypropylene glycols (PPGs) $HO[-CH_2\cdot CHMe\cdot O-]_xH$ have been examined as solutes in benzene for comparison with observations previously made on various other polymers,[1-3] including a number of polyethylene glycols (PEGs).

EXPERIMENTAL

Apparatus, procedures, symbols, and the methods of calculation underlying Table 1 are standard.[4-8] Polypropylene glycol samples, of specified molecular weights, obtained from Koch–Light, Union Carbide, Dow Chemical, and Fluka were used without further purification or fractionation. The measurements listed in Supplementary Publication No. SUP 20547 (5 pp.) ‡ lead to the results and other details shown in Table 1.

DISCUSSION

Physical Properties and Degrees of Polymerisation.— In view of findings with other dissolved polymers,[1-3] the applicability has been explored of empirical con-

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‡ Details of Supplementary Publications are given in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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nections between log x and the physical properties now measured.*

Writing $L = \log x$, $\alpha\varepsilon_1 = (\varepsilon_{12} - \varepsilon_1)/w_2$, $\beta = (d_{12} - d_1)/d_1 w_2$, $\gamma n_1 = (n_{12} - n_1)/w_2$, $\gamma' n_1{}^2 = (n_{12}{}^2 - n_1{}^2)/w_2$, $\delta = (B_{12} - B_1)/B_1 w_2$, and with ${}_\infty r_2$, ${}_\infty p_2$, and ${}_\infty({}_sK_2)$ denoting respectively the specific refraction, polarisation, and Kerr constant at infinite dilution in benzene at 25°, we find from Table 1 equations (1)—(8).

$$\alpha\varepsilon_1 = 6{\cdot}744 - 5{\cdot}172\,L + 1{\cdot}377\,L^2 \qquad (1)$$

$$\beta = 0{\cdot}13321 - 0{\cdot}01219\,L + 0{\cdot}00820\,L^2 \qquad (2)$$

$$\gamma n_1 = 0{\cdot}0157\,L - 0{\cdot}0652 \qquad (3)$$

$$\delta = 0{\cdot}0661 + 2{\cdot}159\,L - 1{\cdot}577\,L^2 \qquad (4)$$

$${}_\infty r_2 = 0{\cdot}0063\,L + 0{\cdot}2569 \qquad (5)$$

$${}_\infty p_2 = 1{\cdot}6236 - 1{\cdot}0713\,L + 0{\cdot}2935\,L^2 \qquad (6)$$

$${}_\infty({}_sK_2) \times 10^{14} = -16{\cdot}80 + 35{\cdot}87\,L - 17{\cdot}56\,L^2 \qquad (7)$$

$$\mu = 4{\cdot}3525 - 3{\cdot}399\,L + 3{\cdot}0332\,L^2 \qquad (8)$$

Table 2 shows ' goodness of fit ' among the quantities considered. Concordance is worst with δ and ${}_\infty({}_sK_2)$. Since Δn is easily determined, equation (3) may be useful for rough estimations of molecular weight (*e.g.* a solution in benzene, with $w_2 = 0{\cdot}0151$, of a PPG sample sold as having M.W. = 2025, showed $\Delta n = n_{12} - n_1 = -0{\cdot}00061$, whence $M_2 = ca.\ 2200$). The factors $\gamma' n_1{}^2$, required in the evaluation of molecular refractions, are adequately predicted as $3\gamma n_1$.

TABLE 1

Total polarisations, molecular refractions, dipole moments, and molar Kerr constants at infinite dilution

Solute	PPG I	PPG II	PPG III	PPG IV	PPG V	PPG VI
$\alpha\varepsilon_1$	3·39	2·40	2·34	2·09	1·96	1·85
β	0·1288	0·1305	0·1313	0·1340	0·1365	0·1384
$-\gamma$	0·0347	0·0294	0·0293	0·0287	0·0254	0·0247
δ	0·802	0·246	0·191	−0·257	−0·795	−1·36
$10^{12}{}_\infty({}_mK_2)$	3·78	1·85	1·27	+50·9	−199	−421
${}_\infty P_2$/cm^3	374	748	884	1377	1989	2567
R_D/cm^3	105	266	319	531	803	1070
μ/D *	$3{\cdot}5_9$	$4{\cdot}7_8$	$5{\cdot}1_8$	$6{\cdot}3_3$	$7{\cdot}4_8$	$8{\cdot}4_0$

* Calculated assuming distortion polarisations of 1·05 R_D.

Apparent Dipole Moments.—The moments now found agree with others deduced earlier by Loveluck,[9] who applied Guggenheim's methods [10] to undisclosed measurements on solutions in benzene of the various polymers. The polarities of polypropylene glycols increase with x slightly less rapidly than do those of polyethylene glycols,[1] $\mu_{obs}{}^2$ being given for the two series respectively by $0{\cdot}934\,x + 6{\cdot}97$ and $1{\cdot}224\,x + 7{\cdot}86$. The values of $\mu_{obs}{}^2/x$ when x is large lead, through equations developed by Marchal and Benoit [11] and assumptions that all C·C·O and C·O·C angles are tetrahedral, to estimated mean cosines of 0·46 and 0·28 for the angles between the planes containing the first and second and second and third bonds of any set of three successive bonds in the main chains of each polymer. Such mean cosines will have magnitudes from 0 to ±1 according as the chain bonds can rotate freely or are fixed in rigid planar conformations. Evidently, as concluded by Loveluck and clearly indicated by space-filling scale models, internal flexibility is restricted in both polymers but more severely in the polypropylene than the polyethylene glycols. That the $(\mathrm{C{\cdot}C{\cdot}O})_x$ backbones may contain zig-zag sections which are planar [12] in the PPGs and helical [13] in the PEGs is suggested by X-ray studies on the corresponding solid phases.

Kerr Effects and Polarisabilities.—The PPGs, like the PEGs, display a change in sign of their electric birefringences as molecular weights are increased, the inversions occurring when x is *ca.* 16 with the PPGs or *ca.* 50 with the PEGs. Such behaviour is not obviously foreseeable from the attempts [14-19] to deal theoretically with polarisability anisotropies of flexible macromolecules. Qualitatively, it suggests that the freely-jointed models, considered in refs. 14 and 15, are unsuitable, since the specific Kerr constants of PPGs and PEGs are not independent of the molecular weights. Other treatments [16-19] forecast ${}_mK$ values in terms of segment anisotropies and/or various geometrical and statistical parameters. Ishikawa and Nagai [17] have recently predicted the general form of graphs of ${}_mK/x$ *versus* x for the PEGs; analogous arguments should be applicable also to the PPGs. From ref. 1, and from this paper, observed ${}_mK/x$ quotients in the two cases respectively can be reproduced approximately by $17{\cdot}6 - 0{\cdot}457\,x + 0{\cdot}00206\,x^2$ for PEGs and $1{\cdot}076 - 0{\cdot}055\,x - 0{\cdot}00070\,x^2$ for PPGs. Curves based upon these expressions only distantly resemble in shape those marked C by the Japanese authors [17] in their Figures 5 and 6.

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* The heading to Table 4 of ref. 1 should define $\log(M_x/200)$ as L, not log L.

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Nagai *et al.*[16,17] and Dows[18] ascribe some of the discrepancy between theory and experiment to ' excluded volume ' effects, among which are deviations of average polymer-chain conformations from those expected if perturbing influences of solvents were absent. The sign inversions noted above may easily be so explained: if each of the $CH_2{\cdot}CH_2{\cdot}O{\cdot}C$ and $CH_2{\cdot}CHMe{\cdot}O{\cdot}C$ segments is regarded as planar and with an ' ether-like ' moment of 1·3/D. acting along the bisector of the C·O·C angle, then the quantities $2b_{xx} - b_{yy} - b_{zz}$ will be, for both segments, given by $4{\cdot}71 \cos^2\theta - 1{\cdot}57$, where the C·C·C and C·O·C angles are 2θ, b_{xx} is the polarisability in the x direction (collinear with μ_{COC}), b_{zz} is the polarisability in the z direction (perpendicular to the C·C·O·C plane), and when the anisotropic polarisabilities of C–H, C–C, and C–O bonds as listed by Le Fèvre[20] are used. The contributions which individual segments may make to the anisotropy of a macromolecule incorporating them must involve the segmental polarisabilities (b_{xx}, b_{yy}, and b_{zz}), and the signs and magnitudes of observed molar Kerr constants should reflect, at least partially, summations of factors such as $\mu_x^2(2b_{xx} - b_{yy} - b_{zz})$. It is therefore relevant that when 2θ is 109, 110, 120, or 122°, $2b_{xx} - b_{yy} - b_{zz}$ becomes respectively $+0{\cdot}02$, $-0{\cdot}02$, $-0{\cdot}39$, or $-0{\cdot}46 \times 10^{-24}$ cm^3. Such results are reconcilable with experiment. By assuming that the molecular polarisability ellipsoids of PEGs and PPGs have semi-axes $b_1 \neq b_2 = b_3$ and that the resultant moments are μ_1 (with $\mu_2 = \mu_3 = 0$) we obtain (using[8] the molar Kerr constants, refractions, *etc.*, recorded for the PEGs in ref. 1 and for the PPGs in Table 1 of this paper) estimates of b_1 and b_2 as in Table 3. The quotients b_1/x and b_2/x are close to the magnitudes of the b_{xx} values and the means of the b_{yy} and b_{zz} values calculable for planar $CH_2{\cdot}CH_2O{\cdot}C$ and $CH_2{\cdot}CHMe{\cdot}O{\cdot}C$ segments. For 2θ values near the tetrahedral angle b_{xx}, b_{yy} and b_{zz} lie around 4·3, 4·8, 3·8, and 6·1, 6·4, 5·8 in the two series. That the measured $_{\mathrm{m}}K$ values are not larger is explained by the low segmental anisotropies; a trivial widening of 2θ can account for the observed changes of algebraic sign.

TABLE 2

Observed and calculated quantities compared

	PPG I	PPG II	PPG III	PPG IV	PPG V	PPG VI
$\alpha\varepsilon_1$ (calc.) *	3·38	2·45	2·33	2·05	1·93	1·89
β (calc.) *	0·1288	0·1307	0·1313	0·1339	0·1364	0·1385
$-\gamma n_1$ (obs.)	0·052	0·044	0·044	0·043	0·038	0·037
$-\gamma n_1$ (calc.)	0·052	0·045	0·045	0·041	0·038	0·036
δ (calc.) *	0·777	0·340	0·190	−0·333	−0·856	−1·289
$_\infty r_2$ (obs.)	0·261	0·266	0·266	0·266	0·268	0·268
$_\infty r_2$ (calc.)	0·262	0·265	0·265	0·267	0·268	0·269
$_\infty p_2$ (obs.)/cm^3	0·935	0·748	0·736	0·688	0·663	0·642
$_\infty p_2$ (calc.)/cm^3	0·932	0·748	0·724	0·670	0·650	0·646
$10^{14}{}_\infty({}_sK_2)$ (obs.)	0·94	0·19	0·11	−2·55	−6·63	−10·52
$_\infty({}_sK_2)$ (calc.)	0·78	0·77	0·06	−3·09	−6·84	−10·16
μ (calc.)/D *	3·60	4·75	5·20	6·29	7·42	8·34

* For observed values see Table 1.

TABLE 3

Polarisability semi-axes *

Solute †	$(b_1 - b_2)$	$(b_1 + 2b_2)$	b_1	b_2	x	b_1/x	b_2/x
PEG 200	0·61	54·22	18·48	17·87	4·1	4·51	4·36
PEG 300	0·36	83·03	27·92	27·56	6·4	4·36	4·30
PEG 800	0·45	218·70	73·20	72·75	17·8	4·11	4·09
PEG 1500	0·11	408·37	136·20	136·09	33·7	4·04	4·04
PEG 4000	−0·18	950·94	316·86	317·04	78·0	4·06	4·06
PEG 6000	−0·34	1913·91	637·74	638·08	153·0	4·17	4·17
PPG I	0·02	118·61	39·55	39·53	6·59	6·00	6·00
PPG II	0·01	300·48	100·17	100·16	16·93	5·92	5·92
PPG III	0·00	360·36	120·12	120·12	20·38	5·89	5·89
PPG IV	−0·12	599·84	199·87	199·99	34·17	5·85	5·85
PPG V	−0·32	907·10	302·15	302·47	51·41	5·88	5·88
PPG VI	−0·54	1208·72	402·55	403·09	68·66	5·86	5·87

* Polarisabilities b_1 or b_2 are in 10^{-24} cm^3. † Source data for the PEGs are in ref. 1.

[2/1155 *Received, 22nd May,* 1972]

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