295. *Molecular Polarisability. The Specific Kerr Constants and Polarisations of Various Polystyrenes dissolved in Carbon Tetrachloride.*

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Styrene, and four polystyrenes with (viscosity) molecular weights up to 250,000, have been examined. Empirical relations between $\log_{10}(M_x/M)$ and ${}_{\infty}p_2$, r_2, β, or ${}_{\infty}({}_{s}K_2)$ can be established. The polystyrenes are considered to be polar molecules with moments given roughly by $\bar{\mu}^2 = 0{\cdot}56N\mu^2$, where N is the number of phenyl groups per molecule and μ is 0·35 D. The anisotropy of polystyrenes diminishes with increase of molecular weight and is always less than that of the monomer. Calculations from link and other polarisabilities indicate that the smaller polystyrenes are relatively more extended than are the larger. Present observations are qualitatively reconcilable with known data concerning the polystyrenes (streaming double refraction, depolarisation of scattered light, etc.).

Hitherto the shapes or configurations of macromolecules in solution have largely been deduced from viscosity, diffusion, sedimentation, osmotic pressure, dielectric dispersion, light scattering, or flow birefringence. Conclusions from different methods applied to the same solute have not always been consistent, so additional techniques should be valuable. The Kerr effect[1] appears particularly relevant, and we now report results for polystyrenes in carbon tetrachloride. We do not regard these polystyrenes as isotactic.

Experimental

Apparatus and Methods.—These were as described in the references indicated: dielectric constants,[2] electric double refractions,[1,3] extrapolation procedures and calculations.[1,3,4,5] Refractive indexes were measured on an Abbé refractometer. Experimental techniques are described in refs. 1, 3, and 4, wherein also the symbols are defined. Carbon tetrachloride was dried ($CaCl_2$) and fractionated through a 1 m. column packed with glass helices.

Solutes.—Styrene was distilled, to remove stabiliser, before use (b. p. 34—35°/10 mm. or 145°/760 mm.). The four polystyrenes, designated *A*, *B*, *C*, and *D*, were obtained as follows: *A* by the polymerisation of styrene in carbon tetrachloride containing aluminium chloride;[6] *B* by using stannic chloride and Williams's directions;[7] *C* by the heating together at 100° for

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[1] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.

[2] Buckingham, Chau, Freeman, Le Fèvre, Narayana Rao, and Tardif, *J.*, 1956, 1405.

[3] Le Fèvre and Le Fèvre, *J.*, 1953, 4041.

[4] Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953.

[5] Harris, Le Fèvre, and Sullivan, *J.*, 1953, 1622.

[6] Jordan and Mathieson, *J.*, 1952, 611.

[7] Williams, *J.*, 1938, 246, 1046.

2 hr. of styrene with 1% w/w of benzoyl peroxide. Polymers *A*, *B*, and *C* were purified by precipitation from their solutions in carbon tetrachloride by methanol, filtration, and drying to constant weight. Sample *D* was "Starex," given to us by C.S.R. Chemicals Pty. Ltd. Infra-red spectra (of mulls in "Nujol" or solutions in carbon tetrachloride, on a Perkin-Elmer No. 21 spectrometer) conformed with published [8] data for polystyrene and with one another, save that *C* displayed a very weak absorption in the region appropriate to C=O groups. Presumably catalyst fragments were incorporated in the polymer since Barson and Bevington [9] (cf. Bevington and Brooks [10]) found that [*carboxy*-^{14}C]benzoyl peroxide catalyses the production, in benzene at 60°, of radioactive polystyrenes; they conclude that, of the radicals which initiate polymerisation, 85% are benzoate and 15% are phenyl.

TABLE 1. *Dielectric constants * and densities * of solutions in carbon tetrachloride at 25°.*

Styrene monomer

10^6w_2 ...	5566	10,432	16,418	17,235
ε	—	2·2309	2·2332	2·2336
d_4^{25}	1·5778	1·5724	1·5655	1·5646

Whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}3788$; $\sum\Delta d/\sum w_2 = -1{\cdot}162$

Polystyrene A

10^6w_2 ...	5040	8120	13,100	14,760	21,000	21,420
ε	2·2305	2·2325	2·2361	—	—	—
d^2	1·5805	1·5780	1·5740	1·5731	$1{\cdot}5683_5$	1·5677

Whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}6893$; $\Delta d = -0{\cdot}7891w_2 + 0{\cdot}035w_2^2$

Polystyrene B

10^6w_2 ...	3806	4210	5621	5876	7870	10,025	11,195	11,600	15,630	21,490
ε	2·2295	2·2302	2·2304	2·2306	2·2333	2·2336	2·2353	2·2355	2·2365	2·2407
d_4^{25}	1·5821	1·5809	1·5810	1·5807	1·5787	1·5783	1·5770	1·5762	1·5740	1·5699

Whence $\Delta\varepsilon = 0{\cdot}7422w_2 - 5{\cdot}19w^2$; $\Delta d = -0{\cdot}6809w_2 + 0{\cdot}168w_2^2$

Polystyrene C

10^6w_2 ...	4420	5508	5817	7818	9099	9728	10,863	12,472	13,200	15,873
ε	2·2298	2·2306	2·2306	2·2318	2·2325	2·2327	2·2328	2·2335	2·2339	2·2349
d_4^{25}	1·5821	1·5813	1·5808	1·5806	1·5791	1·5782	1·5784	1·5771	1·5775	1·5763

Whence $\Delta\varepsilon = 0{\cdot}7107w_2 - 14{\cdot}0w_2^2$; $\Delta d = -0{\cdot}6471w_2 + 7{\cdot}39w_2^2$

Polystyrene D

10^6w_2 ...	4150	4662	5937	6412	7165	8245	10,376	13,106	13,341	13,572
ε	2·2297	2·2299	—	2·2312	2·2320	—	2·2335	2·2352	2·2357	—
d_4^{25}	1·5815	1·5813	1·5804	1·5807	1·5796	1·5788	1·5779	1·5774	1·5761	1·5749
10^6w_2 ...	15,335	17,084	22,176	25,850	28,002					
ε	—	—	—	2·2433	—					
d_4^{25}	1·5738	1·5725	1·5689	1·5665	1·5633					

Whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}6407$; $\Delta d = -0{\cdot}5724w_2 - 0{\cdot}062w_2^2$

* For $w_2 = 0$, $\varepsilon = 2{\cdot}2270$, $d_4^{25} = 1{\cdot}5845$.

Molecular weights were estimated viscosimetrically at 25°, the equations used being, for benzene solutions [6] of *A*:

$$(\eta_{sp}/c)_{c\to 0} = 0{\cdot}0115 + 1{\cdot}81 \times 10^{-5}M$$

(where *c* is the concentration in g. per 100 c.c. of solution), for carbon tetrachloride solutions [7] of *B* and *C*:

$$\eta_{sp}/c = 2{\cdot}5 \times 10^{-2}n + 0{\cdot}2$$

(where *c* is the concentration in base-moles l.$^{-1}$ and *n* is the average degree of polymerisation), and for carbon tetrachloride solutions [11] of "Starex":

$$(\eta_{sp}/c)_{c\to 0} = 1{\cdot}7 \times 10^{-4}M^{0{\cdot}69}$$

(where *c* is in g. per 100 c.c.).

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[8] American Petroleum Institute Research Project 44, Nat. Bur. Stand., Washington, 1950, No. 171.

[9] Barson and Bevington, *J. Polymer Sci.*, 1956, **20**, 133.

[10] Bevington and Brooks, *ibid.*, 1956, **22**, 257.

[11] Outer, Carr, and Zimm, *J. Chem. Phys.*, 1950, **18**, 830.

Experimentally, the left-hand sides of the above equations were respectively 0·0269, $0{\cdot}798_5$, $2{\cdot}12_5$, and 0·902 (for *A* and *D* extrapolation [12] was performed graphically, and for *B* and *C* the values shown are means of η_{sp}/c), whence weight-average molecular weights are 900 for *A*, 2500 for *B*, 8000 for *C*, and 250,000 for *D*.

TABLE 2. *Electric birefringences and refractive indexes of solutions in carbon tetrachloride * at 25°.*

Styrene monomer

$10^5 w_2$ ...	1081	1894	1957	3564	4186	5435
$10^7 \Delta B$ ...	0·020	0·035	0·039	0·067	0·084	0·106
$10^4 \Delta n_D$ ...	16	29	29	52	62	79

Whence $10^7 \Delta B = 1{\cdot}88_5 w_2 + 1{\cdot}4_4 w_2{}^2$; $\sum \Delta n / \sum w_2 = 0{\cdot}147$

Polystyrene A

$10^5 w_2$ ...	701	897	1476	2100	2142	2384	2863
$10^7 \Delta B$ ...	0·006	0·008	0·013	$0{\cdot}017_5$	0·018	—	0·021
$10^4 \Delta n_D$ ...	—	—	—	45	46	52	—

Whence $10^7 \Delta B = 1{\cdot}010 w_2 - 9{\cdot}13 w_2{}^2$; $\sum \Delta n / \sum w_2 = 0{\cdot}216$

Polystyrene B

$10^5 w_2$ ...	274	322	508	1147	1526	2014	2518
$10^7 \Delta B$ ...	—	0·003	0·005	0·011	0·012	0·015	0·018
$10^4 \Delta n_D$ ...	6	—	9	22	32	—	—

Whence $10^7 \Delta B = 1{\cdot}00_1 w_2 - 11{\cdot}9 w_2{}^2$; $\sum \Delta n / \sum w_2 = 0{\cdot}200$

Polystyrene C

$10^5 w_2$ ...	1007	1528	2173	2477	2532	2970	3588	3872
$10^7 \Delta B$ ...	0·005	0·008	0·016	0·018	0·018	0·019	0·021	0·022
$10^4 \Delta n_D$ ...	—	—	—	54	54	62	72	

Whence $10^7 \Delta B = 0{\cdot}773_6 w_2 - 4{\cdot}76 w_2{}^2$; $\sum \Delta n / \sum w_2 = 0{\cdot}209$

Polystyrene D

$10^5 w_2$ ...	716	717	777	946	1573	1743	2097	2111	2294	3722
$10^7 \Delta B$ ...	0·004	0·004	0·006	0·009	0·011	0·012	0·014	0·014	0·019	0·025
$10^4 \Delta n_D$ ...	—	—	15	—	37	—	—	51	—	82

Whence $10^7 \Delta B = 0{\cdot}752_1 w_2 - 1{\cdot}94 w_2{}^2$; $\sum \Delta n / \sum w_2 = 0{\cdot}226$

* For $w_2 = 0$, $B_1 = 0{\cdot}070 \times 10^{-7}$, $n_D^{25} = 1{\cdot}4575$.

Dielectric constants, densities, electric birefringences, and refractive indexes for the monomer and polystyrenes *A*, *B*, *C*, and *D*, are recorded in Tables 1 and 2. Table 3 presents results.

TABLE 3. *Specific polarisations, refractions, and Kerr constants at infinite dilution in carbon tetrachloride.*

Solute	M_2	$(\alpha\varepsilon_1)_{w=0}$	$(\beta)_{w=0}$	γ	$(\delta)_{w=0}$	${}_\infty p_2$ (c.c.)	r_2 (c.c.)	$10^{12}{}_\infty({}_sK_2)$
Styrene	104·1	0·379	−0·733	0·101	26·93	0·3577	0·3462	$0{\cdot}212_5$
Polystyrene *A*	900	0·689	−0·498	0·148	14·43	0·3475	0·3283	0·116
,, *B*	2500	0·742	−0·430	0·137	14·30	0·3405	0·3113	0·114
,, *C*	8000	0·711	−0·408	0·143	11·05	0·3333	0·3106	0·090
,, *D*	250,000	0·641	−0·361	0·155	10·74	0·3172	0·3081	0·087

DISCUSSION

Styrene.—Of the seven references to styrene given by Wesson [13] one deals with the gas and six with the polarisation in solution in benzene. Gorman, Davis, and Gross [14] quote in addition ${}_TP_{30}$ as 37·9 c.c. in carbon tetrachloride—apparently the only previous result in this solvent. Sakurada and Lee's [15] paper is not cited. Everard, Kumar, and Sutton [16] (since ref. 13 appeared) reported the polarisation in benzene at 25° to be 37·0 c.c.—a value

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[12] Martin, *J. Polymer Sci.*, 1953, **10**, 126.

[13] Wessen, "Tables of Electric Dipole Moments," Technology Press, Massachusetts Institute of Technology, 1948.

[14] Gorman, Davis, and Gross, *Physikal. Z.*, 1938, **39**, 181.

[15] Sakurada and Lee, *Z. phys. Chem.*, 1939, *B*, **43**, 245.

[16] Everard, Kumar, and Sutton, *J.*, 1951, 2807.

in harmony with ours (37·2 c.c.) in carbon tetrachloride at the same temperature. Sutton and his co-workers comment on the smallness of moment indicated (R_D is *ca.* 36·5 c.c.) but conclude that it is probably not zero. Von Hippel and Wesson [17] find $\mu = 0{\cdot}12 \pm 0{\cdot}03$ D by the dielectric loss method.

Polystyrenes.—The dielectric polarisation of polystyrenes was examined by Gallay [18] and by Sakurada and Lee.[15] Both investigations were made in benzene as solvent; they disagree in that by the former the specific polarisation of the monomer is less, and by the latter greater, than the observed values for the polymers (see Table 4).

TABLE 4. *Specific polarisations of styrene and polystyrenes in benzene previously reported.*

	Gallay [18]				Sakurada and Lee [15]		
M	104	2820	7750	23,000	104	12,900	42,900
Sp. polarisn. × 10 (c.c.)	3·83	5·74	4·57	3·60	3·678	3·335	3·410

Table 3 shows that, in carbon tetrachloride, ${}_{\infty}p_2$ diminishes as M increases. A smooth relation between ${}_{\infty}p_2$ and $\log_{10}(M_x/M)$ (or $\log_{10} M_x$) can be extracted empirically, as also for the specific refraction, density factor β, and specific Kerr constant ${}_{\infty}({}_sK_2)$ (the last two at infinite dilution). Table 5 summarises these findings, and present equations of possible use in the estimation of molecular weights or degrees of polymerisation, as density or refractive-index measurements are no more difficult to make than those involved in the conventional viscosity method.

TABLE 5. *Relations * between properties and* log (M_x/M).

Density: $(\beta)_{w_2=0} = -0{\cdot}733 + 0{\cdot}283L - 0{\cdot}052L^2$
Specific refraction: $r_2 = 0{\cdot}346 - 0{\cdot}027L + 0{\cdot}005L^2$
Specific polarisation: ${}_{\infty}p_2 = 0{\cdot}3577 - 0{\cdot}0104L - 0{\cdot}0006L^2$
Specific Kerr constant: ${}_{\infty}({}_sK_2) = (0{\cdot}21 - 0{\cdot}11L + 0{\cdot}02L^2) \times 10^{-12}$

Polystyrene	β (calc.)	β (obs.)	r_2 (calc.)	r_2 (obs.)	${}_{\infty}p_2$ (calc.)	${}_{\infty}p_2$ (obs.)	${}_{\infty}({}_sK_2)$ (calc.)	${}_{\infty}({}_sK_2)$ (obs.)
A	−0·514	−0·498	0·325	0·328	0·347	$0{\cdot}347_5$	0·13	0·12
B	−0·444	−0·430	0·318	0·311	0·342	$0{\cdot}340_5$	0·10	0·11
C	−0·385	−0·408	0·312	0·311	0·336	0·333	0·08	0·09
D	−0·371	−0·361	0·312	0·308	0·316	0·317	0·08	0·09

* $L = \log_{10}(M_x/M)$.

On the basis of the polarisations listed in Table 3 it is difficult to decide whether polystyrenes should be adjudged polar or non-polar. Were r_2 identical with the specific distortion polarisation, then $\mu = 0{\cdot}22\,[M_2(p_2 - r_2)]^{0\cdot5}$ would be, for the monomer and specimens *A*, *B*, *C*, and *D*, in turn, $0{\cdot}2_4$, 0·9, 1·9, 3·0, and *ca.* 10 D. Gallay [18] and Sakurada and Lee [15] proceeded thus and respectively reported moments, rising with molecular weights, from 0·56 to 8·61 (maximum M, 23,000) and 0·1 to 1·83D (maximum M, 42,900). However, in Table 3 one only has to take ${}_DP$ as $1{\cdot}03R$ to make the moment of " Starex " appear zero. In the absence of information concerning the correct ${}_DP/R$ ratios for the polystyrenes it is interesting to apply Debye and Bueche's theory.[19] By this the average moment $\bar{\mu}$ of a polymer molecule is given by:

$$\bar{\mu}^2 = (\mu^2 N)\,[1 + 2p\cos\beta\cos\gamma/(1 - p^2)]$$

where a moment " comes off " every other carbon atom at an angle γ with the preceding C–C bond and an angle β with the following C–C bond, p is the cosine of the valency angle (*i.e.*, 1/3 for a C–C chain), and N is the number of dipoles on the chain; free rotation is assumed (*i.e.*, each chain carbon atom rotates freely on the valency cone, restricted only by the C–C–C bond distances' and angles' being preserved). Insertion of β = *ca.* 70° and γ = *ca.* 110° requires $\bar{\mu}^2/N\mu^2$ to be 0·92. The obvious value for μ is that for ethylbenzene, whose structure most closely resembles the $-CH_2-CHPh-$ group making up the polystyrenes. Two estimates of $\mu_{\text{ethylbenzene}}$ are available,[13] 0·58 D for the gas and 0·35 D

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[17] Von Hippel and Wesson, *Ind. Eng. Chem.*, 1946, **38**, 1121.
[18] Gallay, *Kolloid Z.*, 1931, **57**, 1.
[19] Debye and Bueche, *J. Chem. Phys.*, 1951, **19**, 589.

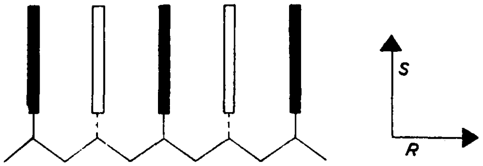
for the liquid. Adopting the lower of these we obtain the figures under $\bar{\mu}_{\text{free}}$ in Table 6. Since Debye and Bueche found $\bar{\mu}^2/N\mu^2$ for poly-*p*-chlorostyrene to be 0·56, not 0·92, by experiment, calculations on this basis are also included under $\bar{\mu}_{\text{restr.}}$. Rough " order of magnitude " agreement between the three sets of μ's is seen, supporting a conclusion that the polystyrenes are polar molecules.

TABLE 6. *Estimations of mean moments of polystyrenes, complete or limited flexibility being assumed.*

Polystyrene	N	$\bar{\mu}_{\text{free}}$	$\bar{\mu}_{\text{restr.}}$	$\bar{\mu}_{\text{expt.}}$*
A	9	1·0	0·8	0·9
B	25	1·7	1·3	1·9
C	80	3·0	2·3	2·0
D	2500	17	13	10

* Maximum estimates by uncorrected refractivity method.

Extant evidence on their configurations consistently indicates them to be not completely flexible; detailed information on this point, however, varies. Debye and Bueche [19] infer for poly-*p*-chlorostyrene that the chain repeats itself every four C–C links and that each component moment vibrates about a mean position through a free angle of *ca.* 65°. It is reasonable to suppose that the configuration of a polystyrene will resemble that of its *p*-chloro-derivative. *X*-Ray work [20, 21, 22] has revealed no clear signs of order in *solid* polystyrene, but this is probably irrelevant since it is known that in a solution the solvent can cause uncoiling or extension of the solute.[23] Bueche,[24] from light-scattering studies, decided that polystyrene of *M ca.* 10^6 in benzene or carbon tetrachloride shows a considerable degree of stiffening, corresponding to oscillations around C–C bonds of about 200° instead of the 360° required for complete flexibility. Doty, Affens, and Zimm,[25] by light-scattering and other methods, considered the r.m.s. separations of the ends of polystyrene molecules to be *at least* 3·5 times as large as those expected for " random walk " free-rotation no-hindrance structures. Using scale models of polystyrene, Outer, Carr, and Zimm [11] noted that during intramolecular rotation only about 100° was clear before a phenyl group collided with other portions of the chain.



During the present work measurements of the electric double refraction of polystyrene have been made for the first time (Errera, Overbeck, and Sack [26] having failed to observe an effect with a 10% solution in benzene of a specimen of *M ca.* 30,000). The results in Table 3 provide molar Kerr constants at infinite dilution and molecular refractions; these, combined with the estimates of dipole moments in the fifth column of Table 6, permit calculation of semi-axes of the apparent polarisability ellipsoids for the samples *A* to *D*, provided that two semi-axes are equal to each other. Such an assumption seems intuitively justifiable with molecules as large as those under consideration. It can be formally investigated by imagining a polystyrene chain unfolded to the maximum extent allowed by the normal C–C–C angles (see the Figure, in which phenyl groups and the C–C bonds linking them to the zig-zag backbone are projecting alternately above and below the plane

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[20] Katz, *Trans. Faraday Soc.*, 1936, **32**, 86.
[21] Bunn, *J.*, 1947, 297.
[22] Charlesby, *J. Polymer Sci.*, 1953, **10**, 201.
[23] Bawn, " The Chemistry of High Polymers," Butterworths, London, 1948, p. 168.
[24] Bueche, *J. Amer. Chem. Soc.*, 1949, **71**, 1452.
[25] Doty, Affens, and Zimm, *Trans. Faraday Soc.*, 1946, **42***B*, 66.
[26] Errera, Overbeck, and Sack, *J. Chim. phys.*, 1935, **32**, 681.

of the paper at angles of 55°). Polarisabilities along three mutually perpendicular directions R, S, T then follow (by methods often illustrated before [1, 27]) as:

$$b_R = N\,[4b_L^{CC}/3 + 2b_T^{CC}/3 + b_T^{CC} + b_3^{Ph} + 8b^{CH}]$$
$$b_S = N\,[b_L^{CC} + 2b_T^{CC} + b_1^{Ph}/3 + 2b_2^{Ph}/3 + 8b^{CH}]$$
$$b_T = N\,[7b_T^{CC}/3 + 2b_L^{CC}/3 + 2b_1^{Ph}/3 + b_2^{Ph}/3 + 8b^{CH}]$$

where N denotes the number of phenyl groups. Insertion of the values [27, 28] $b_1^{Ph} = b_2^{Ph} = 0{\cdot}733$, $b_3^{Ph} = 0{\cdot}352$, $b_L^{CC} = 0{\cdot}0986$, $b_T^{CC} = 0{\cdot}0274$, $b^{CH} = 0{\cdot}0635$ (all $\times\ 10^{-23}$ c.c.) then yields $10^{23}b_R = 1{\cdot}037N$, $10^{23}b_S = 1{\cdot}394N$, and $10^{23}b_T = 1{\cdot}371N$. Thus even for the configuration sketched, two semi-axes (S and T) show near-equality and exceed the third (R). Since, in reality, configurations are probably between this extreme on one hand, and a random coil (for which $b_R = b_S = b_T$) on the other, the assumption made above (that two semi-axes are equal) may be safely used to reduce the three " unknowns " (b_1, b_2, b_3) to two ($b_1 = b_2$, b_3). From the geometry of a molecule as in the Figure the resultant dipole moment will act in the direction S; following our usual convention b_1 is therefore along S, b_2 along T, and b_3 along R. The data of Table 3 provide numerical values for $2b_1 + b_3$ and for $\theta_1 + \theta_2$; in its expanded form (see ref. 1) the last quantity can yield the difference $b_1 - b_3$, for which alternative solutions are obtained (as the equation involved is quadratic).

Table 7 shows the individual semi-axes resulting, those produced by taking $b_1 - b_3$ as negative being in parentheses. In the light of the foregoing discussion we believe $b_1 - b_3$ is properly regarded as positive. Table 8 compares the b's so obtained with those required by $b_1 = b_2 = 1{\cdot}38N$, and $b_3 = 1{\cdot}04N$. The predictions are correct in order of magnitude. Table 8 also suggests that the polystyrenes of lower molecular weights are relatively more extended than those of higher molecular weight.

TABLE 7. *Polarisability semi-axes and anisotropies of polystyrenes A, B, C, D.*

Sample	$10^{23} \times (2b_1 + b_3)$	$10^{23}b_1$	$10^{23}b_3$	b_1/b_3 *	$10^3\delta^2$
A	35·1	12·08 (11·02)	10·98 (13·10)	1·10	1·96
B	92·5$_5$	31·23 (29·01)	30·09 (34·53)	1·04	0·30
C	295·5	98·92 (94·11)	97·63 (106·7)	1·01	0·04
D	9159	3054 (3011)	3051 (3137)	1·00	*ca.* 0

* b_1/b_3 for the configuration of the Figure is about 1—3.

TABLE 8. *Comparison of semi-axes calculated and found.*

Polystyrene	*A*	*B*	*C*	*D*
N	9	25	80	2500
b_1 (calc.)	12·4	34·5	110	3450
,, (found)	12·1	31·2	98·9	3054
b_3 (calc.)	9·4	26·0	83·2	2600
,, (found)	11·0	30·1	97·6	3051

As the molecular weight rises the anisotropy diminishes. This is displayed by the ratios b_1/b_3 and by the calculated values of $10^3\delta^2$ (Table 7); it is moreover consistent with published observations on the depolarisation of light scattered by polystyrene solutions. Zvetkov,[29] in a study of the polymerisation of styrene, has noted that the optical anisotropy (indicated by depolarisation factors, Δ; see ref. 30 for definitions) of the macromolecules is much less than that of the monomer. Doty and Kaufman,[31] using solutions in toluene and

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[27] Le Fèvre and Le Fèvre, *J.*, 1956, 3549.
[28] Le Fèvre and Le Fèvre, *J.*, 1954, 1577.
[29] Zvetkov, *Acta Physicochim. U.R.S.S.*, 1946, **21**, 188.
[30] Le Fèvre and Rao, *J.*, 1957, 3644.
[31] Doty and Kaufman, *J. Phys. Chem.*, 1945, **49**, 583.

ethyl methyl ketone, report that larger molecules are more isotropic. High scattering power and negligible depolarisation are described by Carr and Zimm[32] for solutions of commercial polystyrenes (Dow Styron) in butanone, dichloroethane, or toluene.

Under the conditions used to detect flow birefringence (cf. review by Cerf and Scheraga[33] for references) polystyrene usually[34] behaves negatively, *i.e.*, the refractive index of the molecule appears less along than across its length. This also is to be expected from calculations above especially if the polymer is additionally stretched from the random-coil type of configuration by the action of the tensions and pressures exerted under the velocity gradients imposed in such experiments (cf. Derf,[35] Zvetkov and Savvon[36]). The flow birefringence of polystyrenes in relation to their molecular weights does not seem to have been fully studied. Zvetkov and Frisman[37] examined monomer–polymer mixtures at different stages of the polymerisation process and found the initially positive birefringences to diminish and change sign as the reaction proceeded. According to Čopič[34] a polystyrene of $M = 3 \times 10^5$ (roughly that of our "Starex") was negative at all velocity gradients in dioxan, although a sample of $M = 8 \times 10^6$ only became negative at higher gradients (when presumably deformation was occurring of what, by inference from Table 7, would seem to be an isotropic, albeit flexible, molecule.

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[32] Carr and Zimm, *J. Chem. Phys.*, 1950, **18**, 1616.
[33] Cerf and Scheraga, *Chem. Rev.*, 1952, **51**, 185.
[34] Čopič, *J. Polymer Sci.*, 1956, **20**, 593.
[35] Cerf, *ibid.*, 1954, **12**, 15, 35.
[36] Zvetkov and Savvon, *Zhur. tekh. Fiz.*, 1956, **26**, 348; *Chem. Abs.*, 1957, **51**, 31e.
[37] Zvetkov and Frisman, quoted in ref. 33.