112. *Molecular Polarisability: the Molar Kerr Constants, Apparent Dipole Moments, etc., of Indene and Eight Polyindenes as Solutes in Benzene.*

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The apparent dipole moments and molar Kerr constants are reported for eight polyindenes with molecular weights between 400 and 4200. Empirical connections are found between degrees of polymerisation and various physical properties, including m. p.s. The moments appear rather insensitive to molecular weights. The molar Kerr constants change algebraic signs as the molecular weight increases from 2700 to 3500. No definite conformational pattern for the polyindenes can be inferred from present measurements. The observed molar Kerr constant of indene can be satisfactorily predicted from the known polarisabilities of benzene and the C–C, C=C, and C–H bonds.

ELECTRIC-BIREFRINGENCE measurements [1,2] of solutions of macromolecular polyvinyls have so far always indicated low anisotropies of polarisability for the solutes, even when the smallest repeating units in the polymers separately display this property quite strongly. This is understandable since with incompletely flexible chains the higher the degree of polymerisation (D.P.) the wider will be the variations of the angles between the principal axes of the ellipsoids of the individual segments and some arbitrary line (*e.g.*, the end-to-end line in the polymer molecule). Unfortunately the polyvinyl halides, polyacrylates, etc., studied earlier,[2] have all had high D.P.s and it seemed of interest, therefore, to examine cases where specimens having relatively small molecular weights could be readily obtained. For reasons given in refs. 3 and 4 the polyindenes seemed suitable.

EXPERIMENTAL

Solutes.—Indene, dried over magnesium sulphate, was twice fractionated (30 cm. " Quickfit " Dufton column) in a nitrogen atmosphere. The cut having b. p. 181°/760 mm., n_D^{25} 1·5755, d_4^{25} 0·9813, was stored under nitrogen in sealed tubes at 0° in the dark.

Polymers I—III, of low molecular weight, were prepared thermally: monomer (60 g.) and benzoyl peroxide (0·6 g.) were heated at 180—200° for 24 hr. under reflux in a slow stream of oxygen-free nitrogen. The light brown viscous material obtained on cooling was dissolved in 1 l. of benzene and fractionally precipitated by the addition of 100 c.c. of absolute ethanol, followed by 175 c.c. and 300 c.c. to the first and the second filtrate, respectively. Each of the three samples was then redissolved in benzene and the process repeated. Finally the polymers were dried to constant weight in a vacuum.

Polymers IV—VIII, of higher molecular weight, were produced catalytically: monomer (100 c.c.), diluted by an equal volume of chloroform and stirred, was treated drop-by-drop with a 20% solution (15 c.c.) of stannic chloride in chloroform. The mixture became red and the excess of chloroform was boiled off. After 1 hr. the brown mass was poured into ethanol; the polyindenes thus separated were extracted by benzene and reprecipitated by ethanol several times to remove catalyst residues. The white mixture so obtained was divided into five portions by dissolution in benzene and successive dilution with 50 c.c. lots of ethanol. The solids were filtered off and dried in a vacuum to constant weight.

The molecular weights of fractions I—VIII were determined cryoscopically in benzene. Analyses for carbon fell between 92 and 94%, with *ca.* 7% of hydrogen (Calc. for C_9H_8: C, 93·1; H, 6·9%). M. p.s were taken in Mason's apparatus; they increased gradually with the molecular weight and lay individually within ranges of 3—4°. The mid-points of these m. p.

[1] Le Fèvre, Le Fèvre, and Parkins, *J.*, 1958, 1468; 1960, 1814.
[2] Le Fèvre and Sundaram, *J.*, 1962, 1494, 4003; 1963, 1880, 3188.
[3] Mark and Raff, " High Polymeric Reactions." Interscience Publ. Inc., New York, 1941, p. 350.
[4] Whitby and Katz, *J. Amer. Chem. Soc.*, 1928, **50**, 1160; *Canad. J. Res.*, 1931, **4**, 344.

ranges are roughly rectilinear with the logarithms of the degrees of polymerisation; D.P.s calculated from the empirical equation,

$$\log (\text{D.P.}) = 0.0934 + 0.005156(\text{m. p.})$$

are included in Table 1 to illustrate this statement.

TABLE 1.

Molecular weights, melting-point ranges, and degrees of polymerisation of polyindene fractions.

Polymer sample	M	M. p. range	D.P. from M	D.P. calc. from m. p. range	Polymer sample	M	M. p. range	D.P. from M	D.P. calc. from m. p. range
I	406	83—87°	3·5	3·4	V	2314	234—237°	20·0	20·2
II	565	116—120	4·9	5·0	VI	2671	250—253	23·0	24·4
III	863	152—156	7·4	7·7	VII	3480	267—270	30·0	29·9
IV	1546	193—196	13·3	12·4	VIII	4150	280—283	36·0	34·8

Measurements and Results.—Table 2 shows the following details for solutions in benzene, at 25°, containing weight-fractions w_2 of indene or its polymers: ΔB, the difference between

TABLE 2.

Refractive indexes, dielectric constants, electric birefringences, etc., of indene and its polymers in benzene at 25°.

Solute: Indene.

$10^5 w_2$	4845	6014	7463	9895	13,292	15,256	18,516
$10^4 \Delta n$	37	45	55	72	99	113	139
$10^4 \Delta n^2$	109	133	162	213	293	334	411
d_{12}	0·87891	0·88016	0·88172	0·88432	0·88810	0·89028	0·89385
ε_{12}	2·3037	2·3126	2·3214	2·3337	2·3613	2·3735	2·3899
$10^{10} \Delta B$	71	91	109	166	230	231	314

whence $\Sigma\Delta n/\Sigma w_2 = 0.074$; $\Sigma\Delta n^2/\Sigma w_2 = 0.220$; $\Sigma\Delta d/\Sigma w_2 = 0.1073$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0.649$; $\Sigma\Delta B/\Sigma w_2 = 1.61 \times 10^{-7}$.

Solute: Polyindene 1.

$10^5 w_2$	1012	2103	3540	5599	8209	10,849
$10^4 \Delta n$	12	23	41	64	95	129
$10^4 \Delta n^2$	35	68	121	189	281	382
d_{12}	0·87602	0·87829	0·88155	0·88606	0·89205	0·89868
ε_{12}	2·2797	2·2877	2·2982	2·3134	2·3324	2·3503
$10^{10} \Delta B$	6	11	20	35	47	63

whence $\Sigma\Delta n/\Sigma w_2 = 0.116$; $\Sigma\Delta n^2/\Sigma w_2 = 0.344$; $\Sigma\Delta d/\Sigma w_2 = 0.2231$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0.724$; $\Sigma\Delta B/\Sigma w_2 = 0.584 \times 10^{-7}$.

Solute: Polyindene II.

$10^5 w_2$	2938	5433	8824	10,777	12,980	14,540	17,190
$10^4 \Delta n$	35	64	105	128	155	174	206
$10^4 \Delta n^2$	104	190	311	380	460	517	612
d_{12}	0·88032	0·88582	0·89325	0·89799	0·90302	0·90599	0·91239
ε_{12}	2·2917	2·3080	2·3297	2·3429	2·3575	2·3672	2·3850
$10^{10} \Delta B$	12	23	38	46	45	63	75

whence $\Sigma\Delta n/\Sigma w_2 = 0.119$; $\Sigma\Delta n^2/\Sigma w_2 = 0.354$; $\Sigma\Delta d/\Sigma w_2 = 0.2231$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0.653$; $\Sigma\Delta B/\Sigma w_2 = 0.431 \times 10^{-7}$.

Solute: Polyindene III.

$10^5 w_2$	1027	1923	2476	3143	3811	4107
$10^4 \Delta n$	12	23	30	39	44	48
$10^4 \Delta n^2$	36	68	89	115	130	142
d_{12}	0·87613	0·87805	0·87936	0·88090	0·88238	0·88308
ε_{12}	2·2787	2·2840	2·2874	2·2914	2·2953	2·2973
$10^{10} \Delta B$	3·0	5·5	7·2	9·4	11·7	12·0

whence $\Sigma\Delta n/\Sigma w_2 = 0.119$; $\Sigma\Delta n^2/\Sigma w_2 = 0.352$; $\Sigma\Delta d/\Sigma w_2 = 0.2250$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0.601$; $\Sigma\Delta B/\Sigma w_2 = 0.296 \times 10^{-7}$.

TABLE 2. *(Continued.)*

Solute: Polyindene IV.

$10^5 w_2$	1143	1212	1824	2351	2811
$10^4 \Delta n$	14	15	22	29	34
$10^4 \Delta n^2$	42	45	65	86	101
d_{12}	0·87643	0·87660	0·87799	0·87932	0·88030
ε_{12}	2·2784	2·2788	2·2822	2·2847	2·2870
$10^{10} \Delta B$	1·2	1·4	2·0	2·4	2·9

whence $\Sigma\Delta n/\Sigma w_2 = 0\cdot122$; $\Sigma\Delta n^2/\Sigma w_2 = 0\cdot363$; $\Sigma\Delta d/\Sigma w_2 = 0\cdot2317$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0\cdot521$; $\Sigma\Delta B/\Sigma w_2 = 0\cdot106 \times 10^{-7}$.

Solute: Polyindene V.

$10^5 w_2$	1026	2011	2881	3504	4715	5460	6853	9220
$10^4 \Delta n$	12	24	35	43	59	67	83	113
$10^4 \Delta n^2$	36	74	104	127	174	198	245	354
d_{12}	0·87623	0·87852	0·88047	0·88207	0·88489	0·88645	0·89002	0·89603
ε_{12}	2·2773	2·2820	2·2858	2·2887	2·2949	2·2973	2·3049	2·3156

whence $\Sigma\Delta n/\Sigma w_2 = 0\cdot122$; $\Sigma\Delta n^2/\Sigma w_2 = 0\cdot362$; $\Sigma\Delta d/\Sigma w_2 = 0\cdot2363$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0\cdot467$.

$10^5 w_2$	3504	5460	6853	9220	11,469	13,256
$10^{10} \Delta B$	−1·8	12·7	−3·5	−4·5	−5·8	−6·7

whence $\Sigma\Delta B/\Sigma w_2 = -0\cdot050 \times 10^{-7}$.

Solute: Polyindene VI.

$10^5 w_2$	1629	2124	2632	3107	3304	3874
$10^4 \Delta n$	19	25	31	37	39	46
$10^4 \Delta n^2$	56	74	92	109	115	136
d_{12}	0·87764	0·87869	0·88000	0·88121	0·88163	0·88306
ε_{12}	2·2783	2·2823	2·2845	2·2865	2·2875	2·2902
$10^{10} \Delta B$	−1·6	−2·2	−2·6	−3·0	−3·3	−4·0

whence $\Sigma\Delta n/\Sigma w_2 = 0\cdot118$; $\Sigma\Delta n^2/\Sigma w_2 = 0\cdot349$; $\Sigma\Delta d/\Sigma w_2 = 0\cdot2365$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0\cdot446$; $\Sigma\Delta B/\Sigma w_2 = -0\cdot100 \times 10^{-7}$.

Solute: Polyindene VII.

$10^5 w_2$	1423	1824	2133	2748	3255	3466
$10^4 \Delta n$	17	24	26	33	40	44
$10^4 \Delta n^2$	50	71	77	98	118	130
d_{12}	0·87716	0·87818	0·87885	0·88027	0·88154	0·88208
ε_{12}	2·2790	2·2807	2·2823	2·2848	2·2874	2·2885
$10^{10} \Delta B$	−2·9	−3·6	−4·3	−5·5	−6·6	−7·0

whence $\Sigma\Delta n/\Sigma w_2 = 0\cdot124$; $\Sigma\Delta n^2/\Sigma w_2 = 0\cdot366$; $\Sigma\Delta d/\Sigma w_2 = 0\cdot2376$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0\cdot456$; $\Sigma\Delta B/\Sigma w_2 = -0\cdot201 \times 10^{-7}$.

Solute: Polyindene VIII.

$10^5 w_2$	1823	2445	2812	3105	3407
$10^4 \Delta n$	21	30	32	38	41
$10^4 \Delta n^2$	62	89	95	112	121
d_{12}	0·87813	0·87958	0·88070	0·88118	0·88167
ε_{12}	2·2807	2·2835	2·2851	2·2864	2·2878
$10^{10} \Delta B$	−5	−6	−7	−8	−9·4

whence $\Sigma\Delta n/\Sigma w_2 = 0\cdot119$; $\Sigma\Delta n^2/\Sigma w_2 = 0\cdot352$; $\Sigma\Delta d/\Sigma w_2 = 0\cdot2374$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0\cdot449$; $\Sigma\Delta B/\Sigma w_2 = -0\cdot260 \times 10^{-7}$.

the Kerr constant of a solution and solvent; Δn and Δn^2, the corresponding data for the refractive indices and their squares (with Na light); and ε_{12} and d_{12}, the dielectric constants and densities, respectively, of each solution. Apparatus, techniques, and methods of calculation are described in refs. 5 and 6. Symbols have been recently listed in *J.*, 1962, 1494. Polarisations, dipole moments, molar Kerr constants, etc., deduced from Table 2, follow as Table 3.

[5] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953, Ch. 2.
[6] Le Fèvre and Le Fèvre, (*a*) *Rev. Pure Appl. Chem.*, 1955, **5**, 262; (*b*) Ch. XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ. Inc., New York, 3rd edn., Vol. I, p. 2459.

TABLE 3.

Polarisations, refractions, dipole moments, and molar Kerr constants of indene and its polymers at infinite dilution in benzene at 25°.

Solute	Indene	I	II	III	IV	V	VI	VII	VIII
$\alpha\varepsilon_1$	0·649	0·724	0·653	0·601	0·521	0·467	0·446	0·456	0·449
β	0·1227	0·2553	0·2554	0·2575	0·2651	0·2704	0·2707	0·2719	0·2716
γ	0·050	0·078	0·080	0·079	0·082	0·082	0·079	0·083	0·080
δ	3·926	1·424	1·052	0·722	0·259	−0·122	−0·244	−0·490	−0·634
∞p_2 (c.c.)	0·4211	0·3901	0·3766	0·3662	0·3486	0·3365	0·3324	0·3340	0·3328
∞r_2 (c.c.)	0·3359	0·3151	0·3171	0·3159	0·3155	0·3136	0·3110	0·3139	0·3113
$10^{14}({}_s K_2)$	33·60	13·18	10·60	8·27	4·98	1·63	1·425	−0·51	−1·55
M_2	116	406	565	863	1546	2314	2671	3480	4150
$10^{12}({}_m K_2)$	39·0	53·5	59·9	71·4	77·0	37·7	37·9	−17·1	−64·3
${}_T P$ (c.c.)...	48·9	158·4	212·8	316·0	538	779	888	1162	1381
R_D (c.c.)...	39·0	127·9	179·2	272·6	448	726	831	1092	1292
${}_o P$ (c.c.)...	7·9	24·1	24·7	29·7	26·7	16·8	15·7	15·3	24·7
μ (D) * ...	0·62₃	1·08	1·10	1·21	1·14	0·91	0·88	0·87	1·10

* Calc. by assuming the distortion polarisation to be $1·05 R_D$.

DISCUSSION

Polarity and Polarisability of Indene.—The literature contains four [7-10] estimates of the dipole moment of indene. These range from 0·40 to 0·85 D, the two [7,9] values obtained in benzene being 0·40 and 0·67 D. Our redetermination approaches that recorded in ref. 9, and would be identical if $_D P$ were $1·02 R_D$ instead of $1·05 R_D$. The molecular refraction calculated from bond data [11] for the D line is 37·68 c.c., compared with the 38·96 c.c. computed from the measurements in Table 1; a polarisability exaltation Δb of some 0·152 unit is thus indicated. (Polarisabilities are quoted here and subsequently as 10^{-23} c.c. units.)

The deduction *a priori*, from the polarisability ellipsoids for benzene [12] and the C–H, C–C, and C=C bonds,[13] of b_1, b_2, and b_3 for indene is handicapped by lack of structural information for this hydrocarbon. After consideration of details given in ref. 14 for fluorene, isatin, dibromoindane, etc., we take inter-valency angles as 120° in the 6-ring and as for fluorene in the 5-ring (*viz.*, $a = 105·6°$, $b = e = 109·6°$, $c = d = 107·6°$). The mutually perpendicular axes X, Y, and Z required to define the locations of b_1, b_2, and b_3, and μ_1, μ_2, and μ_3 are placed with Y parallel to the 8,9-bond and X at 90° to Y in the molecular plane. Neither the direction of operation of Δb nor μ_{res} is known with certainty. Regarding indene as a disubstituted benzene suggests that Δb might be applied along the X-axis, in which case usual procedures [6b,15] yield semi-axes and direction cosines with X, Y, and Z, respectively, as:
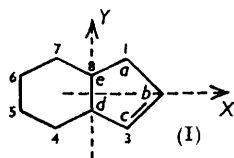
$$b_1 = 1·771_5 \qquad 0·7771 \qquad 0·6293 \qquad 0$$
$$b_2 = 1·608 \qquad -0·6293 \qquad 0·7771 \qquad 0$$
$$b_3 = 1·022 \qquad 0 \qquad 0 \qquad 1$$

If μ_{res} also acts along X, then $\mu_1 = 0·48_4$ D, $\mu_2 = 0·39_2$ D, $\mu_3 = 0$, $10^{35}\theta_1 = 5·52_9$, $10^{35}\theta_2 = 2·65_7$, and $10^{12}{}_m K$ calc. $= 38·6_3$. Alternatively, in view of the known reactivity of the

[7] Gallay, *Kolloid-Z.*, 1931, **57**, 1.
[8] Lee, *J. Soc. Chem. Ind. Japan*, 1940, **43**, Suppl., 190.
[9] Syrkin and Shott-L'vova, *Acta Physicochim. U.R.S.S.*, 1944, **19**, 379.
[10] Narasimha Rao, *Ind. J. Phys.*, 1955, **29**, 398.
[11] Vogel, Cresswell, Jeffrey, and Leicester, *J.*, 1952, 514.
[12] Aroney and Le Fèvre, *J.*, 1960, 3600.
[13] Le Fèvre, *J. Proc. Roy. Soc. N.S.W.*, 1961, **95**, 1.
[14] Sutton *et al.*, "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.* No. 11, 1958.
[15] Eckert and Le Fèvre, *J.*, 1962, 1081.

methylene group at 1 in (I), μ_{res} may be inclined towards the line joining C-1 to the mid-point of the 3,9-bond; at coincidence, μ_{res} would be at $33°$ to b_1, then $\mu_1 = 0.52_3$ D, $\mu_2 = 0.33_9$ D, $\mu_3 = 0$, $10^{35}\theta_1 = 5.52_9$, $10^{35}\theta_2 = 3.92_2$, and $10^{12}{_m}K$ calc. $= 39.74$. Each of these predicted ${_m}K$'s is close to that observed (39.0×10^{-12}). When Δb is applied along the direction of μ_{res} the forecast ${_m}K$ is 40.6×10^{-12}, while when Δb, μ_{res} and b_1 are all parallel ${_m}K$ calc. becomes 48.7×10^{-12}. Of the four approaches the last appears least appropriate, but the relative insensitivity of ${_m}K$ makes a choice between the other three unjustified.

Physical Properties and Molecular Weights of Polyindenes.—As before, with poly(vinyl halides), poly(methyl acrylates), and methacrylates, etc.,[1,2] a tendency can be seen for most of the measured quantities of Table 2 to change smoothly with increasing molecular weight. With L as the logarithm of the degree of polymerisation, empirical equations expressing the dielectric constant, density, and electric birefringence factors, and specific polarisations and Kerr constants, in terms of L emerge as:

$$\alpha\varepsilon_1 = 0.910 - 0.344L$$

$$\beta d_1 = 0.2075 + 0.0215L$$

$$\delta B_1 = 1.020 - 0.825L$$

$$_\infty(p_2) = 0.422 - 0.063L$$

$$_\infty({_s}K_2) = 20.3 - 14.1L$$

Calculated and found values are compared in Table 4. Unlike previous cases,[1,2] for which quadratic relations were needed, the physical properties of these polyindenes show straight-line dependences upon L. The refractive index factors, specific refractions, and dipole moments (γn_1, $_\infty r_2$, and μ, respectively) are found to be nearly constant throughout the molecular weight range studied.

TABLE 4.

Calculated and observed values of $\alpha\varepsilon_1$, βd_1, etc., for polyindenes.

| Polymer	I	II	III	IV	V	VI	VII	VIII
$\alpha\varepsilon_1$ calc.	0.723	0.673	0.610	0.523	0.463	0.441	0.402	0.376
obs.	0.724	0.653	0.601	0.521	0.467	0.446	0.456	0.450
βd_1 calc.	0.2192	0.2223	0.2262	0.2317	0.2355	0.2368	0.2373	0.2409
obs.	0.2231	0.2231	0.2250	0.2317	0.2363	0.2365	0.2376	0.2374
δB_1 calc.	0.571	0.453	0.301	0.092	−0.052	−0.104	−0.199	−0.262
obs.	0.584	0.431	0.296	0.106	−0.050	−0.100	−0.201	−0.260
$_\infty({_s}K_2)$ calc.	12.7	10.6	8.0	4.5	2.0	1.1	−0.5	−1.6
obs.	13.2	10.6	8.3	5.0	1.6	1.4	−0.5	−1.55
$_\infty P_2$ calc. ...	0.3877	0.3787	0.3671	0.3511	0.3401	0.3342	0.3289	0.3241
obs. ...	0.3901	0.3766	0.3662	0.3486	0.3365	0.3324	0.3340	0.3328

Apparent Dipole Moments of Polyindenes.—Sakurada and Lee,[16] using results obtained by Gallay[7] and Lee,[8] quoted moments of 1.37, 1.74, 1.73, 1.91, and 2.18 D for polyindenes having degrees of polymerisation (D.P.) of 5.2, 7.4, 8.9, 9.8, and 12.8, respectively. These differ from those now reported in Table 3 in being higher generally, and tending to increase as the D.P. exceeds *ca.* 9. Regarding the first difference: this may originate partly in the (unrecorded) assumptions made concerning distortion polarisations in ref. 16 since for the four lower polymers there listed, the specific polarisations are in rough agreement with ours:

D.P.	5.2	7.4	8.9	9.8	12.8
$_\infty p_2$ obsd.[16]	0.368	0.376	0.354	0.353	0.252
$_\infty p_2$ calc. as 0.422—$0.063L$	0.377	0.367	0.362	0.359	0.352

Regarding the second difference: the present work carries D.P.s beyond 12.8, the highest studied by Sakurada and Lee, up to 36; there is no noticeable change of the trend of $_\infty p_2$ to fall slowly with D.P.; in fact, as our polymer IV, with a D.P. of 13.3 (*i.e.*, resembling

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

that of 12·8 in ref. 16), has $_\infty p_2 = 0.349$ c.c. (calc. 0·351 c.c.), we question whether 0·252 is not a misprint for 0·352. From reported bond refractions,[11] the R_D's expected for poly-indenes I—VIII are 126, 176·5, 266·5, 479, 720, 828, 1080, and 1297 c.c., respectively; these are not seriously at variance with the R_D's from experiment (Table 3); for a D.P. of 12·8 the R_D should be 461 c.c. corresponding to a specific refraction of 0·310 c.c.; this exceeds the specific polarisation of 0·252 c.c. given in ref. 16, but would be in harmony with 0·352 c.c. as now suggested.
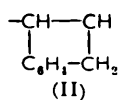
−CH—CH
| |
C_6H_4−CH_2
(II)

Indane may be used as replica of the smallest repeating unit (II) in the polyindenes; its dipole moment, determined in benzene by Sidgwick and Springall,[17] is 0·53 D. The magnitudes of $\mu^2_{polymer}/$(degree of polymerisation) (0·53)[2] fall rapidly as the D.P. rises:

Polymer	I	II	III	IV	V	VI	VII	VIII
Quotient	1·2	0·88	0·69	0·32	0·14	0·12₃	0·10	0·12

and, according to arguments of Debye and Bueche,[18] qualitatively indicate a diminution of flexibility with increase in molecular weight.

The relative insensitivity of μ to M_2 (cf. Table 3), considered with evidence provided by Whitby and Katz[4] (*viz.*, that polyindenes absorb only two bromine atoms per mol.), suggests a general structure for these polymers in which a (presumably terminal) double bond is attached to chains made up of units as (II) so oriented mutually that the resultant polarity of the $(C_9H_8)_n$ portion is always small and roughly independent of n.

Leybold or Catalan models of indene and indane suggest that the most reasonable construction of a polyindene is to join the monomers so that each holds two neighbours at the ends of its 2,3-bond by one link which ascends, and by another which descends, from the 1,2,3-plane. This helical arrangement with every fourth residue in a plane *ca.* 3·9 Å under that of the first appears as a sterically possible extreme form; in reality it is more probable that the residues are disposed propellor-wise by twists about their junctions, and unless these twists are always in the same sense a regular helix cannot be expected. The models make it clear that the opportunities for internal rotations decrease rapidly with rises in the degree of polymerisation.

Molar Kerr Constants of Polyindenes.—These values (see Table 3) display an unusual trend, rising to a maximum for polymer IV and thereafter growing smaller, becoming negative for specimens VII and VIII. However, the quotients $10^{12}{}_mK/$(degree of poly-merisation) show greater continuity, diminishing from +15·3 through 12·2, 9·65, 8·82, 1·90, 1·64, −0·59, to −1·79, respectively, for polyindenes I—VIII; thus the anisotropy per monomeric unit appears to be a minimum between $M_2 = 2670$ and 3480 (the same behaviour is seen from the δ's or $_sK_2$'s of Table 3). A negative $_mK$ almost certainly implies that the solute concerned is polar (*i.e.*, that in these cases the moments of *ca.* 1 D recorded are not wholly due to anomalous atomic or vibration[19] polarisations; cf. p. 292 of ref. 6a). The inversion of the algebraic signs of the $_mK$'s can be explained in two obvious ways: when M_2 increases, b_2 may become greater than b_1, or alternatively, the direction of μ_{res} may change; perhaps both effects occur together. As in previous papers,[2] an attempt to gauge the anisotropies of polymers I—VIII can be made by assuming for the solutes polarisability ellipsoids of rotation in which the resultant dipole moments act parallel to the major semi-axes b_1. The totals $b_1 + 2b_2$ are available from the R_D's of Table 3 and the squares of the differences $b_1 - b_2$ from the $_mK_2$'s. Taking signs con-sistent with those of the observed molar Kerr constants, we have:

Polymer:	I	II	III	IV	V	VI	VII	VIII
$10^{23}(b_1 + 2b_2)$	14·51	20·21	30·80	55·17	82·05	93·82	123·31	145·90
$10^{23}(b_1 - b_2)$	0·31	0·35	0·40	0·45	0·35	0·35	−0·23	−0·73

[17] Sidgwick and Springall, *J.*, 1936, 1532.
[18] Debye and Bueche, *J. Chem. Phys.*, 1951, **19**, 589.
[19] Coop and Sutton, *J.*, 1938, 1269.

and the separate values of b_1 and b_2 follow directly. Comparisons with analogous calculations [2] for poly(vinyl chloride), poly(vinyl bromide), poly(methyl methacrylate), etc., suggest that the polyindenes are the most anisotropically polarisable of the polyolefins examined to date. Despite this, however, we have failed to find any conformational pattern, among the many which would be permitted by present results, that appears to be uniquely indicated; as with the polymers in ref. 2, Kerr effect measurements are disappointingly uninformative in this respect.