

Optical Anisotropy of Polystyrene and Its Low Molecular Analogues

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Depolarized Rayleigh scattering (DRS) of benzene, toluene, cumene, and *t*-butylbenzene, 2,4-diphenylpentane (DPP), 2,4,6-triphenylheptane (TPH), and atactic polystyrenes (PS) with average degrees of polymerization of 21, 38 and 96 have been measured in carbon tetrachloride at $\lambda = 632.8$ nm and $T = 25^\circ\text{C}$. The optical anisotropies γ^2 deduced from the DRS of benzene and toluene are consistent with results obtained by LeFèvre and co-workers from the electric and magnetic birefringence. The anisotropy attributable to the phenyl group is altered markedly by methyl substitution in passing from benzene to toluene. Further substitution on the methyl group has only a minor effect. Optical anisotropies of PS and its oligomers DPP and TPH are calculated from the polarizability tensor for cumene, chosen as the closest analogue of the repeating unit of PS. Values of $\langle\gamma^2\rangle$ computed on this basis by averaging over the conformations of meso and racemic DPP, of the mixture of isomers comprising TPH, and of atactic PS are in good agreement with the results of the DRS measurements. $\langle\gamma^2\rangle$ for PS calculated as a function of stereochemical constitution decreases from 97 \AA^6 to 30 \AA^6 in passing from syndiotactic to isotactic chains.

Depolarized Rayleigh scattering is known to be sensitive to molecular geometry and hence to conformation. Calculations reported by Tonelli, Abe and Flory¹ demonstrated the possibility of using $\langle\gamma^2\rangle$, the mean-squared optical anisotropy determined by depolarized Rayleigh scattering (DRS), as a conformational probe in vinyl-polymers, specifically in polypropylene and in polystyrene. Recently Fourche and Jacq² have measured the DRS of 2,4-diphenylpentane and of polystyrene of different chain lengths using radiation of wavelength $\lambda = 546$ nm. Their experimental procedure departs from the one described in detail in the preceding paper.³ In particular, they did not correct for collisionally-induced scattering. Consequently, their reported optical anisotropies may be appreciably greater than the values attributable to intrinsic molecular scattering by the polystyrene chain.³ In order to obtain agreement between theoretical calculations and their values for $\langle\gamma^2\rangle$, Fourche and Lemaire⁴ were led to postulate conformational characteristics that are difficult to reconcile with molecular models and estimated conformational energies. For meso-2,4-diphenylpentane in its *tg*-conformation, for example, it was concluded that both phenyl groups are rotated by 20° with respect to their symmetric position, appreciable departures from this angle being forbidden. For the racemic form in its *gg*-conformation, random rotations were postulated for both phenyl groups, over a mean range of $\pm 15^\circ$ from their symmetric orientations. This latter behaviour is consistent with models, but no basis is evident for the constraints invoked to explain their results for the meso diastereomer.

Recently, spectra of the depolarized Rayleigh line have been measured for solutions of atactic polystyrenes by Bauer, Brauman and Pecora.⁵ They also determined the

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integrated intensities at $\lambda = 488$ nm and obtained values 25 to 30 % lower than Fourche and Jacq² found at $\lambda = 546$ nm. This difference was attributed by Bauer *et al.* to Fourche and Jacq's failure to eliminate collision-induced scattering, and to various experimental deficiencies.

In the investigation reported in this paper we have applied the methods described in the preceding communication³ to the determination of the optical anisotropies $\langle \gamma^2 \rangle$ of polystyrene and its oligomers dissolved in carbon tetrachloride. Corrections for collision-induced scattering are introduced by procedures set forth in detail in that paper, hereinafter designated as (I). First, however, we measured the DRS of a series of simple aromatic hydrocarbons in order to evaluate the optical anisotropy tensor appropriate to the units of the polystyrene chain. The configurational statistics of the polystyrenes are treated according to the two-state model recently put forward by Yoon, Sundararajan and Flory,⁶ which replaces the traditional three-state model⁷ for this polymer chain.

EXPERIMENTAL

MATERIALS AND PROCEDURES

Spectrograde carbon tetrachloride and benzene (Matheson, Coleman and Bell) and reagent grade (99 %) toluene, cumene and t-butylbenzene (Aldrich Chemicals) were used without further purification.

Fifty grams of the diastereometric mixture of 2,4-diphenylpentane were synthesized according to the method of Overberger and Bonsignore.⁸ Separation of the diastereomers was performed by rectification on a Nester-Faust annular still. The diastereomers were identified by 60 MHz proton-n.m.r.,⁹ and their chemical purity was confirmed to be at least 99 % by gas chromatography.

A diastereomeric mixture of 2,4,6-triphenylheptane was kindly provided by Drs. D. Lim and S. Kolinsky of the Institute of Macromolecular Chemistry, Prague. Gas chromatographic analysis showed it to consist of the three diastereomers in proportions as follows; 14 % isotactic (meso, meso), 50 % heterotactic (meso, racemic), and 36 % syndiotactic (racemic, racemic). It was used without further purification.

Samples of atactic polystyrene of average molecular weight 2 200, 4 000 and 10 000 with relatively narrow molecular weight distributions ($M_w/M_n < 1.1$ for all) were obtained from Pressure Chemicals, Pittsburgh, Pa. They were used without fractionation or purification.

Solutions of the samples were prepared and their depolarized scattering intensities at 632.8 nm measured following the methods of Patterson and Flory¹⁰ with the refinements set forth in the preceding paper.³ In order to estimate the contribution of collision-induced scattering to the total depolarized Rayleigh scattering (DRS), intensities were measured using the two interference filters having band half-widths of 18 and 53 cm^{-1} , respectively.³ The attenuation factors $f(\sigma, b)$ were evaluated according to eqn (23) of the preceding paper.³ Alms, Bauer, Brauman and Pecora¹¹ find $b = 1.5 \text{ cm}^{-1}$ and 0.8 cm^{-1} for benzene and toluene, respectively, from which we obtain $f_1 \equiv f(18, b) = 0.92$ and 0.96 and $f_2 \equiv f(53, b) = 0.97$ and 0.98 for these liquids. For cumene and t-butylbenzene we assume $b \approx 0.5 \text{ cm}^{-1}$, from which it follows that $f_1 \approx 0.97$ and $f_2 \approx 0.99$. For substances of higher molecular weight, and hence of smaller b , these factors were set equal to unity.

Following the procedure in the preceding paper, we set the ratio g_1/g_2 of the corresponding attenuation factors for the collisionally-induced scattering equal to 0.438, this being the value appropriate for dilute solutions in carbon tetrachloride.³

RESULTS

MONOMERIC COMPOUNDS

All measurements were conducted on solutions in carbon tetrachloride at a temperature of 25°C. Intensities determined with each of the two interference filters served for the evaluation of $R_{\text{HV},\text{mol}}$ and of $R_{\text{HV},\text{col}}$ through use of eqn (I-21) and (I-22),

respectively, of the preceding paper.³ The former represents the Rayleigh ratio for intrinsic molecular DRS by the solution, and the latter that due to collision-induced scattering. The portion of the former, *i.e.*, $\Delta R_{\text{HV},\text{mol}}$, that is attributable to the solute in the solution was calculated according to eqn (I-24). The corresponding quantity $\Delta R_{\text{HV},\text{col}}$, representing the contribution of the solute to the induced scattering, was calculated by use of the analogue of eqn (I-24) for the induced scattering. Substitution of $\Delta R_{\text{HV},\text{mol}}$ into eqn (I-25) yielded the "apparent" squared optical anisotropy γ_{app}^2 of the solute at the concentration of measurement. The subscript is appended to acknowledge possible effects of solute-solute correlations at finite concentrations. For solutes of variable conformation, we employ the symbol $\langle \gamma^2 \rangle_{\text{app}}$ in which the configurational average is denoted by angle brackets.

Results for benzene, toluene, cumene and *t*-butylbenzene are plotted against the volume fractions ϕ_2 of solute in fig. 1. With the exception of toluene, the dependences on concentration are small. Each set of results admits of reliable extrapolation to obtain the intercept γ^2 at infinite dilution, which we take to be the molecular anisotropy of the molecule devoid of effects due to intermolecular correlations or of intermolecularly induced anisotropies. These values are presented in the second column of table 1. The precision of the intercepts is about $\pm 2\%$. Estimation of all sources of error indicates a range of error of about $\pm 5\%$.

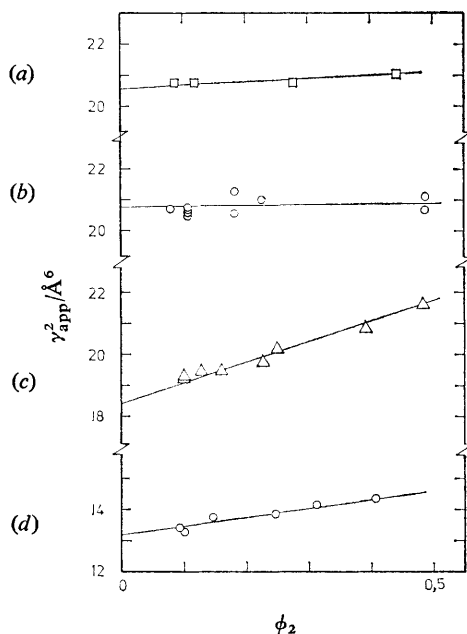


FIG. 1.—Apparent optical anisotropies of four aromatic compounds in carbon tetrachloride at 25°C plotted against the volume fractions ϕ_2 of solute; $\lambda = 632.8$ nm. All values of γ^2 are obtained from DRS corrected for collision-induced scattering. (a) \square , *t*-butylbenzene; (b) \circ , cumene; (c) \triangle , toluene; (d) \circ , benzene.

In the third column of table 1 we show values of the ratios $\Delta R_{\text{HV},\text{col}}/\Delta R_{\text{HV}}$ extrapolated to infinite dilution (compare table 4 of the preceding paper).³ The quantity ΔR_{HV} is the total DRS attributable to the solute in absence of a filter that would attenuate either component. Division of the molecular optical anisotropy γ^2 in the preceding column by the difference of this ratio from unity yields the figures

TABLE 1.—OPTICAL ANISOTROPIES OF SIMPLE AROMATIC COMPOUNDS
(at infinite dilution in CCl_4 ; $T = 25^\circ\text{C}$; $\gamma = 632.8\text{ nm}$)

compound	$\gamma^2/\text{\AA}^6$	$\frac{\Delta R_{\text{HV, col}}}{\Delta R_{\text{HV}}}$	$\gamma^2 \left(\frac{\Delta R_{\text{HV}}}{\Delta R_{\text{HV, mol}}} \right) / \text{\AA}^6$
benzene	13.2	0.57	30.7
toluene	18.4	0.52	38.3
cumene	20.8	0.46	38.5
t-butylbenzene	20.5	0.50	41.0

in the last column of table 1. They represent the values that would be obtained for γ^2 from measurements of the combined intensity if no measures were taken for elimination of collisional scattering. Unanu  and Bothorel¹² reported values of 36, 43.5, 45 and 46.8 \AA^6 for γ^2 for these four hydrocarbons, respectively. Their measurements also were carried out in carbon tetrachloride, but at a wavelength $\lambda = 546\text{ nm}$ and *without filters*. If the dispersions are similar to that found by Lalanne, Martin and Bothorel¹³ for neat liquid benzene, correction to $\lambda = 633\text{ nm}$ would lower these values by $\sim 18\%$. The figures given in the last column of table 1 are in reasonable accord with their results when adjusted in this way. However, the differences between Unanu  and Bothorel's values for γ^2 and ours, deduced from the intrinsic molecular scattering and given in the second column of table 1, is large. Induced scattering, even for these optically anisotropic molecules, accounts for about half of the total DRS.

A more direct comparison can be made with measurements on neat liquid benzene carried out by Lalanne, Martin and Bothorel¹³ with $\lambda = 632.8\text{ nm}$. They report $\gamma^2 = 25.1\text{ \AA}^6$ at 25°C , this result having been derived from the total DRS intensity. Using filters and applying the foregoing procedure, we obtain $\gamma^2 = 10.2\text{ \AA}^6$, which may be compared with $\gamma^2 = 13.2\text{ \AA}^6$ for benzene at infinite dilution in carbon tetrachloride (see table 1). (Effects of intermolecular correlations are included in the former figure, but their magnitude is relatively small in this instance.) Multiplication by the ratio $R_{\text{HV}}/R_{\text{HV, mol}}$ gives 26.9 \AA^6 , in good agreement with the value derived by Lalanne *et al.*¹³ from the gross DRS. The importance of adopting appropriate procedures for elimination of the induced scattering is again underscored.³

POLYSTYRENE AND ITS OLIGOMERS

Experimental measurements of the DRS by polystyrene and its oligomers $\text{CH}_3-(\text{CHC}_6\text{H}_5-\text{CH}_2)_x-\text{H}$, in carbon tetrachloride solutions were treated similarly. Results are presented in fig. 2, where the ratio $x^{-1}\langle\gamma^2\rangle_{\text{app}}$ of the configurational average of the square of the optical anisotropy to the degree of polymerization is plotted against the volume fraction of the solute. Within limits of the experimental errors, these ratios are independent of concentration. They depend appreciably on chain length only when x is small; the asymptotic value for large x appears to be approached even at $x = 20$. The end groups in these atactic polymers differ from those in the molecular formula as written above, but at the prevailing average chain lengths ($x \geq 21$) their contributions are not significant.

Values of the ordinates of the horizontal lines drawn through the various sets of points are recorded in the second column of table 2. The results for the first member of the series, cumene, are taken from table 1. For the succeeding entries the combined error is again estimated to be $\pm 5\%$. Ratios given in the fourth column were calculated as described above. They decrease slightly with the size of the hydrocarbon molecule (see also table 1). The error that would attend evalu-

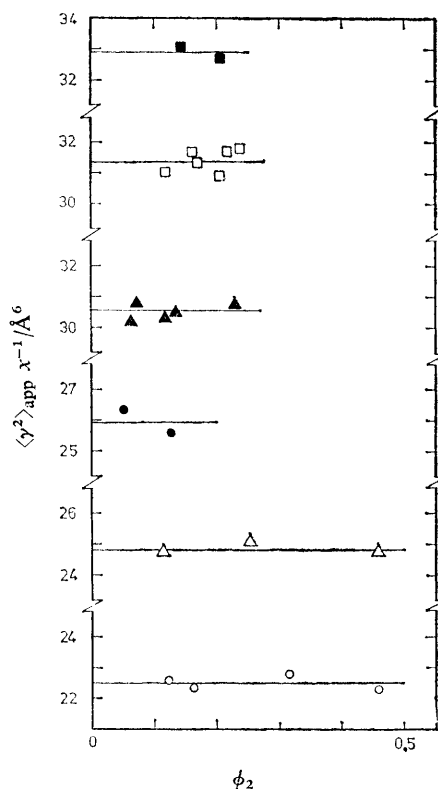


FIG. 2.—Optical anisotropies per monomer unit of atactic polystyrenes of various chain lengths and of oligomers in carbon tetrachloride at $\lambda = 632.8$ nm and $T = 25^\circ\text{C}$ plotted against volume fractions ϕ_2 of solute. ■, $\bar{x} = 96$ atactic; □, $\bar{x} = 38$ atactic; ▲, $\bar{x} = 21$ atactic; ●, $x = 3$, mixture of diastereomers in the proportions isotactic : syndiotactic : heterotactic = 14 : 36 : 50; △, $x = 2$, 92 % racemic; ○, $x = 2$, 80 % meso.

TABLE 2.—OPTICAL ANISOTROPIES OF POLYSTYRENE AND ITS OLIGOMERS

x	stereochem. config.	$\langle \gamma^2 \rangle x^{-1}$ $/\text{\AA}^6$	$\frac{\Delta R_{\text{HV, col}}}{\Delta R_{\text{HV}}}$	$\gamma^2 \left(\frac{\Delta R_{\text{HV}}}{\Delta R_{\text{HV, mol}}} \right) / \text{\AA}^6$
1 (cumene)		20.8	0.46	38.2
2	m	21.8 ^a	0.39	35.9
2	r	25.0 ^a	0.38	40.3
3	mixture ^b	26.0	0.37	41.5
21	atactic	30.5	0.37	48.6
38	atactic	31.3	0.34	47.5
96	atactic	33	0.33	49.4

^a extrapolated to $w_m = 0$ and 1 from diastereomeric mixtures with $w_m = 0.08$ and 0.80, respectively.

^b isotactic : heterotactic : syndiotactic = 14 : 50 : 36.

ation of $\langle \gamma^2 \rangle$ if collisional scattering were not eliminated is large, as indicated by comparison of columns three and five. From the differences between these columns, it will be apparent that the induced scattering per chain unit is nearly independent of x over the entire range.

The presence of a substantial contribution to the DRS from collisional processes

confirms the results of Bauer, Braumann and Pecora⁵ for atactic polystyrene in carbon tetrachloride obtained with radiation of $\lambda = 488$ nm. Our value of 1.5-1.6 for the ratio $\langle \gamma^2 \rangle / x \gamma_{\text{cumene}}^2$ is lower than their result, 2.2-2.4, determined interferometrically with a 85 cm^{-1} bandpass filter in the emergent beam.

The much larger values of $\langle \gamma^2 \rangle$ reported by Fourche and Jacq² for the diastereomeric dimers and for atactic polystyrene can be reconciled approximately with our results if allowance is made for their failure to eliminate induced scattering. A more perplexing discordance occurs in the relative values of $\langle \gamma^2 \rangle$ for the meso and racemic isomers. According to our results (table 2) $\langle \gamma^2 \rangle$ for the racemic isomer exceeds that for the meso form by 15 %, whereas they find $\langle \gamma^2 \rangle$ for meso to be greater by 5 %. The purity and stereochemical configurations of our compounds were established both by chromatographic analysis and by n.m.r. measurements (see above).

ANALYSIS OF RESULTS

BENZENE

The anisotropic part of the optical polarizability tensor for benzene can be written

$$\hat{\alpha}_{\text{benzene}} = \Delta\alpha_{\text{benzene}}^{\dagger} \text{diag} \left(\frac{2}{3}, -\frac{1}{3}, -\frac{1}{3} \right) \quad (1)$$

where $\Delta\alpha_{\text{benzene}}^{\dagger}$ is the difference between the polarizability along the cylindrical axis perpendicular to the ring and the polarizability in the plane of the ring. It follows from eqn (I-5) of the preceding paper³ that $\gamma_{\text{benzene}}^2 = (\Delta\alpha_{\text{benzene}}^{\dagger})^2$.² The experimental value for γ^2 in table 1 gives $\Delta\alpha_{\text{benzene}}^{\dagger} = -3.63 \text{ \AA}^3$. This result can be put to test by using it to estimate the Kerr constant ${}_mK$ and the Cotton-Mouton constant ${}_mC$, values of which have been determined by LeFèvre and co-workers¹⁴⁻¹⁶ under conditions comparable to those used above for the determination of γ^2 .

We adopt the definition of the molar Kerr constant as the difference between the molar polarization parallel and perpendicular to the field divided by the square of the strength of the local field. Expressed thus, it is given by¹⁷⁻¹⁹

$${}_mK \equiv (4\pi/3)N\Delta\alpha_E/E_{\text{eff}}^2 \\ = \left(\frac{2\pi N}{15} \right) \left[\frac{\mu^T \hat{\alpha} \mu}{(kT)^2} + \left(\frac{\epsilon - 1}{\tilde{n}^2 - 1} \right) \frac{\text{Tr} \hat{\alpha} \hat{\alpha}}{kT} + \frac{4\mu\beta_h}{3kT} + \frac{2}{3}\gamma_h \right] \quad (2)$$

where $\Delta\alpha_E$ is the average difference between the polarizability of the molecule parallel and perpendicular to the field; N is Avogadro's number; μ is the permanent dipole moment, μ^T is its transpose and μ is its magnitude; ϵ is the static dielectric constant of the medium and \tilde{n} is its refractive index at the wavelength λ ; $E_{\text{eff}} = (\epsilon + 2)E_0/3$ is the effective local field produced by the static external field E_0 . The third and fourth terms in eqn (2) express the contributions from the "first" and "second" hyperpolarizability, respectively.^{18, 19} The quantity $\mu\beta_h$ represents the sum of elements of the inner product $\mu_i \beta_{ijk}$ of the dipole moment and the first hyperpolarizability tensor. Similarly, γ_h is the sum of the symmetric elements γ_{tjjj} of the fourth order tensor that expresses the second hyperpolarizability¹⁸ (not to be confused with γ). Molar Kerr constants defined on the foregoing basis differ from those of LeFèvre and his co-workers¹⁷ by a factor of 9. Numerical values of ${}_mK$ quoted below have been altered to conform with eqn (2).

For nonpolar molecules, the first and third terms in eqn (2) are zero. The second term can be evaluated from the results of the DRS measurements since $\text{Tr} \hat{\alpha} \hat{\alpha} = 2\gamma^2/3$. The fourth term, though small, may be appreciable for nonpolar molecules for which the electric birefringence is relatively low. This second hyperpolarizability term is

the only identifiable source of the electric birefringence in spherically symmetric molecules. It accounts for virtually all of the electric birefringence of carbon tetrachloride,^{20*} and for about two-thirds of ${}_mK$ for the lower n-alkanes dissolved in carbon tetrachloride.²¹ Although the electric birefringences of these liquids are small, ${}_mK$ for carbon tetrachloride amounts to about one-sixth that of benzene.^{17, 20}

From the value of γ^2 deduced above for benzene in carbon tetrachloride, one obtains $58.5(\pm 3) \times 10^{-12} \text{ cm}^5 \text{ statvolt}^{-2} \text{ mol}^{-1}$ at $\gamma = 633 \text{ nm}$ for the second term in eqn (2). The molar Kerr constant, ${}_mK = 60 \times 10^{-12}$ at $\lambda = 589 \text{ nm}$, as determined by LeFèvre and Radom¹⁴ in carbon tetrachloride at 25°C , does not differ significantly from this value. (The difference in wavelength is unimportant). The comparison suggests that the hyperpolarizability term is exceptionally small for benzene. A contribution from this source at least as great as that for carbon tetrachloride or for the n-alkanes might have been expected. One should observe, however, that the coefficient γ_h for this highly anisotropic molecule comprises three separate components¹⁸ γ_{uij} involving pairwise combinations of the two nonequivalent molecular axes. The signs of these components being unknown, approximate mutual cancellation cannot be ruled out.

The corresponding contribution of hyperpolarizability to the magnetic birefringence²² of anisotropic molecules is quite negligible.^{15, 23} Hence, the term expressing the induced polarization alone suffices. The molar Cotton-Mouton constant is given with negligible error therefore by

$${}_mC = (2\pi N/15 kT) \text{Tr}(\hat{\alpha}\hat{\chi}) \quad (3)$$

which corresponds to the second term of eqn (2). Here $\hat{\chi}$ is the anisotropic part of the magnetic susceptibility tensor.

The anisotropy of the magnetic susceptibility of benzene may be specified by $\Delta\chi_{\text{benzene}}^\dagger$ defined analogously to $\Delta\alpha_{\text{benzene}}^\dagger$. The magnetic susceptibility of crystalline benzene yields²⁴ $\Delta\chi_{\text{benzene}}^\dagger = -99 \times 10^{-37} \text{ J G}^{-2} \text{ molecule}^{-1}$. From this result in conjunction with the foregoing value of $\Delta\alpha_{\text{benzene}}^\dagger$, we obtain ${}_mC = 1.47(\pm 0.05) \times 10^{-15} \text{ cm}^3 \text{ G}^{-2} \text{ mol}^{-1}$ at $\lambda = 632.8 \text{ nm}$ and a temperature of 25°C . This may be compared with LeFèvre and Murthy's¹⁵ experimental value of $1.49 \times 10^{-15} \text{ cm}^3 \text{ G}^{-2} \text{ mol}^{-1}$ measured in carbon tetrachloride at 20°C and $\gamma = 589 \text{ nm}$. The close agreement confirms the value of $\Delta\alpha_{\text{benzene}}^\dagger = -3.63 \text{ \AA}$ obtained from the intrinsic DRS of benzene in carbon tetrachloride. It lends credence to the indication above that the electric hyperpolarizability of benzene is very small.

HOMOLOGUES OF BENZENE

For the analysis of aromatic compounds $\text{R}-\text{C}_6\text{H}_5$ it is convenient to take the X -axis in the direction of the $\text{C}^{\text{al}}-\text{C}^{\text{ar}}$ bond. The reference frame is specified in fig. 3. These are the principal axes of the phenyl group. They are also the principal axes of toluene and *t*-butylbenzene, and can be employed for cumene as well. For these hydrocarbon molecules with the exception of cumene (*cf. seq.*), and for the phenyl group in general, the anisotropic part of the polarizability tensor can be written as follows, the axes being taken in the order X, Y, Z :

$$\hat{\alpha} = \Delta\alpha \text{diag} \left(\frac{2}{3}, -\frac{1}{3}, -\frac{1}{3} \right) + \Delta\alpha^\dagger \text{diag} \left(0, \frac{1}{2}, -\frac{1}{2} \right) \quad (4)$$

where

$$\Delta\alpha = \alpha_x - (\alpha_y + \alpha_z)/2 \quad (5)$$

* From the residual DRS for liquid carbon tetrachloride after correction for induced scattering,³ we estimate that the contribution of the residual optical anisotropy accounts for no more than 3 % of ${}_mK$ for liquid carbon tetrachloride.

is the excess polarizability parallel to the X -axis compared to the mean polarizability transverse thereto, and

$$\Delta\alpha^\dagger = \alpha_y - \alpha_z \quad (6)$$

expresses the departure from cylindrical symmetry about the X -axis.

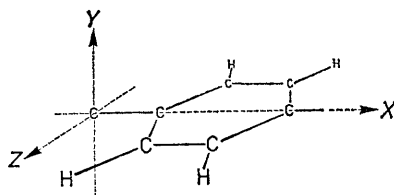


FIG. 3.—The phenyl group in its coordinate system XYZ .

For the benzene molecule with $\alpha_z = \alpha_x$, we have

$$\Delta\alpha_{\text{benzene}} = -\frac{1}{2}\Delta\alpha_{\text{benzene}}^\dagger. \quad (7)$$

If the polarizability of the phenyl group were unaffected by substitution, $\Delta\alpha$ and $\Delta\alpha^\dagger$ for this group would be interrelated through these equations and a single parameter would suffice. However, the magnitude of the anisotropy attributable to the aromatic ring is affected markedly by substitution, as shown below; cylindrical symmetry about the Y -axis is eliminated also. For these reasons, we introduce the tensor $\hat{\alpha}_{\phi\text{H}}$ to represent the phenyl group as it exists in a given derivative of benzene. It is determined by parameters $\Delta\alpha_{\phi\text{H}}$ and $\Delta\alpha_{\phi\text{H}}^\dagger$ defined analogously to the molecular quantities $\Delta\alpha$ and $\Delta\alpha^\dagger$ defined above. The tensor $\hat{\alpha}_{\phi\text{H}}$ represents the combination $\text{C}_6\text{H}_5\text{—H}$, with the polarizability of the benzene ring perturbed precisely as it is in the given homologue. Thus, we assign the secondary effects of substitution exclusively to the phenyl group as distinct from the associated bonds and groups. This artifice is introduced for convenience and is of no consequence otherwise.

On the basis of the valence-optical scheme,²⁵ according to which the polarizability tensor comprises the sum of contributions characteristic of the constituent bonds or groups,³ the tensor $\hat{\alpha}$ for toluene is determined by the quantities

$$\left. \begin{aligned} \Delta\alpha_{\text{toluene}} &= \Delta\alpha_{\phi\text{H}} + \Gamma_{\text{CC}} \\ \Delta\alpha_{\text{toluene}}^\dagger &= \Delta\alpha_{\phi\text{H}}^\dagger \end{aligned} \right\}. \quad (8)$$

For tetrahedral bond angles,

$$\Gamma_{\text{CC}} = \Delta\alpha_{\text{CC}} - 2\Delta\alpha_{\text{CH}} \quad (9)$$

where $\Delta\alpha_{\text{CC}}$ and $\Delta\alpha_{\text{CH}}$ are the anisotropies of the C—C and C—H bonds; see eqn (I-3). Departures from tetrahedral bonding do not affect this quantity significantly.¹⁰ The tensor $\hat{\alpha}_{\text{toluene}}$ is given by eqn (4) with these quantities substituted for $\Delta\alpha$ and $\Delta\alpha^\dagger$ therein. It follows [see eqn (I-5)] that

$$\gamma_{\text{toluene}}^2 = (\Delta\alpha_{\phi\text{H}} + \Gamma_{\text{CC}})^2 + \frac{3}{4}(\Delta\alpha_{\phi\text{H}}^\dagger)^2. \quad (10)$$

The net contribution of the tertiary butyl group in *t*-butylbenzene should be nil according to the valence-optical scheme in the approximation that the difference between an aliphatic-aryl and an aliphatic-aliphatic C—C bond can be ignored. The tensor $\hat{\alpha}_{\text{t-Bu}\phi}$ for the *t*-butylbenzene molecule should, on this basis, equate to that of benzene. In anticipation of substantial substitution effects, we adhere to the procedure above, $\Delta\alpha_{\phi\text{H}}$ and $\Delta\alpha_{\phi\text{H}}^\dagger$ being chosen to represent the phenyl group as it exists in this molecule. Then

$$\gamma_{\text{t-Bu}\phi}^2 = (\Delta\alpha_{\phi\text{H}})^2 + \frac{3}{4}(\Delta\alpha_{\phi\text{H}}^\dagger)^2. \quad (11)$$

Rotation of the isopropyl group of cumene about the X -axis in fig. 3 is restricted by steric repulsions between hydrogens on the methyl groups and the *ortho*-CH groups of phenyl to a small range centred around the conformation in which the methyl groups are symmetrically disposed on either side of the plane of the phenyl ring, the latter being coplanar with the methine C—H bond.^{6, 26, 27} We let β denote the departure of the torsional angle about this bond from its value, $\beta = 0$, for this preferred conformation. If the bond angles at the aliphatic carbons are tetrahedral, the anisotropy attributable to replacement of H—C^{ar} of benzene by the isopropyl group (CH₃)₂CH—C^{ar} can be taken to be the resultant of replacing one of the methyl groups of *t*-butyl by H. This is expressed by the cylindrical tensor ³— $\Gamma_{CC} = 2\Delta\alpha_{CH} - \Delta\alpha_{CC}$ having its symmetry axis along the methine C—H bond. It follows that the anisotropy tensor for cumene expressed in the coordinate system of the phenyl group (see fig. 3) is

$$\begin{aligned}\hat{\alpha}_{\text{cumene}} = & \Delta\alpha_{\phi H} \text{diag} \left(\frac{2}{3}, -\frac{1}{3}, -\frac{1}{3} \right) + \\ & \Delta\alpha_{\phi H}^{\dagger} \text{diag} \left(0, \frac{1}{2}, -\frac{1}{2} \right) - \\ & \Gamma_{CC} R_{X, \beta} R_{Y', \theta} \text{diag} \left(\frac{2}{3}, -\frac{1}{3}, -\frac{1}{3} \right) R_{Y', \theta}^T R_{X, \beta}^T\end{aligned}\quad (12)$$

where $R_{Y', \theta}$ is the rotation matrix through angle θ about an axis Y' that is perpendicular to the C—H and C—C^z bonds; θ is the supplement of the C—C—C bond angle of the isopropyl group; $R_{X, \beta}$ is the matrix that takes account of rotation of the isopropyl group through angle β about the X -axis, β being measured from the preferred conformation. Taking $\pi - \theta$ to be the tetrahedral angle, we obtain

$$\begin{aligned}\gamma_{\text{cumene}}^2 = & (\Delta\alpha_{\phi H})^2 + \frac{3}{4}(\Delta\alpha_{\phi H}^{\dagger})^2 + \Gamma_{CC}^2 + \\ & \frac{2}{3}\Delta\alpha_{\phi H}\Gamma_{CC} + \frac{4}{3}(1-2\langle\sin^2\beta\rangle)\Delta\alpha_{\phi H}^{\dagger}\Gamma_{CC}.\end{aligned}\quad (13)$$

We let $\Gamma_{CC} = 0.53 \text{ \AA}^3$, as found previously.¹⁰ If $\Delta\alpha_{\phi H}$ and $\Delta\alpha_{\phi H}^{\dagger}$ are evaluated according to eqn (7) with $\Delta\alpha_{\phi H}^{\dagger} = -3.63 \text{ \AA}^3$, then eqn (10), (11) and (13) give

$$\begin{aligned}\gamma_{\text{toluene}}^2 &= 15.4 \text{ \AA}^6 \\ \gamma_{\text{cumene}}^2 &= 11.6 \text{ \AA}^6 \\ \gamma_{\text{t-Bu}\phi}^2 &= 13.2 \text{ \AA}^6.\end{aligned}$$

(The value quoted for cumene was calculated with $\beta = 0$. If, instead, the rotation of the phenyl group in cumene is constrained by a square potential within the range $-20^\circ < \beta < 20^\circ$, then γ_{cumene}^2 is raised to 11.9 \AA^6 .) All of these values are substantially lower than the results of experiment as given in table 1. Thus, $\Delta\alpha_{\phi H}$ and $\Delta\alpha_{\phi H}^{\dagger}$ for the derivatives of benzene cannot be identified with those for benzene itself. The conclusions of Volkenstein²⁵ and of Le Fèvre²⁸ that conjugated systems do not conform to the valence-optical scheme are thus confirmed.

Experimental values of ${}_mK$ and of ${}_mC$ have been reported for toluene, but not for cumene and *t*-butylbenzene. These results, in conjunction with γ^2 , may be used to evaluate the parameters $\Delta\alpha_{\phi H}$ and $\Delta\alpha_{\phi H}^{\dagger}$ that characterize the phenyl group in toluene.

The solid line in fig. 4 represents the locus of solutions of eqn (10) that satisfy γ^2 observed for toluene. The dashed curve represents solutions of eqn (2) that give ${}_mK = 123 \times 10^{-12} \text{ cm}^5 \text{ statvolt}^{-2} \text{ mol}^{-1}$ as found by Aroney, Huang, LeFèvre and Ritchie²⁹ from measurements in carbon tetrachloride at 25°C with $\lambda = 589 \text{ nm}$. For these calculations we have taken $\mu = 0.34 \text{ D}$;²⁹ the hyperpolarizability terms in eqn (2) have been ignored. Owing to the presence of a dipole moment μ , the first hyperpolarizability, as well as the second, may contribute to ${}_mK$. The small value

of μ suggests that the former term should be small. By inference from the results for benzene, one may expect the contribution of the second hyperpolarizability to be small also. Nevertheless, the presence of hyperpolarizabilities of unknown magnitude and sign confers a latitude of uncertainty on values of the parameters calculated from ${}_mK$. Since μ is small, the curve (dashed) in fig. 4 for the electric birefringence is dominated by the induced polarization. It resembles the curve (solid) for the optical anisotropy, therefore, and their point of intersection is poorly defined.

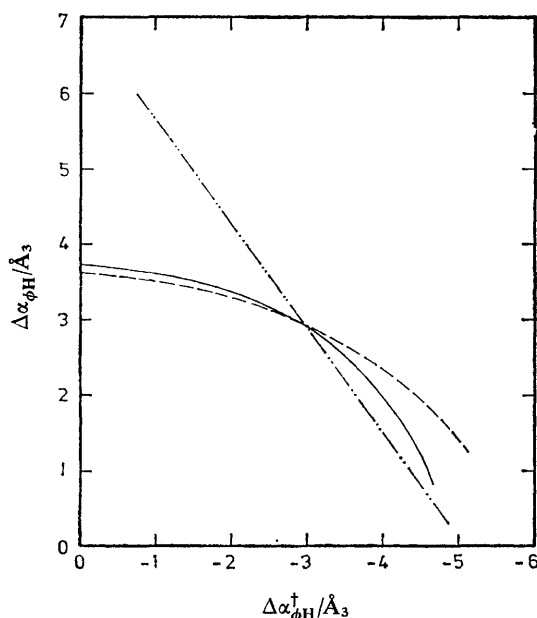


FIG. 4.—Values for $\Delta\alpha_{\phi H}$ and $\Delta\alpha_{\phi H}^\dagger$ required to fit experimental results for toluene as follows: —, DRS with $\gamma^2 = 18.4 \text{ \AA}^6$; ---, electric birefringence with ${}_mK = 123 \text{ cm}^5 \text{ statvolt}^{-2} \text{ mol}^{-1}$; - . . -, magnetic birefringence with ${}_mC = 1.70 \times 10^{-15} \text{ cm}^3 \text{ G}^{-2} \text{ mol}^{-1}$. See text.

The dot-dashed curve in fig. 4 has been calculated according to eqn (3) from Cheng, Murthy and Ritchie's¹⁶ result ${}_mC = 1.70(\pm 0.01) \times 10^{-15} \text{ cm}^3 \text{ G}^{-2} \text{ mol}^{-1}$, for toluene in carbon tetrachloride at 20°C with $\lambda = 589 \text{ nm}$. The required magnetic susceptibility tensor $\hat{\chi}$ was evaluated from bond and group susceptibilities on the assumption that they are additive. This assumption has been shown by Schmalz, Norris and Flygare³⁰ to hold in satisfactory approximation for aromatic hydrocarbons. Adopting notation corresponding to that for the electric polarizability, we have

$$\left. \begin{aligned} \Delta\chi_{\text{toluene}} &= -\frac{1}{2}\Delta\chi_{\phi H}^\dagger + \Delta\chi_{CC} - \Delta\chi_{CH} + \Delta\chi_{CH_3} \\ \Delta\chi_{\text{toluene}}^\dagger &= \Delta\chi_{\phi H}^\dagger \end{aligned} \right\}. \quad (14)$$

These quantities, being analogues of $\Delta\alpha_{\text{toluene}}$ and $\Delta\alpha_{\text{toluene}}^\dagger$ of eqn (8), define the anisotropic part of the magnetic anisotropy tensor $\hat{\chi}$ for toluene according to eqn (4). Substitution of $\Delta\chi_{\phi H}^\dagger = -99 \times 10^{-37} \text{ J G}^{-2} \text{ molecule}^{-1}$ (see above), $\Delta\chi_{CC} = 12.8 \times 10^{-37}$, $\Delta\chi_{CH} = 4.2 \times 10^{-37}$ and $\Delta\chi_{CH_3} = -4.7 \times 10^{-37}$ from the tabulations of Schmalz *et al.*³⁰ gives $\Delta\chi_{\text{toluene}} = 53.4 \times 10^{-37}$ and $\Delta\chi_{\text{toluene}}^\dagger = -99 \times 10^{-37}$, all in the stated

units. Introduction of the tensor thus determined into eqn (3) in conjunction with the observed value of ${}_mC$ quoted above yields the linear relation between $\Delta\alpha_{\phi H}$ and $\Delta\alpha_{\phi H}^\dagger$ for the phenyl group shown in fig. 4.

The intersection of the locus for solution of ${}_mC$ with the other two curves occurs at $\Delta\alpha_{\phi H} = 2.95 \text{ \AA}^3$ and $\Delta\alpha_{\phi H}^\dagger = -3.0 \text{ \AA}^3$. These values correspond to $\Delta\alpha_{\text{toluene}} = 3.5 \text{ \AA}^3$ and $\Delta\alpha_{\text{toluene}}^\dagger = -3.0 \text{ \AA}^3$ for the toluene molecule. They compare satisfactorily with LeFèvre and Radom's¹⁴ values of 3.2 \AA^3 and -3.3 \AA^3 , respectively. The parameters $\Delta\alpha_{\phi H}$ and $\Delta\alpha_{\phi H}^\dagger$ found for the benzene group in toluene differ appreciably from the values for the benzene molecule, namely, $\Delta\alpha_{\text{benzene}} = 1.83 \text{ \AA}^3$ and $\Delta\alpha_{\text{benzene}}^\dagger = -3.63 \text{ \AA}^3$. The near-coincidence of the intersection of the line for the magnetic birefringence with the other curves suggests that the net contribution of the hyperpolarizabilities to ${}_mK$ may be small.

The loci of solutions $\Delta\alpha_{\phi H}$, $\Delta\alpha_{\phi H}^\dagger$ for the values of γ^2 observed for cumene and t-butylbenzene are compared with the locus for toluene in fig. 5. The solid curve representing toluene in fig. 5 corresponds to the solid curve in fig. 4. It is apparent that a common solution does not exist; a different pair of parameters $\Delta\alpha_{\phi H}$ and $\Delta\alpha_{\phi H}^\dagger$ is required for cumene and t-butylbenzene than for toluene.

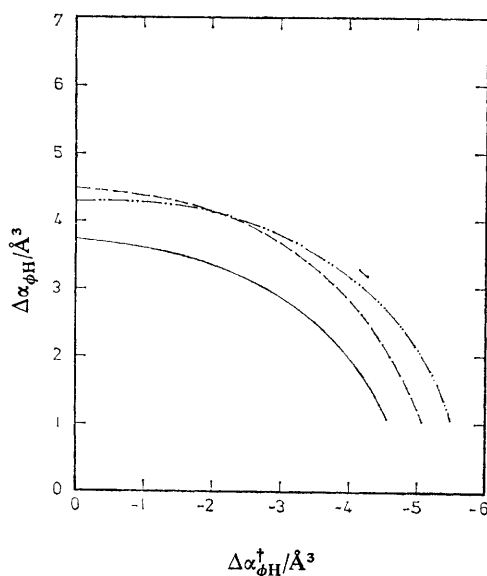
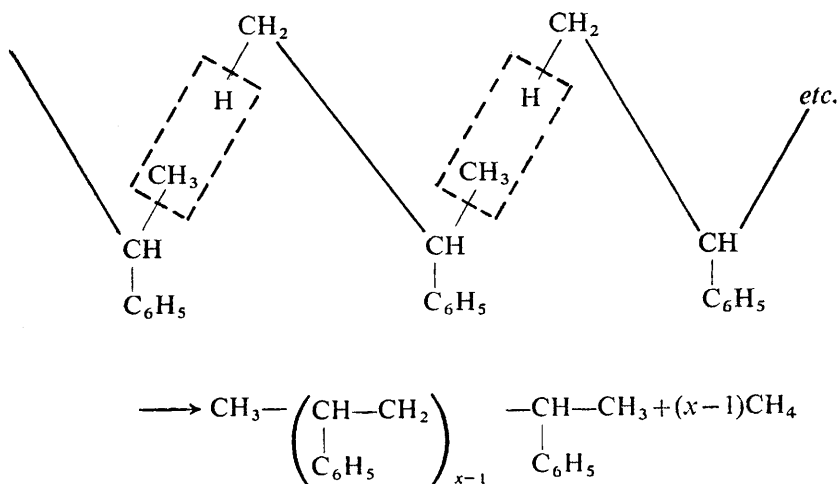


FIG. 5.—Values for $\Delta\alpha_{\phi H}$ and $\Delta\alpha_{\phi H}^\dagger$ required to fit the experimental γ^2 for: —, toluene; ---, t-butylbenzene; - · - ·, cumene.

In order to proceed, we make the reasonable assumption that the anisotropy of the benzenoid group about the x -axis is unaffected by substitution on the methyl group of toluene. We therefore take $\Delta\alpha_{\phi H}^\dagger = -3.0 \text{ \AA}^3$ for the aromatic ring as it occurs in cumene and in t-butylbenzene, as well as in toluene. On this basis $\Delta\alpha_{\phi H} = 3.85 \text{ \AA}^3$ for the phenyl group in both cumene and t-butylbenzene. We rely on these results for the analysis of the polystyrene chain below.

POLYSTYRENE

Let the polymer be formed from molecules of cumene by elimination of methane according to the following hypothetical process :



On the plausible assumption that the optical anisotropy of the phenyl group is not affected appreciably in the process, and in the approximation that bond angles about the participating carbon atoms are tetrahedral, the optical anisotropy is unaffected by this condensation in which pairs of collinear $\text{CH}-\text{CH}_3$ and $\text{C}-\text{H}$ bonds are converted to $\text{CH}-\text{CH}_2$. This follows from the isotropy of methane and the associated relation $\Delta\alpha_{\text{CH}_3} = -\Delta\alpha_{\text{CH}}$. It will be apparent also from the cylindrical symmetry of the methyl group that $\hat{\alpha}_{\text{ps}}$ for the polystyrene chain will be the sum of the tensors $\hat{\alpha}_{\text{cumene}}$ for any orientation of the cumene molecules which complies with the stated condition of collinearity of the bonds involved in the elimination of methane. Hence, $\hat{\alpha}_{\text{ps}}$ is given by this sum of tensors for any conformation of the polystyrene chain, it being understood that the orientations of the constituent tensors are taken into account. We, therefore, identify the anisotropy tensor for the repeating unit $-\text{CH}(\text{C}_6\text{H}_5)-\text{CH}_2-$ with $\hat{\alpha}_{\text{cumene}}$.

It will be expedient to express this tensor in the cartesian reference frame defined by the pair of skeletal bonds $\text{CH}_2-\text{CH}-\text{CH}_2$, the x -axis being taken along the second bond of the pair and the y -axis in the plane defined by these bonds with the direction of the y -axis acute to the CH_2-CH bond. The direction of the z -axis is chosen to complete a right- or a left-handed cartesian system, depending on the chirality of the second bond.^{31, 32} Let the pair of skeletal bonds be serially indexed $i-1$ and i , respectively. The x_i and y_i axes of the indicated reference frame are shown in fig. 6. Also shown is the X -axis of the reference frame in fig. 3 employed for the expression of $\hat{\alpha}_{\text{cumene}}$ according to eqn (12). Transformation from the reference frame XYZ embedded in the phenyl group to the reference frame (also right-handed) $x_i y_i z_i$ requires rotation about the Y -axis through the angle ψ , followed by rotation about the axis Z (or axis z_i) through the angle $\pi - \xi$. These angles are defined in fig. 6. To the skeletal bond angle $\pi - \theta''$ at the tertiary carbon we assign the value 112° . Hence, $\xi = (\pi - \theta'')/2 = 56^\circ$. On the further assumption that all bond angles $\angle \text{CCC}$ at the tertiary carbon are equal to 112° , one obtains $\psi = 47.9^\circ$. Finally, we take $\beta = 0$, which is tantamount to fixing the phenyl group in its preferred

orientation about the axis of the C—C^{ar} bond. The error is negligible if the average range of β does not exceed about $\pm 20^\circ$.

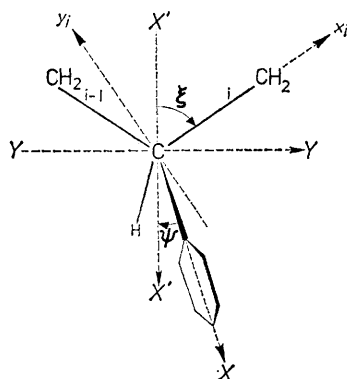


FIG. 6.—Relationship between the respective coordinate systems embedded in the phenyl group and affixed to the skeletal bond i .

Application of the foregoing transformations to eqn (12) with the various angles assigned the values stated above, with $\Delta\alpha_{\phi H} = 3.85 \text{ \AA}^3$ and $\Delta\alpha_{\phi H}^\dagger = -3.0 \text{ \AA}^3$, and with $\Gamma_{CC} = 0.53 \text{ \AA}^3$ yields

$$\hat{\alpha}_i \equiv \hat{\alpha}' = \begin{bmatrix} -1.376 & -1.825 & 0.778 \\ -1.825 & 0.099 & -1.153 \\ 0.778 & -1.153 & 1.277 \end{bmatrix} \times 10^{-24} \text{ cm}^3 \quad (15)$$

for the optical anisotropy tensor associated with a skeletal bond such as bond i in fig. 6. This being the first bond of a dyad pair, we designate it, in a generic sense, by a single prime as above.³³

For a given spatial configuration of the chain, as specified by skeletal bond angles* $\pi - \theta_i$ and the torsional angles φ_i for each internal skeletal bond i , the optical anisotropy parameter γ^2 is given by³³⁻³⁶

$$\gamma^2 = \frac{3}{2} \mathbf{P}_{[1]} \mathbf{P}_2^{(n-2)} \mathbf{P}_{[n]} \quad (16)$$

where $\mathbf{P}_2^{(n-2)}$ stands for the serial product of the $n-2$ generator matrices \mathbf{P}_i commencing with \mathbf{P}_2 for bond 2. For each internal bond, \mathbf{P}_i is defined according to

$$\mathbf{P}_i = \begin{bmatrix} 1 & 2\hat{\alpha}^R(\mathbf{T} \otimes \mathbf{T}) & \hat{\alpha}^2 \\ \mathbf{0} & (\mathbf{T} \otimes \mathbf{T}) & \hat{\alpha}^C \\ 0 & \mathbf{0} & 1 \end{bmatrix}_i, \quad 1 < i < n. \quad (17)$$

The initial matrix $\mathbf{P}_{[1]}$ is the first row of \mathbf{P}_i with $i = 1$, and $\mathbf{P}_{[n]}$ is the last column of \mathbf{P}_i with $i = n$. \mathbf{T}_i is the transformation from the reference frame for bond $i+1$ to that for bond i . The self-direct product $\mathbf{T} \otimes \mathbf{T}$ may be condensed to 6×6 order as set forth elsewhere.³⁵ The row $\hat{\alpha}_i^R$ and the column $\hat{\alpha}_i^C$ comprising the elements of $\hat{\alpha}_i$ are correspondingly condensed to orders 6×1 and 1×6 , respectively.³⁵ Finally, $\hat{\alpha}_i^2 = \hat{\alpha}_i^R \hat{\alpha}_i^C$. The resulting matrix \mathbf{P}_i is of order 8×8 .

* The adoption of an angle other than symmetrical tetrahedral for $\angle CCC$ at the methylene of the chain skeleton vitiates identification of the anisotropy tensor for the repeat unit with $\hat{\alpha}_{\text{cumene}}$ according to the procedure above. The error can be identified with alteration of $\angle HCC$ for the C—H bond eliminated in the hypothetical process of joining pairs of cumene molecules. It is trivial, however, for departures of θ' from the tetrahedral value that do not exceed 5 % (cf. *seq.*).

Since the optical anisotropy of the repeat unit is allocated in its entirety to the first bond of a dyad by the procedure described above, the generator matrix \mathbf{P}' for such a bond is given by eqn (17) with eqn (15) for $\hat{\alpha}'$ substituted therein. The transformation \mathbf{T}' in \mathbf{P}' relates the reference frame for the second bond of the dyad to the first.

The generator matrix \mathbf{P}'' for the second bond of a dyad is given by

$$\mathbf{P}'' = \begin{bmatrix} 1 & \mathbf{0} & 0 \\ \mathbf{0} & \mathbf{T}'' \otimes \mathbf{T}'' & \mathbf{0} \\ 0 & \mathbf{0} & 1 \end{bmatrix} \quad (18)$$

obtained from eqn (17) with $\hat{\alpha}$ null. Here \mathbf{T}'' represents the transformation from the reference frame for the first bond of the following dyad into the reference frame of the second bond of the dyad considered.

Inasmuch as the bonds flanking the tertiary carbon are necessarily of opposite chirality, \mathbf{T}'' must take into account the fact that it relates right- and left-handed reference frames when these are defined in the manner stated above.^{26, 31} Thus, if \mathbf{T} is the transformation between coordinate systems of the same hand, it follows that the transform \mathbf{T}'' is of the form \mathbf{T}^* where

$$\mathbf{T}^* = \mathbf{T} \text{diag} (1, 1, -1)$$

regardless of the stereochemical character of the dyad. Since the bonds within a *meso* dyad are also of opposite chirality, \mathbf{T}'_m must likewise be identified with \mathbf{T}^* . The bonds of a racemic dyad are of the same chirality, hence \mathbf{T}'_r is of the character \mathbf{T} .

Calculations of the conformational energies⁶ of *meso* and racemic dyads of polystyrene reveal four minima of accessible energy for each dyad. In table 3 we give their averaged locations,⁶ expressed as the rotations φ' and φ'' from the *trans* conformation, the sign of the rotation being measured according to the chirality of the bond³¹ (see above). Included also are the partition functions or statistical weights $U_{\kappa\lambda}$, attributable to each minimum or rotational state, with κ and λ either *trans* (*t*) or *gauche* (*g*). The $U_{\kappa\lambda}$ were evaluated by integrating the Boltzmann factor of the energy over the energy surface surrounding the minimum. These data are taken from ref. (6).

TABLE 3.—ROTATIONAL ISOMERIC STATES AND STATISTICAL WEIGHTS FOR DYADS OF THE POLYSTYRENE CHAIN^a

state	<i>meso</i>		<i>racemic</i>	
	$\varphi', \varphi''/\text{deg}$	$U_{\kappa\lambda}$ ^b	$\varphi', \varphi''/\text{deg}$	$U_{\kappa\lambda}$ ^b
<i>tt</i>	20, 20	0.04	10, 10	1
<i>tg</i> ^c	5, 110	0.64	20, 90	0.03
<i>gg</i>	90, 90	0.02	105, 105	0.40

^a From Yoon *et al.*, ref. (6); ^b evaluated for a temperature of 25°C; ^c the *gt* state corresponds to *tg* with φ' and φ'' interchanged.

Elements of the statistical weight matrices \mathbf{U}'_m and \mathbf{U}'_r are furnished by the entries in table 3. The statistical weight matrix for the first bond of the dyad in relation to the preceding bond is given by

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix} \quad (19)$$

without regard for the characters, *meso* or racemic, of the dyads thus joined. Hence,

the configuration partition function for the chain is obtained from the serial product of matrices $(U'U'')_k$ for successive dyads k , where $k = 1$ to $x-1$; *i.e.*,

$$Z = U_{11}(U'U'')_1^{(x-1)}U_{x1} \quad (20)$$

$$\left. \begin{aligned} U_{11} &= \begin{bmatrix} 1 & 0 \end{bmatrix} \\ U_{x1} &= \begin{bmatrix} 1 \\ 1 \end{bmatrix} \end{aligned} \right\} \quad (21)$$

and U''_k is U''_m or U''_r as dictated by the character of dyad k .

The statistical mechanical average of γ^2 is given by ^{33,35}

$$\langle \gamma^2 \rangle = \left(\frac{3}{2}\right)Z^{-1} \mathcal{P}_{11} \mathcal{P}_1^{(x-1)} \mathcal{P}_{x1} \quad (22)$$

where

$$\mathcal{P}_k = (U' \otimes E_8) \begin{bmatrix} U''_{tt}(P'P'')_{tt} & U''_{tg}(P'P'')_{tg} \\ U''_{gt}(P'P'')_{gt} & U''_{gg}(P'P'')_{gg} \end{bmatrix} \quad (23)$$

is the generator matrix for dyad k , which may be meso or racemic. Here, E_8 is the identity of order eight, and U''_{tt} , U''_{tg} , *etc.*, are elements of the statistical weight matrix U'' , these elements being given in table 3. The generator matrices P' and P'' are formally defined by eqn (17) and (18); the transformations T' and T'' therein are determined by θ' and θ'' , which we set equal to 66° and 68° , respectively, and by the values of ϕ' and ϕ'' given in table 3 for the state specified by subscripts. The torsional angles ϕ' and ϕ'' entering P' and P'' , as well as the values of U'' , *etc.*, depend on the stereochemical character of dyad k (see table 3).

The terminal matrices in eqn (22) are

$$\left. \begin{aligned} \mathcal{P}_{11} &= U_{11} \otimes P_{11} \\ \mathcal{P}_{x1} &= U_{x1} \otimes P_{x1} \end{aligned} \right\} \quad (24)$$

with

$$P_{11} = \text{row}(1, 0 \dots 0)$$

and

$$P_{x1} = \text{col}(\hat{\alpha}^2, \hat{\alpha}^c, 1)$$

as follows from eqn (18) and (17), respectively, and the definitions of P_{11} and P_{n1} given above.

TABLE 4.—OPTICAL ANISOTROPIES CALCULATED FOR POLYSTYRENE AND ITS OLIGOMERS

x	tacticity	$\langle \gamma^2 \rangle_{x-1} / \text{\AA}^6$	
		calc'd	obs'd
2	m	17.8	21.8
	r	27.5	25.0
3	mixture ^a	27.1	26.0
≥ 20	$w_m = 0.4 \pm 0.1$	37 ± 5	32 ± 1
∞	(m) _{∞} isotactic	29.9	—
	(r) _{∞} syndiotactic	96.9	—

^a isotactic: heterotactic: syndiotactic = 14:50:36

Results of calculations carried out using these relations are presented in table 4 and fig. 7. For isotactic and syndiotactic chains, serial multiplication was performed using the generator matrices, U'' and P_k , for meso and for racemic dyads, respectively. Atactic chains in which the expectation of a meso dyad is w_m , where $0 < w_m < 1$, and in which the sequencing of dyads is random (Bernoullian) were generated by Monte Carlo methods. Calculations of $\langle \gamma^2 \rangle$ were carried out on the sequences thus

generated, the appropriate matrix $\mathcal{P}_{\text{meso}}$ or $\mathcal{P}_{\text{racemic}}$ being selected according to the character of each dyad. Averages were taken for twenty chains at each composition and chain length. Standard deviations are shown by vertical bars in fig. 7. The single entry for the atactic polymer in table 4 represents the mean of closely agreeing calculations within the range $w_m = 0.3-0.5$ and for $x = 20, 40$ and 100 .

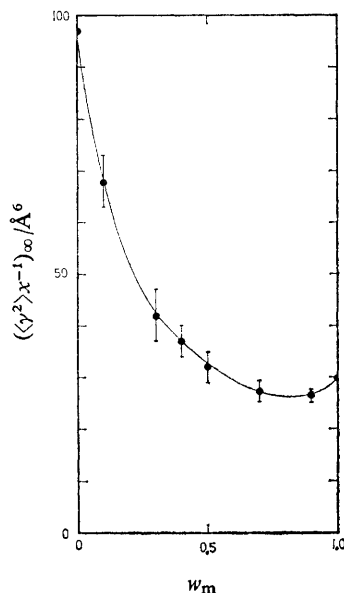


FIG. 7.—Calculated optical anisotropies of polystyrene plotted against the fraction w_m of meso dyads in random (Bernoullian) chains. Averages for 20 Monte Carlo chains are denoted by \bullet . The vertical bars represent standard deviations for each set of 20 chains. See text for parameters used.

The value calculated for $\langle\gamma^2\rangle$ for the meso “dimer” exceeds that for the racemic form (table 4), in agreement with our experimental results. Although the mean of $\langle\gamma^2\rangle_m$ and $\langle\gamma^2\rangle_r$ obtained by calculation is in good agreement with experiment, their difference, according to the calculations, is considerably greater than observed. Agreement for the trimer is good. Calculated values for the atactic polymer are greater than those observed, but the difference is within both the range of experimental error and uncertainties in the calculations, including uncertainties in the stereochemical composition.

The effects on the calculations of alterations in the statistical weights given in table 3 have been examined in detail. Variations within allowable ranges, as established previously by analysis of other properties of polystyrene and its oligomers,⁶ affect the calculated results by $<5\%$.

According to the evaluations shown in fig. 7, $\langle\gamma^2\rangle x^{-1}$ for the syndiotactic chain is nearly five times the value for cumene. It decreases rapidly with incorporation of meso dyads. Over the range from atactic ($w_m = 0.5$) to isotactic ($w_m = 1.0$) it changes little, and is only about three-halves of γ^2 for cumene.* In this range the correlation between group tensors for units comprising the chain is positive but small

* Fourche and Jacq² found $\langle\gamma^2\rangle$ for isotactic polystyrene of high molecular weight to be ~ 10 times $\langle\gamma^2\rangle$ for the atactic polymer. Experiments on the isotactic material were rendered difficult by its very low solubility. Measurements were therefore restricted to low concentrations, and incomplete dispersion of the crystalline polymer may have vitiated the results.

according to the calculations. The marked sensitivity of $\langle \gamma^2 \rangle$ to tacticity in the syndiotactic range is especially noteworthy. An explanation of the difference between $\langle \gamma^2 \rangle x^{-1}$ for the syndiotactic and isotactic chains is included in the Discussion of the following paper.³⁷

Although the experiments on polystyrene are meagre, in conjunction with the results for the oligomers they warrant the conclusion that the optical anisotropies for this series of chain molecules are consistent with the group anisotropic polarizability tensors determined from DRS measurements on low molecular hydrocarbons bearing a single phenyl group, and, in particular, with the tensor for cumene. The rotational isomeric state analysis of the polystyrene chain recently published⁶ gains further support from this study.

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