from the second term in eq 37 yield similar values of a for both isotactic and syndiotactic chains. Moreover, they display only a small dependence on $\Delta\phi$ from 0 to 10° and on ω from 0 to 0.2. All results fall within the range $a = -1.7 \pm 0.2$. With substitution of this for a in eq 38, we observe that a square-well potential confining χ to the range $\pm 20°$ would reduce the magnitude of Γ_2 only by about 7%. The actual range of variation of χ is almost certainly smaller than would correspond to a square well $\pm 20°$ in breadth. Hence, we conclude that the correction for rotation of the phenyl group must be quite small and may be insignificant.

Experimental strain-birefringence studies on crosslinked atactic polystyrene networks swollen with solvents have been carried out by Tsvetkov and coworkers.[26] By extrapolation of measurements at various concentrations, these results yield a value of about -170×10^{-25} cc for Δa of eq 4. Hence, Γ_2 (exptl) $\approx -100 \times 10^{-25}$ cc. Calculated values in the vicinity of $f_r = 0.5$ are about -135×10^{-25} cc for $\Delta\phi = 0°$ and $\omega = 0.05$; see Figure 8. Increase of $\Delta\phi$ to 10° lowers the magnitude to about -125×10^{-25} cc according to calculations not reproduced in detail here. Allowance for torsional oscillation of the phenyl group would lower the magnitude of this figure somewhat, perhaps to -115 to -120×10^{-25} cc. The agreement with experiment is quite satisfactory.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research Contract No. F 44620-69-C-0058.

Optical Anisotropy of Vinyl Polymer Chains. II. Depolarized Scattering by Polypropylene and Polystyrene

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Received December 26, 1969

ABSTRACT: The depolarization of light scattered at 90° by polypropylene (PP) and polystyrene (PS) is treated according to rotational isomeric state theory. Numerical calculations are carried out as functions of the statistical weight parameter ω governing interactions of second order, of the locations of the rotational states, of the chain length expressed by the number x of repeat units, and of the stereochemical composition expressed by the fraction f_r of racemic dyads. The intensity of the depolarized scattering per repeat unit rapidly approaches an asymptotic value with x, except for $\omega = 0$ in the case of stereoregular chains ($f_r = 0$ or 1). Admission of disfavored conformations to the extent represented by $\omega = 0.05$ renders the scattering for PP fairly insensitive to f_r. The calculations on PS chains indicate a much stronger dependence on f_r within the range $0.4 < f_r < 1$. The depolarized scattering of 2,4-dimethylpentane found experimentally by Clement and Bothorel is in good agreement with calculations for the PP oligomer with $x = 2$. Experimental results suitable for comparison with the calculations for high polymeric chains are unavailable at present.

The depolarization of light scattered by polymer molecules in solution has been treated according to rotational isomeric state theory by Jernigan and one of the present authors[1,2] and by Nagai.[3] Like the strain birefringence, the depolarization is determined by the anisotropy of the polarizability tensor. It depends on a particular invariant of that tensor and therefore is not related in any direct way to the strain birefringence. The group polarizabilities derived in the preceding paper[4] (hereafter referred to as I) may be employed however for the formulation of this invariant, which may then be averaged over all configurations of the chain by well-established methods.[2]

The treatment and calculations for polypropylene (PP) and polystyrene (PS) chains which follow are addressed to depolarization measurements on the polymers and their low-molecular oligomeric homologs, such measurements being carried out either on the pure liquids or on their solutions. The valence optical scheme critically discussed by Volkenstein[5] is adopted, as in the treatment of strain birefringence. Inductive effects on the surrounding molecules, solvent or species of like kind, and the inductive effects of neighboring molecules on the one considered, cannot in general be ignored. If, in the case of a solution, the solvent is optically isotropic, or if orientations of solvent molecules in the neighborhood of the solute are random, then it may be permissible to consider only the so-called microform effects dependent upon the difference between the polarizability tensor for the solute molecule or the polymer unit and the polarizability of the solvent it replaces, due account being taken of the anisometric shape of the solute or unit. The shape of the unit usually is not well defined, especially in relation to the various conformations which the unit may assume.

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[1] R. L. Jernigan and P. J. Flory, *J. Chem. Phys.*, 47, 1999 (1967).

[2] P. J. Flory, "Statistical Mechanics of Chain Molecules," John Wiley & Sons, Inc., New York, N. Y., 1969, pp 353–365.

[3] K. Nagai, *J. Chem. Phys.*, 47, 4690 (1967).

[4] Y. Abe, A. E. Tonelli, and P. J. Flory, *Macromolecules*, 3, 294 (1970).

[5] M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," S. N. Timasheff and M. J. Timasheff, Trans., John Wiley & Sons, Inc., New York, N. Y., 1963, Chapter 7.

This part of the problem does not admit of general treatment; each case must be handled individually. If, however, the polarizability per unit volume of the (isotropic) solvent matches the average polarizability of the polymer, then the microform effect should vanish, as is well known.

Here we assume either that the experimental conditions have been so chosen as to permit the microform effect to be ignored, or that the microform effect (in the given medium) has been included in the group polarizability tensors. In the illustrative calculations presented for PP and PS chains, we tacitly adopt the former alternative inasmuch as the medium is not specified.

The method here employed takes into account the sum of the group polarizability tensors for each and every spatial configuration. Hence, separate account of the *macro*-form effect customarily discussed in reference to particles of specified shape (*e.g.*, ellipsoids of revolution) is obviated by taking the statistical mechanical average over all of these configurations.

Theory

The depolarization of light scattered by a dispersion of particles oriented at random[6,7] depends on the quantity γ^2 defined by[8]

$$\gamma^2 = (^3/_2)\,\mathrm{trace}\,(\hat{\boldsymbol{\alpha}}\hat{\boldsymbol{\alpha}}) \tag{1}$$

where $\hat{\boldsymbol{\alpha}}$ is the traceless polarizability tensor for a particle; *i.e.*, $\hat{\boldsymbol{\alpha}} = \boldsymbol{\alpha} - \bar{\alpha}\mathbf{E}_3$ (compare eq I-14[4]). Thus, for scattering at 90° from the incident beam (and the ensuing discussion refers exclusively to scattering at this angle), the Rayleigh ratio R_{An} of the anisotropic scattering is given by

$$R_{\mathrm{An}} = R_{\mathrm{vh}} = R_{\mathrm{hv}} = R_{\mathrm{hh}} = (16\pi^4\nu/\lambda^4)(\gamma')^2/15 \tag{2}$$

where R_{vh} is the Rayleigh ratio for horizontally polarized scattered light when the incident beam is vertically polarized with respect to the plane defined by the incident and scattered rays; R_{hv} and R_{hh} are the vertically and horizontally polarized components of the scattered radiation when the incident beam is horizontally polarized; λ is the wavelength in a vacuum, ν is the number of molecules per unit volume, and γ' is the effective value of γ in the liquid medium. Assuming a Lorentz-Lorenz internal field, we have $\gamma' = \gamma(\tilde{n}^2 + 2)/3$ where $\tilde{n}$ is the refractive index. On this basis

$$R_{\mathrm{An}} = (16\pi^4\nu/\lambda^4)[(\tilde{n}^2 + 2)^2/9]\gamma^2/15 \tag{2$'$}$$

In the case of a solution, R_{An} may be identified with the increment due to the solute; *i.e.*, it may be considered to represent the difference between the anisotropic scattering of the solution and that attributable to the solvent contained therein.

The isotropic scattering is represented by the Rayleigh ratio R_{vv} for vertically polarized incident and scattered rays. In general, it depends on fluctuations of both density and of composition. Ignoring the general case, we confine our consideration to a very dilute solution of molecules which are large with respect to the solvent, but not so large as to introduce significant differences in phase for rays scattered by different portions of the same molecule. Then the contribution of the solute to scattering at right angles in the limit of infinite dilution can be expressed by

$$R_{\mathrm{vv}} = (16\pi^4\nu/\lambda^4)[(\bar{\alpha}')^2 + (4/45)(\gamma')^2] \tag{3}$$

$$= (16\pi^4\nu/\lambda^4)[(\tilde{n}^2 + 2)/3]^2[\bar{\alpha}^2 + (4/45)\gamma^2] \tag{3$'$}$$

In the latter equation the effective mean polarizability $\bar{\alpha}'$ is replaced on the supposition that the Lorentz-Lorenz internal field obtains. Equations 2 and 3 are of the same form as for the scattering by a gas.

The corresponding expressions for the depolarization ratios for vertically polarized and for unpolarized incident light are, respectively

$$\rho_{\mathrm{v}} = R_{\mathrm{vh}}/R_{\mathrm{vv}} = 3\gamma^2/(45\bar{\alpha}^2 + 4\gamma^2) \tag{4}$$

and

$$\rho = (R_{\mathrm{vh}} + R_{\mathrm{hh}})/(R_{\mathrm{vv}} + R_{\mathrm{hv}}) \tag{5}$$

$$= 6\gamma^2/(45\bar{\alpha}^2 + 7\gamma^2)$$

These equations refer to the scattering at 90° attributable to the high molecular solute in the limit of infinite dilution. They are of the same form as corresponding expressions for 90° scattering by gases.[6,7]

For randomly coiled chains γ^2 must be replaced by its average $\langle\gamma^2\rangle$ over all configurations. This invariant of the polarizability tensor $\boldsymbol{\alpha}$ can be computed according to the matrix multiplication procedure[2] through use of the expression[1,2]

$$\langle\gamma^2\rangle = 2Z^{-1}\mathscr{G}^*\mathscr{P}_1^{(n+1)}\mathscr{G} \tag{6}$$

where Z is the configuration partition function, $\mathscr{G}^*$ and $\mathscr{G}$ are the row and column defined in preceding papers,[1,2,9] and $\mathscr{P}_1^{(n+1)}$ is the serial product of factors[10]

$$\mathscr{P}_i = \begin{bmatrix} \mathbf{U} & (\mathbf{U} \times \hat{\boldsymbol{\alpha}}^{\mathrm{R}})\|\mathbf{T} \times \mathbf{T}\| & (^3/_4)\hat{\alpha}^2\mathbf{U} \\ \mathbf{0} & (\mathbf{U} \times \mathbf{E}_3)\|\mathbf{T} \times \mathbf{T}\| & (^3/_2)\mathbf{U} \times \boldsymbol{\alpha}^{\mathrm{C}} \\ \mathbf{0} & \mathbf{0} & \mathbf{U} \end{bmatrix}_i \tag{7}$$

Here, $\hat{\boldsymbol{\alpha}}_i^{\mathrm{R}}$ and $\hat{\boldsymbol{\alpha}}_i^{\mathrm{C}}$ are the row and column forms of the traceless tensor $\hat{\boldsymbol{\alpha}}_i$, and $\hat{\alpha}_i^2$ is the sum of the squares of its elements, *i.e.*

$$\hat{\alpha}_i^2 = \mathrm{trace}\,(\hat{\boldsymbol{\alpha}}_i\hat{\boldsymbol{\alpha}}_i) = \hat{\boldsymbol{\alpha}}_i^{\mathrm{R}}\hat{\boldsymbol{\alpha}}_i^{\mathrm{C}} \tag{8}$$

These and other quantities in eq 7 are defined elsewhere.[2,9] Group tensors formulated in the preceding paper[4] are directly applicable here (also see the Appendix to this paper).

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(6) S. Bhagavantam, "Scattering of Light and the Raman Effect," Chemical Publishing Co., Brooklyn, N. Y., 1942.

(7) H. C. Van de Hulst, "Light Scattering by Small Particles," John Wiley & Sons, Inc., New York, N. Y., 1957.

(8) R. P. Smith and E. M. Mortensen, *J. Chem. Phys.*, 32, 502, 508 (1960).

(9) Y. Fujiwara and P. J. Flory, *Macromolecules*, 3, 280 (1970).

(10) The computations may be simplified by condensing $\mathbf{T} \times \mathbf{T}$ from 9×9 to 6×6 order, with corresponding reductions in the orders of row and column direct products appearing in eq 7, after the manner cited in ref 20 of the preceding paper.[4] Actual calculations presented here were carried out in this manner.

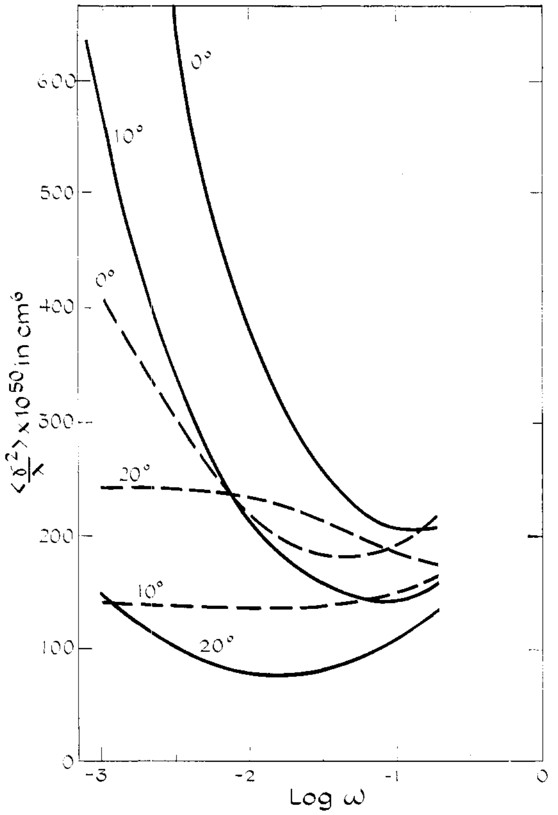

Figure 1. Depolarization anisotropy per unit $\langle\gamma^2\rangle/x$ plotted against log ω for isotactic (solid curves) and syndiotactic (dashed curves) polypropylenes. Calculations carried out for chains of $x = 400$ units using parameters $\eta = 1.00$, $\tau = 0.50$, $\tau^* = 1.00$. Values of $\Delta\phi$ are indicated with each curve.

Results of Numerical Calculations on Polypropylene

The invariant $\langle\gamma^2\rangle$ of the polarizability tensor which characterizes its anisotropy with reference to depolarized scattering was calculated according to eq 6 and 7 for chains of various lengths and stereochemical compositions as specified below. Rotational states were taken at locations defined by $\Delta\phi = 0°$, $10°$, and $20°$ (see I).[4,9] As in I, all calculations on this polymer were carried out for values of the statistical weight parameters as follows: $\eta = 1.00$, $\tau = 0.50$, and $\tau^* = 1.00$, with ω treated as a variable.

The average depolarization anisotropy per repeat unit, represented by the ratio $\langle\gamma^2\rangle/x$, is plotted in Figure 1 against log ω for isotactic (full lines) and for syndiotactic (dashed lines) PP chains. The calculations were carried out for chains of $x = 400$ units. Asymptotic values of the ratio are substantially attained at this chain length in all cases except for very small values of ω. The dependence of $\langle\gamma^2\rangle/x$ on ω for isotactic chains is similar for the several values of $\Delta\phi$, although the magnitude of the ratio decreases as $\Delta\phi$ is increased. Each of the three curves displays a minimum with log ω. In the limit $\omega = 0$, the only acceptable conformations for the isotactic chains are the right- and left-handed helices (the Natta–Corradini 3_1 helices in the case $\Delta\phi = 0°$); hence $\langle\gamma^2\rangle/x$ diverges in this limit. The rate of divergence with decrease in ω is slowed by an increase in $\Delta\phi$, however.

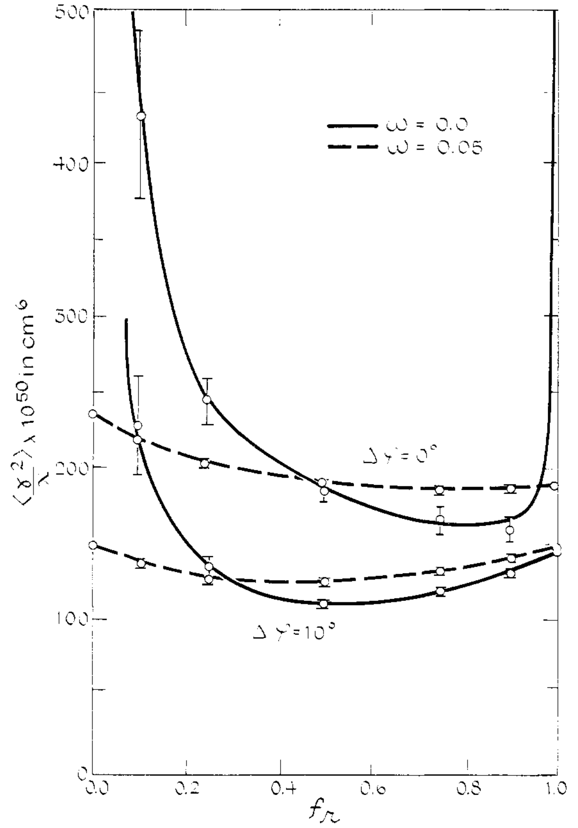

Figure 2. The dependence of $\langle\gamma^2\rangle/x$ on stereochemical composition of PP expressed by the fraction f_r of racemic dyads. Each point within the range $0 < f_r < 1$ represents the average for 15 Monte Carlo chains. Vertical bars denote standard deviations.

For syndiotactic chains the change of $\langle\gamma^2\rangle/x$ with ω depends markedly on $\Delta\phi$. The curve for $\Delta\phi = 0°$ increases without limit with decreasing ω, owing to the suppression of nonplanar conformations, as pointed out in preceding papers.[4,9] Curves for $\Delta\phi = 10°$ and $20°$ display remarkably small dependences on ω within the realistic range of $\omega < 0.10$, and each converges rapidly to a finite asymptotic value as ω decreases.

The results of Monte Carlo calculations of $\langle\gamma^2\rangle/x$ for chains of various stereochemical compositions expressed by the fraction f_r of racemic dyads are presented in Figure 2. Values of ω and $\Delta\phi$ are indicated in the figure. Each point represents the average for 15 Monte Carlo chains consisting of $x = 400$ units. Standard deviations are shown by vertical bars. The configurational average of the anisotropy of the polarizability, represented by $\langle\gamma^2\rangle$, is comparatively insensitive to the stereochemical composition f_r throughout the atactic range. It increases markedly near the isotactic extremity ($f_r = 0$) for $\omega = 0$; it increases abruptly at the syndiotactic extremity if $\Delta\phi = 0°$, for the reasons cited above. An increase of ω to 0.05 renders $\langle\gamma^2\rangle$ insensitive to the stereochemical composition throughout the range $f_r = 0$–1.

In Figure 3, $\langle\gamma^2\rangle/x$ is shown for PP as a function of chain length for isotactic, syndiotactic and atactic ($f_r = 0.5$) chains. All of these calculations were carried out with $\omega = 0.05$. For atactic chains consisting of more than three units, the values shown are

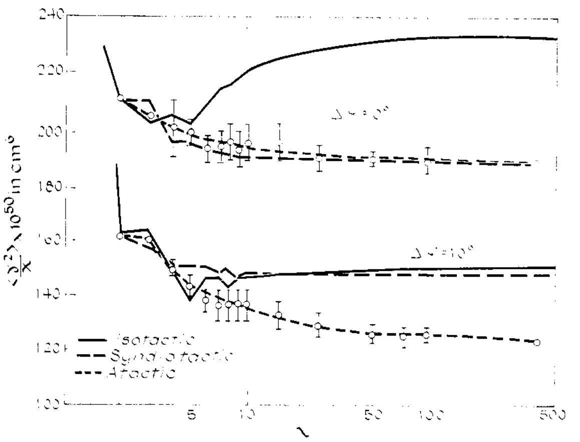

Figure 3. Dependence of $\langle\gamma^2\rangle/x$ on chain length x for isotactic (solid curves), syndiotactic (long dashed curves), and atactic ($f_r = 0.5$; short dashed curves) polypropylenes. Results for atactic PP with $x > 3$ computed for chains generated by Monte Carlo methods; see text. Vertical bars denote standard deviations. All calculations carried out for $\omega = 0.05$.

averages for 15 Monte Carlo chains in each case. It will be observed that $\langle\gamma^2\rangle/x$ approaches its asymptotic value at 10–50 units.

Inasmuch as both $\langle\gamma^2\rangle$ and $\bar{\alpha}$ are of order x, the depolarization ratios ρ_v and ρ (given by eq 4 and 5, respectively) must vanish as $1/x$ for large values of x. The average polarizability α for the propylene unit, C_3H_6, is 58.2×10^{-25} cc. From the results in Figure 3, we find for atactic PP ($f_r = 0.5$) for $\Delta\phi = 0°$ that

$$\rho = (7.5/x) \times 10^{-3},\ x > 15$$

and for $\Delta\phi = 10°$

$$\rho = (4.9/x) \times 10^{-3},\ x > 30$$

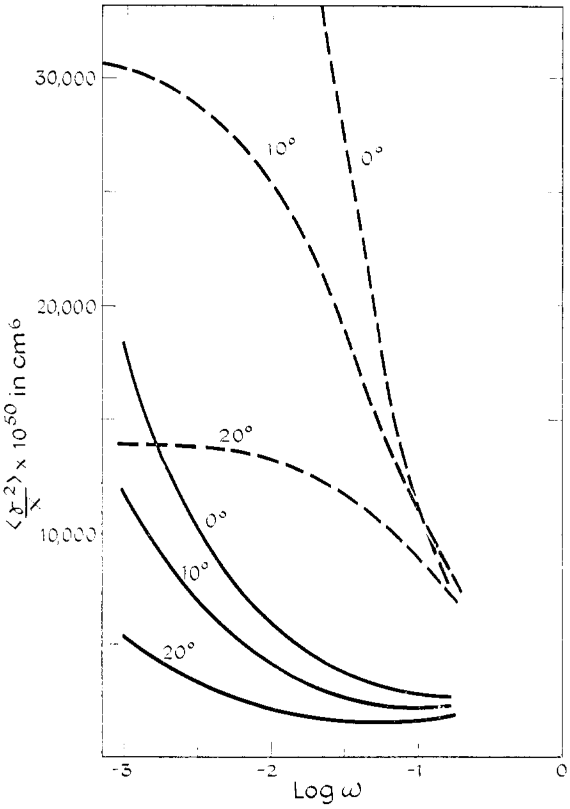

Figure 4. Depolarization anisotropies per unit $\langle\gamma^2\rangle/x$ plotted against log ω for isotactic (solid curves) and syndiotactic (dashed curves) polystyrenes. Values of $\Delta\phi$ are indicated with each curve; $\eta = 1.5$, $\tau = 0.5$, $\tau^* = 1.0$, and $x = 400$.

We are unaware of experimental results on polypropylene with which to compare these calculations. Clement and Bothorel[11] found $\langle\gamma^2\rangle = 332 \times 10^{-50}$ cm^6 for pure liquid 2,4-dimethylpentane, which may be regarded as the dimeric oligomer of PP. Our calculations carried out for $\Delta\phi = 0°$ and $10°$ (see Figure 3) give $\langle\gamma^2\rangle = 420$ and 324×10^{-50} cm^6, respectively, for the dimer. Careful scrutiny of the intramolecular interactions[12] in the several conformations leaves no doubt that $\Delta\phi > 0$; a value in the vicinity of 10° appears plausible. Thus, the agreement between theory and experiment is as good as may be expected in this instance.

Results of Numerical Calculations on Polystyrene

All calculations were carried out using $\eta = 1.5$, $\tau = 0.5$, $\tau^* = 1.0$, and $\chi = 0°$ (see I). Polarizability tensors were taken from the preceding paper (I).[4] In Figure 4 the values of $\langle\gamma^2\rangle/x$ for isotactic and syndiotactic chains ($x = 400$) are plotted against log ω for the several values of $\Delta\phi$ indicated.

Whereas for polypropylene the magnitudes of the anisotropy ratios for isotactic and syndiotactic chains are of the same order in the physically significant range $0.01 \leq \omega \leq 0.1$, the ratios for syndiotactic PS chains are much larger than those for isotactic PS chains. Although the curves for the isotactic PS chains exhibit minima with log ω, the minima are less pronounced than those calculated for PP (Figure 1). Effects of displacing the rotational states by amounts $\Delta\phi > 0°$ from symmetrical locations resemble those found for PP.

The dependence of $\langle\gamma^2\rangle/x$ on f_r is shown in Figure 5 for the values of $\Delta\phi$ and ω indicated. Each of the points on these curves within the range $0 < f_r < 1$ represents the average of computations on 15 Monte Carlo chains consisting of $x = 400$ units. The anisotropy ratio $\langle\gamma^2\rangle/x$ for PS exhibits a stronger dependence on f_r than was found for PP (compare Figure 2). This is consistent with the large difference between the ratios for isotactic and syndiotactic PS chains.

For atactic PS chains the dependence of the ratio on $\Delta\phi$ as well as on ω is small. The three curves shown in Figure 5 are close to one another in the range $0.2 < f_r < 0.8$.

Values of $\langle\gamma^2\rangle/x$ are plotted in Figure 6 against chain length for isotactic, syndiotactic, and atactic ($f_r = 0.5$) PS chains. They were calculated using $\omega = 0.05$ and $\Delta\phi = 0°$. The "atactic" point for $x = 2$ represents the mean for a *meso* (m) and a racemic (r) dimer; the point for $x = 3$ represents the weighted mean for mm, mr, and rr triads; and that for $x = 4$ is the mean for the several tetrads. For longer atactic chains

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[11] C. Clement and P. Bothorel, *J. Chim. Phys.*, **61**, 878 (1964).

[12] See A. Abe, *Polym. J.*, in press.

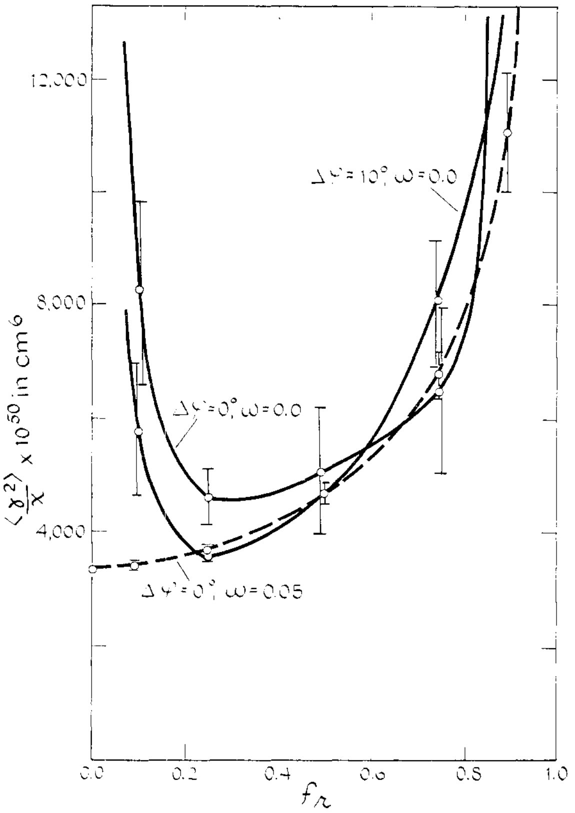

Figure 5. The dependence of $\langle \gamma^2 \rangle/x$ on the stereochemical composition of PS chains as established by Monte Carlo calculations on sets of 15 chains for $0 < f_r < 1$; see legend to Figure 2.

Monte Carlo calculations were carried out on sets of 50 chains for each value of x in the range $5 \leq x \leq 15$ and on 15 chains for x in the range $x \geq 25$. The large standard deviations for short chains are indicative of the marked effect of variations in stereochemical composition and sequence for chains generated subject to the *a priori* probability $f_r = 0.5$. The scale for isotactic and atactic chains is given on the left-hand margin; that for syndiotactic chains is given on the right-hand margin. The large difference in anisotropies between isotactic and syndiotactic chains is manifested even in short chains.

Similar calculations not included here were carried out for atactic chains with $\Delta\phi = 10°$ and $\omega = 0.05$. In keeping with the results presented in Figure 5 for long chains, the effects of these alterations were found to be small.

For atatic chains with $x > 10$, the depolarization ratio (see eq 5) is given approximately by

$$\rho \cong 34 \times 10^{-3}/x$$

Effects of variations in the torsional angle χ specifying rotations of the phenyl group (see Figure I-5 of ref 4), these being symmetrical about $\chi = 0°$,[4] have been investigated by methods given in the Appendix. Results of the computations for several values of $\langle \sin^2 \chi \rangle$ are summarized in Table I. The very large values of $\langle \gamma^2 \rangle/x$ for syndiotactic chains and for isotactic chains subject to $\omega = 0$ are lowered appreciably by variations in the torsional angle. For atactic chains, and for isotactic chains subject to the larger value of ω, the

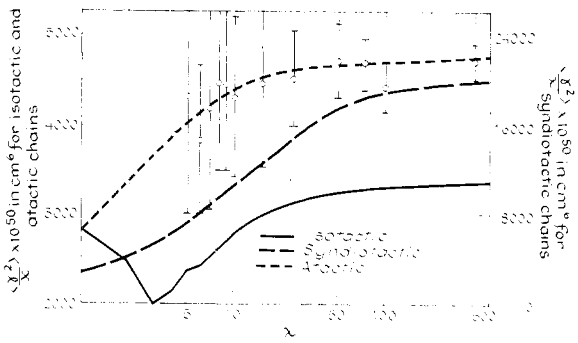

Figure 6. Dependence of $\langle \gamma^2 \rangle/x$ on x for isotactic, syndiotactic and atactic ($f_r = 0.5$) PS chains, with $\omega = 0.05$ and $\Delta\phi = 0°$. See text for details on Monte Carlo calculations for atactic chains.

effects are relatively small. Even for the comparatively large range of χ denoted by $\langle \sin^2 \chi \rangle = 0.08$ they amount to no more than 10%.

Discussion

In general the ratio $\langle \gamma^2 \rangle/x$ rapidly attains its asymptotic value with increase in x. Thus, with the exceptions of isotactic chains subject to $\omega \cong 0$ and of syndiotactic chains subject to $\omega \cong 0$ *and* $\Delta\phi = 0°$, asymptotic values are closely approached for x = 10–100 (see Figures 3 and 6). With the exceptions noted, correlation effects on $\langle \gamma^2 \rangle$ are not of long range. The intensity of depolarized scattering (see eq 3) at fixed weight concentration therefore approaches a constant value at chain lengths that are comparatively low. On the other hand, the depolarization ratio ρ for scattering attributable to the polymeric solute in the dilute solution must decrease with chain length at fixed weight concentrations owing to the increase in the intensity of the vertically polarized component with x at fixed weight concentration, $\bar{\alpha}$ in eq 2 being proportional to x. Thus, whereas the depolarization ratio so defined becomes extremely small for x in the high polymeric range, the absolute intensity of depolarized scattering by the solute (for fixed weight concentration) remains undiminished.

According to the calculations presented in Figures 1 and 2 for PP, effects of ω and $\Delta\phi$ dominate the dependence of the depolarization anisotropy on the stereochemical composition (f_r). The same applies to PS in the isotactic range (Figures 4 and 5). For f_r >

TABLE I
EFFECTS OF SYMMETRICAL FLUCTUATIONS IN THE ROTATION ANGLE OF THE PHENYL GROUP[a]

		$(\langle \gamma^2 \rangle/x) \times 10^{50}$, cm^6		
f_r	ω	$\langle \sin^2 \chi \rangle = 0$	$\langle \sin^2 \chi \rangle =$ 0.04	$\langle \sin^2 \chi \rangle =$ 0.08
0.0	0.0	147,000	127,000	108,000
	0.05	3,360	3,290	3,230
0.5	0.0	5,090 ± 1,140	4,690 ± 990	4,530 ± 680
	0.05	4,710 ± 200	4,430 ± 160	4,170 ± 120
1.0	0.0	279,000	249,000	212,000
	0.05	19,900	17,700	15,700

[a] All calculations carried out for x = 400 units with $\eta = 1.5$, $\tau = 0.5$, $\tau^* = 1.0$, and $\Delta\phi = 0°$.

0.4, however, a strong dependence on f_r predominates. Thus, depolarized scattering may offer a useful method for characterizing stereochemical composition of PS chains in the atactic and syndiotactic ranges. It is to be observed, however, that our calculations have been confined to polymers in which the distribution of *meso* and racemic dyads is random, or Bernoullian. Calculations could of course be carried out for chains of any given stereochemical sequence, statistical or regular.

It is regrettable that suitable experimental results with which to put the foregoing calculations to test are unavailable, except in the instance of the dimeric analog of PP, namely, 2,4-dimethylpentane, discussed above.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research Contract No. F 44620-69-C-0058.

Appendix

The Effect of Random Variations in the Torsional Angle χ. According to the treatment presented for strain birefringence (see especially eq I-33),[4] the polarizability of the CHR–C group subject to a torsional angle χ about the C—R bond is given by

$$\hat{\boldsymbol{\alpha}}'(\chi) = \hat{\boldsymbol{\alpha}}'(\chi = 0) + \Delta\alpha_{\mathrm{R}}(\sin^2 \chi)\boldsymbol{\beta}_{\mathrm{a}} + \Delta\alpha_{\mathrm{R}}(\sin \chi \cos \chi)\boldsymbol{\beta}_{\mathrm{b}} \quad (9)$$

where

$$\boldsymbol{\beta}_{\mathrm{a}} = \boldsymbol{\Omega}_0(\xi', -\psi_{\mathrm{R}})[\mathrm{diag}(0, -1, 1)]\boldsymbol{\Omega}_0(\xi', -\psi_{\mathrm{R}})^{\mathrm{T}} \quad (10)$$

$$\boldsymbol{\beta}_{\mathrm{b}} = \boldsymbol{\Omega}_0(\xi', -\psi_{\mathrm{R}}) \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \boldsymbol{\Omega}_0(\xi', -\psi_{\mathrm{R}})^{\mathrm{T}} \quad (11)$$

with $\Delta\alpha_{\mathrm{R}} = \alpha_{\mathrm{CR};y} - \alpha_{\mathrm{CR};z}$ and $\boldsymbol{\Omega}(\xi', -\psi_{\mathrm{R}})$ given by eq I-26.[4]

If χ is subject to variations, then the average tensor $\hat{\boldsymbol{\alpha}}'$ is obtained from eq 9 by replacement of the trigonometric functions therein by their averages. In the case of the PS chain, the potential affecting χ is symmetric about $\chi = 0$,[4] and we have therefore that

$$\hat{\boldsymbol{\alpha}}' = \hat{\boldsymbol{\alpha}}'(\chi = 0) + \Delta\alpha_{\mathrm{R}}\langle\sin^2 \chi\rangle\boldsymbol{\beta}_{\mathrm{a}} \quad (12)$$

For the treatment of the depolarization (see eq 7) we require also the quantity $\hat{\alpha}_i^2$ defined by eq 8. From eq 9 we obtain, for the case of a symmetric potential such that $\langle\sin \chi \cos \chi\rangle = \langle\sin^3 \chi \cos \chi\rangle = 0$

$$\begin{aligned} \hat{\alpha}'^2 &= \alpha'^2(\chi = 0) + \Delta\alpha_{\mathrm{R}}^2\langle\sin^4 \chi\rangle\boldsymbol{\beta}_{\mathrm{a}}^{\mathrm{R}}\boldsymbol{\beta}_{\mathrm{a}}^{\mathrm{C}} + \\ &\quad \Delta\alpha_{\mathrm{R}}^2\langle\sin^2 \chi \cos^2 \chi\rangle\boldsymbol{\beta}_{\mathrm{b}}^{\mathrm{R}}\boldsymbol{\beta}_{\mathrm{b}}^{\mathrm{C}} + 2\cdot\Delta\alpha_{\mathrm{R}}\langle\sin^2 \chi\rangle \times \\ &\qquad \boldsymbol{\beta}_{\mathrm{a}}^{\mathrm{R}}\hat{\boldsymbol{\alpha}}'^{\mathrm{C}}(\chi = 0) \\ &= \hat{\alpha}'^2(\chi = 0) + 2\cdot\Delta\alpha_{\mathrm{R}}\langle\sin^2 \chi\rangle\boldsymbol{\beta}_{\mathrm{a}}^{\mathrm{R}}\hat{\boldsymbol{\alpha}}'^{\mathrm{C}} \times \\ &\qquad (\chi = 0) + 2\cdot\Delta\alpha_{\mathrm{R}}^2\langle\sin^2 \chi\rangle \end{aligned}$$

since $\boldsymbol{\beta}_{\mathrm{a}}^{\mathrm{R}}\boldsymbol{\beta}_{\mathrm{a}}^{\mathrm{C}} = \boldsymbol{\beta}_{\mathrm{b}}^{\mathrm{R}}\boldsymbol{\beta}_{\mathrm{b}}^{\mathrm{C}} = 2$. Writing $\hat{\boldsymbol{\alpha}}'$ of eq 12 in its row and column forms and introducing them into the equation above, we obtain

$$\hat{\alpha}'^2 = \hat{\boldsymbol{\alpha}}'^{\mathrm{R}} \cdot \hat{\boldsymbol{\alpha}}'^{\mathrm{C}} + 2\Delta\alpha_{\mathrm{R}}^2(\langle\sin^2 \chi\rangle - \langle\sin^2 \chi\rangle^2) \quad (13)$$

The traceless tensor $\hat{\boldsymbol{\alpha}}'$ for a PS chain is given by eq I-37.[4]

The values of $\langle\gamma^2\rangle$ presented in Table I were calculated according to eq 6 and 7 using $\hat{\boldsymbol{\alpha}}'$ and $\hat{\alpha}'^2$ given by eq 12 and 13.

A Dielectric Study of Molecular Relaxation in Polyoxymethylene at High Temperatures

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ABSTRACT: Dielectric loss in polyoxymethylene has been measured at temperatures both below and above the crystalline melting point in order to ascertain the effect of crystalline order on molecular relaxation. Discontinuous changes in the relaxation take place upon melting. At least two relaxation regions are present in the melt. A relaxation region (α) occurs at ~4 GHz and further dispersion above 8 GHz is inferred from the dielectric constant at 8 GHz. The α region is characterized by a low activation energy, single relaxation time, and independence of molecular weight. From a study in the solid of the loss at low frequencies and the dc conductivity it was decided that an α dipolar dispersion region could not be extracted. A statistical mechanical calculation of the static dielectric constant of the melt based on the rotational isomeric state model is in good agreement with the experimental.

The study of relaxations in polymers by such techniques as measurement of the torsion modulus and loss *vs.* temperature has proven to be extremely valuable in understanding and summarizing simply their mechanical properties.[2] Although there exists a considerable body of information on relaxations from a variety of mechanical techniques and from dielectric and nuclear magnetic resonance measurements, the exact nature of the molecular motions underlying these relaxation regions remains relatively obscure. This is particularly true of the crystalline polymers where the role of the considerable recent developments in solid morphology is not clear. In fact, it is not clear how many relaxation regions linear chains without

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(2) N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids," John Wiley & Sons, Inc., New York, N. Y., 1967.