Optical Anisotropy of Vinyl Polymer Chains.
I. Strain Birefringence of Polypropylene and Polystyrene

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ABSTRACT: The theory of strain birefringence is elaborated in terms of the rotational isomeric state model as applied to vinyl polymer chains. Additivity of the polarizability tensors for constituent groups is assumed. Stress-birefringence coefficients are calculated for polypropylene (PP) and for polystyrene (PS) on the basis of the polarizabilities of C–C, C–H, and C_6H_5 given by Denbigh. Statistical weight parameters which affect the incidences of various rotational states are varied over ranges consistent with other evidence. The effects of these variations are explored in detail for isotactic and syndiotactic chains. Critical study of the distances between *ortho* H and C atoms of the phenyl group and other atoms of neighboring CH and CH_2 groups shows the preferred orientation of the phenyl group to be that in which its plane is perpendicular to the plane defined by the adjoining skeletal C–C bonds. This preference holds for all eligible conformations of the chain skeleton. Effects of fluctuations about this preferred orientation on the group polarizability tensor and on the stress-optical coefficient are treated. Stress-optical coefficients of stereoirregular polymers with varying degrees of tacticity are computed by Monte Carlo methods. Results deduced for atactic chains of PP and PS are in agreement with experimental results on these polymers.

The theory of the birefringence produced by strain in amorphous polymer networks was first developed by Kuhn and Grün[1,2] using the freely jointed chain as a model. The intimate connection with the theory of rubber elasticity was at once made apparent. The birefringence and the stress depend on the same function of the strain and of the network structure as expressed by the degree of cross-linking. Thus, within the limitations set by the gaussian approximation for the chain vector distribution, Kuhn and Grün showed that the birefringence should be directly proportional to the tension for simple elongation and independent of the degree of cross-linking.[2] These results of the Kuhn and Grün theory may be shown[3-5] to transcend the unrealities of the freely jointed chain model; they should hold generally for networks of random chains, within the range of deformations in which the Gaussian approximation cited above holds. They are, on the whole, well confirmed by experiments.[2]

The stress-optical coefficient of proportionality between the birefringence and the stress depends, according to the Kuhn and Grün theory, on the optical anisotropy of the hypothetical segment of the freely jointed model chain. Since the segment is a figment of the model, this theory offers no basis for relating the stress-optical coefficient to structural and optical characteristics (polarizabilities) of the real chain and its constituent units. The development of a theory which is capable of relating this property rationally to the chemical structure and configurational characteristics of the chains comprising a network was initiated by Gotlib and Volkenstein[3,4] in their pioneering studies underlying the establishment of the rotational isomeric state model as a basis for dealing more realistically with the configuration-dependent properties of polymeric chains. Nagai[5] refined and extended the theory so that it was possible for him to calculate the stress-optical coefficient for simple polymethylene chains starting with bond polarizabilities and employing the rotational isomeric state scheme with proper account of the dependence of bond rotations on neighbors. Generalization to chains of any length and virtually any structural description was achieved[6-8] by adoption of the matrix multiplication method,[9] successfully developed for generating configurational averages of other properties of polymeric chains.[10] The treatment was put in concise form by two of the present authors in collaboration with Jernigan,[7,8] who presented a method for generating the essential sum $\Sigma_i\langle \mathbf{r}^T\hat{\alpha}_i\mathbf{r}\rangle_0$ of configurational averages as a single serial product of generating matrices. Here $\mathbf{r}$ is the chain vector, $\mathbf{r}^T$ is its transpose, and $\hat{\alpha}_i$ is the traceless polarizability tensor associated with bond i. Nagai[11] recently presented a corresponding treatment in the Lifson–Nagai scheme.

In this paper we apply the methods cited above to two representative vinyl polymers. As in preceding papers on vinyl polymers,[12-14] the role of stereoregularity is given particular attention. The theory, and ac-

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(1) W. Kuhn and F. Grün, *Kolloid-Z.*, **101**, 248 (1942).

(2) L. R. G. Treloar, "The Physics of Rubber Elasticity," 2nd ed, Clarendon Press, Oxford, 1958, Chapter X. See also, *Trans Faraday Soc.*, **43**, 277 (1947).

(3) Yu. Ya. Gotlib, M. V. Volkenstein, and E. K. Byutner, *Dokl. Akad. Nauk SSSR*, **99**, 935 (1954); Yu. Ya. Gotlib, *Zh. Tekhn. Fiz.*, **27**, 707 (1957).

(4) 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.

(5) K. Nagai, *J. Chem. Phys.*, **40**, 2818 (1964).

(6) K. Nagai, *ibid.*, **47**, 2052 (1967).

(7) P. J. Flory, R. L. Jernigan, and A. E. Tonelli, *ibid.*, **48**, 3822 (1968).

(8) See ref 10, pp 365–377.

(9) P. J. Flory, *Proc. Nat. Acad. Sci. U. S.*, **51**, 1060 (1964); P. J. Flory and R. L. Jernigan, *J. Chem. Phys.*, **42**, 3509 (1965).

(10) P. J. Flory, "Statistical Mechanics of Chain Molecules," John Wiley & Sons, Inc., New York, N. Y., 1969.

(11) K. Nagai, *J. Chem. Phys.* **51**, 1265 (1969).

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

(13) Y. Fujiwara and P. J. Flory, *ibid.*, **3**, 288 (1970).

(14) For earlier references to studies on vinyl chains, see the preceding papers of this series, ref 12 and 13. See also ref 10, Chapter VI.

cordingly the calculations carried out through its use, rest on two main premises: (i) the reliability of the rotational isomeric state scheme, especially as applied to vinyl chains, and (ii) the additivity of group polarizability tensors. The former premise[4] has been employed in the treatment of other properties of vinyl chains,[14,15] and of polymer chains representing a variety of structural types.[10] There can be little doubt of its essential validity. The second premise is in need of critical scrutiny, a matter to which we shall devote attention elsewhere. Its validity may ultimately be decided largely on the basis of experimental evidence. The availability of theoretical procedures for handling the configuration-statistical aspects of the problem facilitates confrontation of premise (ii) with experimental observations.

Of the two polymers here considered, polypropylene (PP) possesses a substituent which is cylindrically symmetric about the CH–R axis, and hence the formulation of its group polarizability tensor is comparatively simple. Parameters occurring in the statistical weight matrices employed in preceding papers on vinyl polymers have not been determined for PP, and hence we must rely on crude estimates. The other polymer treated, polystyrene (PS), possesses a substituent with a large optical anisotropy. Though not cylindrically symmetric, one of its principal axes coincides with the CH–R bond. Statistical weight parameters for this polymer are known with sufficient assurance and accuracy from previous studies.[16]

General Theory

Consider a polymeric chain whose end-to-end vector **r** is fixed. Let $\Delta\alpha_r$ denote the difference between the optical polarizabilities along vector **r** and perpendicular to it, this difference being averaged over all configurations consistent with **r**. Inasmuch as the averaged polarizability tensor must be cylindrically symmetric about **r**, it follows that

$$\Delta\alpha_r = (^3/_2)(\alpha_r - \bar{\alpha}) \qquad (1)$$

where α_r is the averaged polarizability along **r** and $\bar{\alpha}$ is the mean polarizability, *i.e.*, $\bar{\alpha} = (^1/_3)\text{trace}\ \boldsymbol{\alpha}$. If X, Y, and Z are the axes of a cartesian coordinate system, then the difference between the components of the polarizability along two of these axes is given, for example, by[2,8]

$$(\alpha_{xx} - \alpha_{yy})_r = \Delta\alpha_r(x^2 - y^2)/r^2 \qquad (2)$$

where x and y are the components of **r** along X and Y, and r is its magnitude. To terms of first order in the extension of the chain[3–5] measured by $r^2/\langle r^2\rangle_0$

$$\Delta\alpha_r = \Gamma_2 r^2/\langle r^2\rangle_0 \qquad (3)$$

where Γ_2 is the constant of proportionality, or, rather, the coefficient of the first term in a series in powers of $r^2/\langle r^2\rangle_0$. For chains of sufficient length, and at extensions not too great, eq 3 suffices. According to the theory of a freely jointed chain[1–2]

$$\Gamma_2 = (^3/_5)\Delta a \qquad (4)$$

where Δa is the difference between the polarizabilities of the hypothetical segment along its length and perpendicular thereto. Whereas we shall evaluate Γ_2 from properties of the real chain, most experimental results have heretofore been interpreted in terms of the freely jointed model. Equation 4 therefore is useful in translating published experimental results to present terms.

By combination of eq 2 and 3

$$\alpha_{xx} - \alpha_{yy} = \Gamma_2(x^2 - y^2)/\langle r^2\rangle_0 \qquad (5)$$

The subscript r has been dropped from the left-hand member of this equation inasmuch as the difference in polarizabilities is a function of components of **r** and not of $r = |\mathbf{r}|$. For the system of chains in a network, it is convenient to identify X, Y, and Z with the principal axes of the deformation gradient $\boldsymbol{\lambda}$ that specifies the state of strain, and therefore also with the principal axes of the macroscopic polarizability, for which we herewith appropriate the symbol $\boldsymbol{\alpha}$. The difference between the polarizabilities of the network along two principal axes is obtained from eq 5 merely by replacing x^2 and y^2 by their average values $\overline{x^2}$ and $\overline{y^2}$ for the system of chains.[2] Thus, making the usual identifications

$$\lambda_x^2 = 3\overline{x^2}/\langle r^2\rangle_0, \text{ etc.} \qquad (6)$$

where λ_x, etc. are the principal extension ratios,[17] we have for the network[2]

$$\alpha_x - \alpha_y = (^1/_3)\nu\Gamma_2(\lambda_x^2 - \lambda_y^2) \qquad (7)$$

where α_x and α_y are the polarizabilities for the *network as a whole* along the indicated principal axes, and ν is the number of chains comprising the network. According to the theory of rubber elasticity,[2] the corresponding difference between principal stresses is

$$\tau_x - \tau_y = (\nu kT/V)(\lambda_x^2 - \lambda_y^2) \qquad (8)$$

where k is Boltzmann's constant, T is the absolute temperature, and V is the volume. From eq 7 and 8

$$\alpha_x - \alpha_y = (\Gamma_2 V/3kT)(\tau_x - \tau_y) \qquad (9)$$

Conversion of this result to the corresponding difference in refractive indexes $\tilde{n}$ through use of the Lorentz–Lorenz relationship yields[1,2]

$$\tilde{n}_x - \tilde{n}_y = B(\tau_x - \tau_y) \qquad (10)$$

where B is the stress-optical coefficient given by

$$B = (2\pi\Gamma_2/27kT)(\tilde{n}^2 + 2)^2/\tilde{n} \qquad (11)$$

$\tilde{n}$ being the mean refractive index. For uniaxial elongation we have[1,2]

$$\Delta\tilde{n} = B\tau \qquad (12)$$

where τ is the axial stress and $\Delta\tilde{n}$ is the birefringence expressed as the difference between the refractive indexes parallel and perpendicular to the stress.

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(15) A. Abe, *J. Amer. Chem. Soc.*, **90**, 2205 (1968).

(16) A. D. Williams and P. J. Flory, *ibid.*, **91**, 3111 (1969).

(17) Present definitions of λ_x, λ_y, and λ_z differ from those used in ref 8. Here we revert to the earlier practice (see P. J. Flory, *Trans. Faraday Soc.*, **56**, 722 (1960); **57**, 829 (1961)) of expressing λ_x etc., relative to the isotropic reference state having a volume such that $\langle r^2\rangle$ averaged over all chains equals the value $\langle r^2\rangle_0$ for the free, unperturbed chain.

The parameter Γ_2, which embodies the characteristics of the polymer chain that determine B, is given generally by[7,8,11]

$$\Gamma_2 = (9/10)\sum_i \langle \mathbf{r}^{\mathrm{T}}\hat{\boldsymbol{\alpha}}_i\mathbf{r}\rangle_0/\langle r^2\rangle_0 \tag{13}$$

where $\mathbf{r}^{\mathrm{T}}$ is the transpose (*i.e.*, the row form) of chain vector $\mathbf{r}$, and $\hat{\boldsymbol{\alpha}}_i$ is the traceless tensor representing the anisotropy of the polarizability associated with bond i of the chain; thus

$$\hat{\boldsymbol{\alpha}}_i = \boldsymbol{\alpha}_i - \bar{\alpha}_i\mathbf{E}_3 \tag{14}$$

where $\boldsymbol{\alpha}_i$ is the polarizability tensor for the ith bond, or group, of the chain, $\bar{\alpha}_i = (^1/_3)\text{trace } \boldsymbol{\alpha}_i$ is its mean value, and $\mathbf{E}_3$ is the identity matrix. The angle brackets with subscripts zero in eq 13 denote averages over all configurations of the free chain. This equation rests solely on the assumption of additivity of the individual tensors $\hat{\boldsymbol{\alpha}}_i$.[5-8]

As we have shown elsewhere[7,8]

$$\sum_i \langle \mathbf{r}^{\mathrm{T}}\hat{\boldsymbol{\alpha}}_i\mathbf{r}\rangle_0 = 2Z^{-1}\mathcal{J}^*\mathcal{Q}_1^{(n+1)}\mathcal{J} \tag{15}$$

where Z, $\mathcal{J}^*$, and $\mathcal{J}$ retain their definitions given previously,[10,12] and $\mathcal{Q}_1^{(n+1)}$ is the serial product of matrices $\mathcal{Q}_i$ defined by [7,8,18,19]

$$\mathcal{Q}_i = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{0} & \mathbf{C} \end{bmatrix}_i \tag{16}$$

where the submatrices, each bearing the subscript i affixed external to the brackets in eq 16, are defined in eq 17–19[18-20]

$$\mathbf{A}_i = \begin{bmatrix} \mathbf{U} & (\mathbf{U}\times\mathbf{l}^{\mathrm{T}})\|\mathbf{T}\| & {}^1/_2(\mathbf{U}\times\mathbf{l}^{\mathrm{T}}\times\mathbf{l}^{\mathrm{T}})\|\mathbf{T}\times\mathbf{T}\| \\ \mathbf{0} & (\mathbf{U}\times\mathbf{E}_3)\|\mathbf{T}\| & (\mathbf{U}\times\mathbf{E}_3\times\mathbf{l}^{\mathrm{T}})\|\mathbf{T}\times\mathbf{T}\| \\ \mathbf{0} & \mathbf{0} & (\mathbf{U}\times\mathbf{E}_9)\|\mathbf{T}\times\mathbf{T}\| \end{bmatrix}_i \tag{17}$$

$$\mathbf{B}_i = \begin{bmatrix} (\mathbf{U}\times\hat{\boldsymbol{\alpha}}^{\mathrm{R}})\|\mathbf{T}\times\mathbf{T}\| & \mathbf{U}\times[\hat{\boldsymbol{\alpha}}^{\mathrm{R}}(\mathbf{l}\times\mathbf{E}_3)]\|\mathbf{T}\| & {}^1/_2\mathbf{U}[\hat{\boldsymbol{\alpha}}^{\mathrm{R}}(\mathbf{l}\times\mathbf{l})] \\ \mathbf{0} & (\mathbf{U}\times\hat{\boldsymbol{\alpha}})\|\mathbf{T}\| & \mathbf{U}\times[(\mathbf{E}_3\times\mathbf{l}^{\mathrm{T}})\hat{\boldsymbol{\alpha}}^{\mathrm{C}}] \\ \mathbf{0} & \mathbf{0} & \mathbf{U}\times\hat{\boldsymbol{\alpha}}^{\mathrm{C}} \end{bmatrix}_i \tag{18}$$

$$\mathbf{C}_i = \begin{bmatrix} (\mathbf{U}\times\mathbf{E}_9)\|\mathbf{T}\times\mathbf{T}\| & (\mathbf{U}\times\mathbf{l}\times\mathbf{E}_3)\|\mathbf{T}\| & {}^1/_2(\mathbf{U}\times\mathbf{l}\times\mathbf{l}) \\ \mathbf{0} & (\mathbf{U}\times\mathbf{E}_3)\|\mathbf{T}\| & \mathbf{U}\times\mathbf{l} \\ \mathbf{0} & \mathbf{0} & \mathbf{U} \end{bmatrix}_i \tag{19}$$

In these matrices $\hat{\boldsymbol{\alpha}}^{\mathrm{R}}$ and $\hat{\boldsymbol{\alpha}}^{\mathrm{C}}$ are the row and column forms, defined elsewhere, of the tensor $\hat{\boldsymbol{\alpha}}_i$. Thus, $\mathcal{Q}_i$ is a function of the anisotropic part of the polarizability $\boldsymbol{\alpha}_i$ associated with skeletal bond i (*cf.* the following) of the matrix $\mathbf{T}_i$ which effects transformation of a vector expressed in the coordinate system of bond $i + 1$ to its representation in the coordinate system of bond i, and of the statistical weight matrix $\mathbf{U}_i$ for rotational states of bond i in relation to the states of its predecessor, bond $i - 1$.

Formulation of Group Polarizability Tensors for Vinyl Chains

In Figure 1a we show a dyad of a vinyl chain encompassing two asymmetric centers. The choice of a racemic (*dl*) dyad is essentially arbitrary. This selection offers the advantage that both of the coordinate systems x_i, y_i, z_i and x_{i+1}, y_{i+1}, z_{i+1} affixed to skeletal bonds i and $i + 1$ are right-handed according to the conventions enunciated in the first of the present group of papers.[12] The z_i axis (not shown) is directed downward and the z_{i+1} axis upward, both being perpendicular to the plane defined by the adjoining pair of skeletal bonds. In addition to these reference frames, we define two right-handed coordinate systems x', y', z' and x'', y'', z'' as indicated in Figure 1a. Specifically, we locate x' and y' in the plane defined by $C_{i-2}C_{i-1}C_i$ with x' bisecting the angle between the bonds connecting these atoms, *i.e.*, the angle between skeletal bonds $i - 1$ and i. Similarly, x'' and y'' are located in the plane defined by bonds i and $i + 1$, with x'' bisecting the angle between these two skeletal bonds. The axis z' is directed downward; it coincides with z_i. The z'' axis is directed upward, and it coincides with z_{i+1}.

Excluding certain R groups of exceptionally asymmetric shape, we take the C_{i-1}—R and C_{i-1}—H bonds to be in the $x'z'$ plane which bisects the skeletal bond angle at this carbon. The angles $-\psi_{\mathrm{R}}'$ and ψ_{H}' are defined in Figure 1b; they are indicated also in Figure 1a. In keeping with the chirality of reference frame x', y', z' (and also of x_i, y_i, z_i), $-\psi_{\mathrm{R}}'$ and ψ_{H}' are measured in the right-handed sense. Thus, both ψ_{R}' and ψ_{H}' are so defined as to be positive quantities.

The axis x_{R} shown in Figure 1b is taken along the R—C_{i-1} bond. Axes y_{R} and z_{R}, shown in Figure 1c, are perpendicular to this bond, again in directions forming a right-handed system. In most cases of interest, x_{R} will be a principal axis of the polarizability tensor $\boldsymbol{\alpha}_{\mathrm{CR}}$ of group R, including therewith the polarizability of the C_{i-1}—R bond. If this is the case, then it will obviously be possible, and convenient as well, to locate y_{R} and z_{R} in the directions of the other principal axes of this tensor. Even if bond C_{i-1}—R, and therefore x_{R}, is not a principal axis of $\boldsymbol{\alpha}_{\mathrm{CR}}$, the present scheme retains the advantage of introducing explicitly the angle χ (see Figure 1c) which denotes the rotation about this bond. The angle χ will assume importance for any group R which is not cylindrically symmetric with respect to the C—R bond. In any case, we begin by expressing $\boldsymbol{\alpha}_{\mathrm{CR}}$ in the cartesian reference frame x_{R}, y_{R}, z_{R}, where x_{R} coincides with bond R—C_{i-1}, y_{R} and z_{R} being located in the plane perpendicular to x_{R}

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(18) P. J. Flory and Y. Abe, *Macromolecules*, 2, 335 (1969).

(19) The present definition of $\mathcal{Q}_i$ departs from that given earlier (ref 7 and 8) only through the interchanges of third and fourth pseudorows and pseudocolumns. See ref 18.

(20) In carrying out the calculations described in the concluding sections of this paper, advantage was taken of the simplifications which can be achieved by reducing the order of $\mathbf{T}\times\mathbf{T}$ from 9×9 to 6×6, with corresponding reductions of $\mathbf{l}\times\mathbf{l}$, $\mathbf{l}^{\mathrm{T}}\times\mathbf{l}^{\mathrm{T}}$, $\hat{\boldsymbol{\alpha}}^{\mathrm{R}}$, $\hat{\boldsymbol{\alpha}}^{\mathrm{C}}$, etc., as first pointed out by K. Nagai, *J. Chem. Phys.*, **38**, 924 (1963); see also K. Nagai, *ibid.*, **48**, 5646 (1968). These condensations simplify numerical computations.

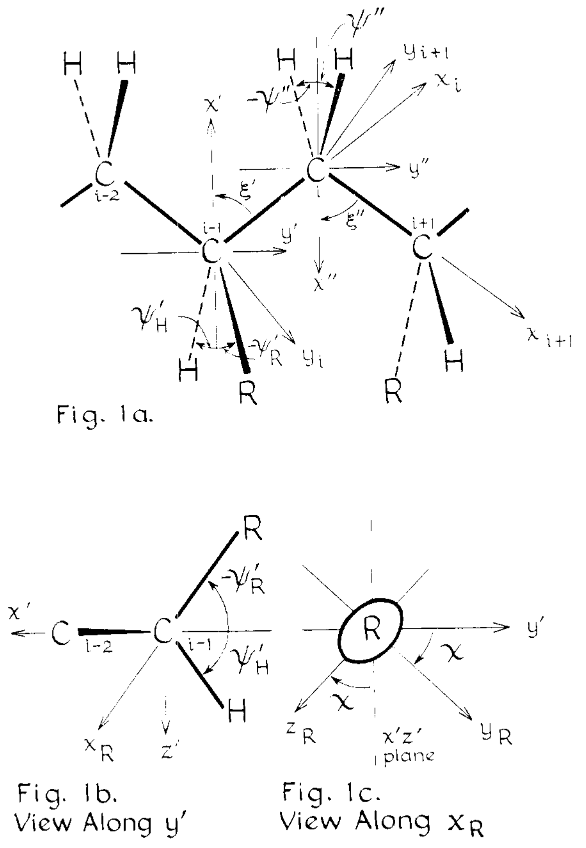

Fig. 1a.

Fig. 1b. View Along y'

Fig. 1c. View Along x_R

Figure 1. Coordinate systems used for the formulation of group polarizability tensors.

in whatever manner may be preferred. For polystyrene, for example, we shall take z_R in the plane of the phenyl group and y_R perpendicular to it; x_R, y_R, and z_R thus specified are principal axes for this group. Then χ will measure the rotation of the plane of the phenyl group from the plane bisecting the skeletal bond angle at C_{i-1}.

We shall combine the polarizability tensor α_{CR} with the polarizabilities associated with bonds C_{i-1}—H and with C_{i-1}—C_i, the latter being the skeletal bond (i) *following* $(CHR)_{i-1}$ in the chain. These three bonds are fixed in the reference frame x_i, y_i, z_i of bond i. Their mutual orientation with respect to the preceding bonds of the chain depends on the supplement θ_{i-1} of the bond angle at C_{i-1} and on the rotation ϕ_{i-1} about bond $i - 1$. It is appropriate therefore to treat these bonds and substituent R as group i of the chain. Accordingly, they will be represented by the polarizability tensor $\boldsymbol{\alpha}_i$ defined as the sum of the specified polarizabilities expressed in the coordinate system of bond i. In circumstances where the serial index i is unimportant, $\boldsymbol{\alpha}_i$ may be denoted by $\boldsymbol{\alpha}'$. The traceless tensor $\hat{\boldsymbol{\alpha}}_i$ formed from $\boldsymbol{\alpha}_i$ expressed in the foregoing manner is the tensor required for the generator matrix $\mathcal{Q}_i$ representing bond i (see eq 16–19). If it is permissible to disregard the serial index, we may represent this matrix by $\mathcal{Q}'$ in keeping with the practice[11–12] of designating the statistical weight matrix associated therewith by $\mathbf{U}'$.

Similarly, we combine the polarizabilities associated with the two pendant C—H bonds at C_i with skeletal C—C bond $i + 1$. These will comprise the group polarizability $\boldsymbol{\alpha}_{i+1}$, which is to be expressed in the coordinate system of bond $i + 1$. It will furnish the traceless tensor $\hat{\boldsymbol{\alpha}}_{i+1}$ required in the generator matrix $\mathcal{Q}_{i+1}$ for bond $i + 1$. Alternatively, if the serial index may be disregarded, we shall denote $\boldsymbol{\alpha}_{i+1}$ and $\hat{\boldsymbol{\alpha}}_{i+1}$ by $\boldsymbol{\alpha}''$ and $\hat{\boldsymbol{\alpha}}''$, respectively, and $\mathcal{Q}_{i+1}$ by $\mathcal{Q}''$ (see below).

In order to transform α_{CR} (which includes the polarizability of C_{i-1}—R; see above) from its representation in the coordinate system x_R, y_R, z_R to the reference frame x_i, y_i, z_i affixed to bond i, we first transform it to the system x', y', z'. This involves a rotation χ about axis x_R, followed by a rotation $-\psi_R'$ about y'. Finally, we transform from x', y', z' to x_i, y_i, z_i. This is achieved through rotation ξ' about the z' axis, which latter coincides with axis z_i. These three transformations may be represented, respectively, by

$$\mathbf{X}(\chi) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\chi & -\sin\chi \\ 0 & \sin\chi & \cos\chi \end{bmatrix} \tag{20}$$

$$\mathbf{\Psi}(\psi) = \begin{bmatrix} \cos\psi & 0 & \sin\psi \\ 0 & 1 & 0 \\ -\sin\psi & 0 & \cos\psi \end{bmatrix} \tag{21}$$

$$\Xi(\xi) = \begin{bmatrix} \cos\xi & \sin\xi & 0 \\ -\sin\xi & \cos\xi & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{22}$$

with $\psi = -\psi_R$ and $\xi = \xi'$. The complete transformation is given by eq 23

$$\mathbf{\Omega}(\xi,\psi,\chi) = \Xi\,\mathbf{\Psi}\,\mathbf{X} = \begin{bmatrix} \cos\xi\cos\psi & \cos\xi\sin\psi\sin\chi + \sin\xi\cos\chi & \cos\xi\sin\psi\cos\chi - \sin\xi\sin\chi \\ -\sin\xi\cos\psi & -\sin\xi\sin\psi\sin\chi + \cos\xi\cos\chi & -\sin\xi\sin\psi\cos\chi - \cos\xi\sin\chi \\ -\sin\psi & \cos\psi\sin\chi & \cos\psi\cos\chi \end{bmatrix} \tag{23}$$

Thus, in the case of the R group in Figure 1, its polarizability tensor expressed in the reference frame of skeletal bond i is

$$(\alpha_{CR})_i = \mathbf{\Omega}(\xi', -\psi_R', \chi)\alpha_{CR}\mathbf{\Omega}^T(\xi', -\psi_R', \chi) \tag{24}$$

where the superscript T denotes the transpose of the orthogonal matrix $\mathbf{\Omega}$.

If the positions of R and H are reversed at atom C_{i-1} in Figure 1, this atom becomes an l instead of a d center according to our arbitrary designations. For the equivalent orientation of the R group about the R–C axis, the arrangement of atoms about the l center is just the mirror reflection, through the $C_{i-2}C_{i-1}C_i$ plane, of their arrangement about the d center in Figure 1. Adherence to the conventions[12] cited above requires a left-handed reference frame for a bond (i) following an l center. Mirror reflection through the $C_{i-2}C_{i-1}C_i$ plane brings about this change also. It follows that the polarizability tensor for the CR group of an l center is identical with that for a d center when each is expressed in the reference frame prescribed for bond i in the respective cases; thus

$$(\boldsymbol{\alpha}_{\mathrm{CR}})_{d;i} = (\boldsymbol{\alpha}_{\mathrm{CR}})_{l;i} = (\boldsymbol{\alpha}_{\mathrm{CR}})_i \qquad (25)$$

This invariance is contingent, of course, upon the foregoing conventions concerning coordinate systems; the polarizability tensors for a d and an l center are not identical when expressed in the same reference frame.

If $\chi = 0$, or if the polarizability of the substituent is cylindrically symmetric about the axis of the pendant bond (*i.e.*, bond C—R), then $\boldsymbol{\Omega}$ reduces to

$$\boldsymbol{\Omega}_0(\xi,\psi) = \boldsymbol{\Xi\Psi}$$
$$= \begin{bmatrix} \cos\xi\cos\psi & \sin\xi & \cos\xi\sin\psi \\ -\sin\xi\cos\psi & \cos\xi & -\sin\xi\sin\psi \\ -\sin\psi & 0 & \cos\psi \end{bmatrix} \qquad (26)$$

The transformation for the polarizability of the C_{i-1}—H bond is obtained by substituting ψ_{H} for ψ in this equation. Hence, the total polarizability associated with the group $(\mathrm{CHR{-}C})_i$ expressed in the reference frame appropriate for skeletal bond i is given in general by

$$\boldsymbol{\alpha}_i = \boldsymbol{\alpha}' = \boldsymbol{\Omega}(\xi',-\psi_{\mathrm{R}}',\chi)\boldsymbol{\alpha}_{\mathrm{CR}}\boldsymbol{\Omega}^{\mathrm{T}}(\xi',-\psi_{\mathrm{R}}',\chi) + \boldsymbol{\Omega}_0(\xi',\psi_{\mathrm{H}}')\boldsymbol{\alpha}_{\mathrm{CH}}\boldsymbol{\Omega}_0^{\mathrm{T}}(\xi',\psi_{\mathrm{H}}') + \boldsymbol{\alpha}_{\mathrm{CC}} \qquad (27)$$

where $\boldsymbol{\alpha}_{\mathrm{CC}}$ is the polarizability of skeletal bond i. As will be apparent, this tensor, when expressed as specified, is invariant to the symmetry of C_{i-1}.

For the $(\mathrm{CH_2{-}C})_{i+1}$ group we have similarly

$$\boldsymbol{\alpha}_{i+1} = \boldsymbol{\alpha}'' = \boldsymbol{\Omega}_0(\xi'',\psi'')\boldsymbol{\alpha}_{\mathrm{CH}}\boldsymbol{\Omega}_0^{\mathrm{T}}(\xi'',\psi'') + \boldsymbol{\Omega}_0(\xi'',-\psi'')\boldsymbol{\alpha}_{\mathrm{CH}}\boldsymbol{\Omega}_0^{\mathrm{T}}(\xi'',-\psi'') + \boldsymbol{\alpha}_{\mathrm{CC}} \qquad (28)$$

This tensor obviously is invariant to reflection through the plane of skeletal bonds i and $i + 1$, and therefore to the direction of the z_{i+1} axis and the chirality of the coordinate system[12] affixed to bond $i + 1$. Hence, $\boldsymbol{\alpha}_{i+1}$, like $\boldsymbol{\alpha}_i$, is invariant to the stereochemical character of the dyad of which it is a part. For a polymer formed from a single monomer, therefore, we may generally represent these tensors by $\boldsymbol{\alpha}''$ and $\boldsymbol{\alpha}'$, respectively, the serial indexes being omitted.

Equations 27 and 28 are quite general. They are applicable also to the formulation of the corresponding traceless tensors $\hat{\boldsymbol{\alpha}}'$ and $\hat{\boldsymbol{\alpha}}''$. These latter are obtained merely by replacing $\boldsymbol{\alpha}_{\mathrm{CR}}$, $\boldsymbol{\alpha}_{\mathrm{CH}}$, and $\boldsymbol{\alpha}_{\mathrm{CC}}$ in the equations by the corresponding traceless tensors $\hat{\boldsymbol{\alpha}}_{\mathrm{CR}}$, $\hat{\boldsymbol{\alpha}}_{\mathrm{CH}}$, and $\hat{\boldsymbol{\alpha}}_{\mathrm{CC}}$.

Owing to the cylindrical symmetry of the polarizabilities contributing to $\boldsymbol{\alpha}''$, the tensor $\hat{\boldsymbol{\alpha}}''$ takes the comparatively simple form shown in eq 29

$$\hat{\boldsymbol{\alpha}}'' = \begin{bmatrix} {}^2\!/_3\Delta\alpha_{\mathrm{CC}} + 2(\cos^2\xi''\cos^2\psi'' - {}^1\!/_3)\Delta\alpha_{\mathrm{CH}} & -2(\sin\xi''\cos\xi''\cos^2\psi'')\Delta\alpha_{\mathrm{CH}} & 0 \\ -2(\sin\xi''\cos\xi''\cos^2\psi'')\Delta\alpha_{\mathrm{CH}} & -{}^1\!/_3\Delta\alpha_{\mathrm{CC}} + 2(\sin^2\xi''\cos^2\psi'' - {}^1\!/_3)\Delta\alpha_{\mathrm{CH}} & 0 \\ 0 & 0 & -{}^1\!/_3\Delta\alpha_{\mathrm{CC}} + 2(\sin^2\psi'' - {}^1\!/_3)\Delta\alpha_{\mathrm{CH}} \end{bmatrix}_{i+1} \qquad (29)$$

where $\Delta\alpha_{\mathrm{CC}}$ and $\Delta\alpha_{\mathrm{CH}}$ are the differences between the polarizabilities along and perpendicular to the respective bonds. It will be observed that

$$\xi' = (\pi - \theta'')/2$$
$$\xi'' = (\pi - \theta')/2 \qquad (30)$$

where $\theta' = \theta_i$ and $\theta'' = \theta_{i-1}$ are the supplements of the skeletal bond angles at carbons i and $i - 1$, respectively. The asymmetry of superscripts in eq 30 is unfortunate but unavoidable. According to eq 29 and 30, the relationship of the tensor $\hat{\boldsymbol{\alpha}}''$ to the anisotropies of the bond polarizabilities depends on the valence angles at C_i as represented by ψ'' and θ'.

The general expression for $\hat{\boldsymbol{\alpha}}'$ that corresponds to eq 29 is excessively cumbersome and need not be reproduced. We shall, however, consider in some detail the case in which x_{R}, y_{R}, and z_{R} are symmetry axes of $\boldsymbol{\alpha}_{\mathrm{CR}}$. We shall not consider χ necessarily to be fixed; it may be subject to variation depending on the rotational potential associated with the C—R bond. It is then advantageous to effect the transformation denoted by $\mathbf{X}(\chi)$ at the outset. The result may be written

$$\mathbf{X}\boldsymbol{\alpha}_{\mathrm{CR}}\mathbf{X}^{\mathrm{T}} = \mathrm{diag}(\alpha_{\mathrm{CR};x},\alpha_{\mathrm{CR};y},\alpha_{\mathrm{CR};z}) + \Delta\alpha_{\mathrm{R}}\begin{bmatrix} 0 & 0 & 0 \\ 0 & -\langle\sin^2\chi\rangle & \langle\sin\chi\cos\chi\rangle \\ 0 & \langle\sin\chi\cos\chi\rangle & \langle\sin^2\chi\rangle \end{bmatrix} \qquad (31)$$

where $\mathrm{diag}(\alpha_{\mathrm{CR};x},\alpha_{\mathrm{CR};y}\alpha_{\mathrm{CR};z})$ is the diagonal matrix having elements as indicated, this matrix being identical with $\boldsymbol{\alpha}_{\mathrm{CR}}$, and

$$\Delta\alpha_{\mathrm{R}} = \alpha_{\mathrm{CR};y} - \alpha_{\mathrm{CR};z} \qquad (32)$$

This quantity is written as $\Delta\alpha_{\mathrm{R}}$ instead of as $\Delta\alpha_{\mathrm{CR}}$ inasmuch as the polarizability of the C—R bond, being cylindrically symmetric, does not contribute to the difference. Thus $\Delta\alpha_{\mathrm{R}}$ characterizes the asymmetry of the R group in the plane perpendicular to the C—R bond. The trigonometric functions in the second term on the right-hand side of eq 31 are shown as averages on the assumption that χ may vary, being constrained by a torsional potential. If, on the contrary, χ is fixed and its value is zero, then this term is null and of course the transformation on the left reduces to the identity operation.

Expressing $\mathbf{X}\hat{\boldsymbol{\alpha}}_{\mathrm{CR}}\mathbf{X}^{\mathrm{T}}$ in corresponding fashion and proceeding as above we obtain

$$\hat{\boldsymbol{\alpha}}' = \hat{\boldsymbol{\alpha}}'(\chi = 0) + \Delta\alpha_{\mathrm{R}}\langle\sin^2\chi\rangle\boldsymbol{\Omega}_0[\mathrm{diag}(0,-1,1)]\boldsymbol{\Omega}_0^{\mathrm{T}} + ({}^1\!/_2)\Delta\alpha_{\mathrm{R}}\langle\sin 2\chi\rangle\boldsymbol{\Omega}_0\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}\boldsymbol{\Omega}_0^{\mathrm{T}} \qquad (33)$$

Here $\hat{\boldsymbol{\alpha}}'(\chi = 0)$ is the tensor which would represent group *i*, expressed in the reference frame of bond *i*, if χ were fixed at zero; *i.e.*, it may be obtained according to eq 27 with $\boldsymbol{\Omega}$ replaced by $\boldsymbol{\Omega}_0$ (see eq 26) in its first term. If the potential affecting χ is symmetric about zero, the last term in eq 33 vanishes. The departure of $\hat{\boldsymbol{\alpha}}'$ from $\hat{\boldsymbol{\alpha}}'$ $(\chi = 0)$ due to fluctuations of χ about $\chi = 0$ is then proportional to $\langle \sin^2 \chi \rangle$. In consequence of this circumstance, Γ_2 will also be linearly dependent upon $\langle \sin^2 \chi \rangle$ for variations in χ symmetrical about $\chi = 0$ (see below).

It follows from the symmetry relations pointed out above, and from the statistical weight matrices **U** and the transformations **T** applicable to *meso* and racemic dyads (see ref 12, and especially eq 15 thereof), that the several matrices $\mathcal{Q}$ required for vinyl chains are formulable from eq 16–19 according to the rules

$$\begin{aligned} \mathcal{Q}_m' &= \mathcal{Q}(\mathbf{U}',\mathbf{T}_*,\hat{\boldsymbol{\alpha}}') \\ \mathcal{Q}_r' &= \mathcal{Q}(\mathbf{U}',\mathbf{T},\hat{\boldsymbol{\alpha}}') \\ \mathcal{Q}_m'' &= \mathcal{Q}(\mathbf{U}_m'',\mathbf{T}_*,\hat{\boldsymbol{\alpha}}'') \\ \mathcal{Q}_r'' &= \mathcal{Q}(\mathbf{U}_r'',\mathbf{T}_*,\hat{\boldsymbol{\alpha}}'') \end{aligned} \tag{34}$$

The matrices $\mathbf{U}'$, $\mathbf{U}_m''$, $\mathbf{U}_r''$, **T**, and $\mathbf{T}_*$ are given in ref 12.

Numerical Calculations for Polypropylene

The following structural data were used. The

$$l_{\mathrm{C-C}} = 1.53\ \text{Å}$$

$$\theta' = \theta'' = \pi - \angle\mathrm{CCR} = 68°$$

$$\pi - \angle\mathrm{CCH} = 73.2° \text{ (tertiary H)}$$

$$\pi - \angle\mathrm{HCH} = 71.0° \text{ (secondary H)}$$

$-CH_3$ group was taken to be tetrahedral.

From the bond polarizabilities of Denbigh[21,22] we obtain

$$\Delta\alpha_{\mathrm{CC}} = (\alpha_{\parallel} - \alpha_{\perp})_{\mathrm{CC}} = 18.6 \times 10^{-25}\ \mathrm{cc}$$

$$\Delta\alpha_{\mathrm{CH}} = -\Delta\alpha_{\mathrm{CH_3}} = 2.1 \times 10^{-25}\ \mathrm{cc}$$

On this basis

$$\hat{\boldsymbol{\alpha}}_{\mathrm{CCH_3}} = \mathrm{diag}(11.0, -5.5, -5.5) \times 10^{-25}\ \mathrm{cc}$$

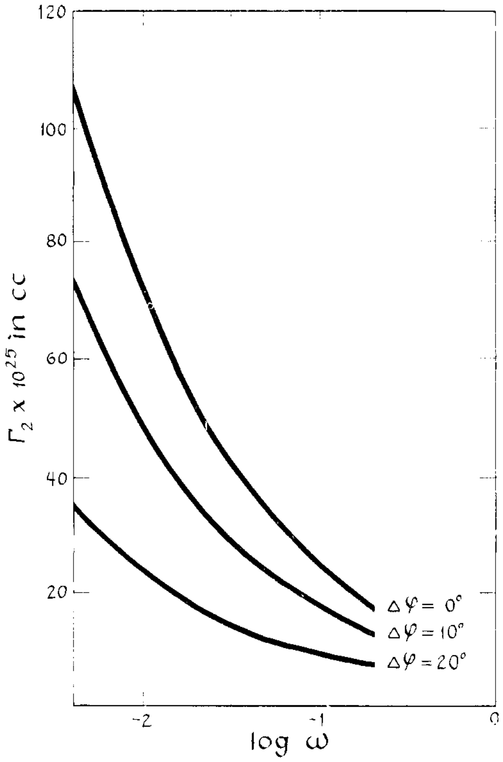

Figure 2. The strain-birefringence coefficient Γ_2 (see eq 3, 7, 11, and 13) calculated for isotactic polypropylene according to eq 13 and 15 using the group polarizability tensors given by eq 35 and 36, the statistical weights $\tau^* = 1.00$, $\tau = 0.50$, $\eta = 1.00$, and the several values of $\Delta\phi$ indicated (see ref 12, eq 2–4 and 13). Results are plotted against the logarithm of the statistical weight parameter ω for four-bond interactions.

From eq 27 and 29 we find

$$\hat{\boldsymbol{\alpha}}' = \begin{bmatrix} 8.69 & -3.69 & 4.07 \\ -3.69 & -6.92 & -6.03 \\ 4.07 & -6.03 & -1.77 \end{bmatrix} \times 10^{-25}\ \mathrm{cc} \tag{35}$$

and

$$\hat{\boldsymbol{\alpha}}'' = \begin{bmatrix} 11.44 & -0.66 & 0.00 \\ -0.66 & -6.62 & 0.00 \\ 0.00 & 0.00 & -4.82 \end{bmatrix} \times 10^{-25}\ \mathrm{cc} \tag{36}$$

The required $\mathcal{Q}'$ and $\mathcal{Q}''$ matrices were constructed according to eq 16–19 and 34. The statistical weight matrices used are given by eq 2–4 of ref 12. Values chosen for the parameters were $\tau^* = 1.00$, $\tau = 0.50$, and $\eta = 1.00$, with various values assigned to ω as indicated below. For some of the calculations the rotational states were displaced from their symmetrical locations by $\Delta\phi = 10$ or 20°, according to the scheme[14] prescribed by eq 13 of ref 12.

Values of Γ_2 calculated for isotactic PP according to eq 13 and 15 are plotted against log ω in Figure 2 for the values of $\Delta\phi$ indicated. These and all other calculations to follow were carried out for chains of 400 units (800 bonds); this length is ample for realization of asymptotic results. A marked dependence on ω is

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(21) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(22) Bond polarizabilities for C—C and C—H bonds advanced by various investigators differ widely. However, it is the appropriate combinations of the anisotropies of these polarizabilities which is important in any given application. Thus, in the case of a tetrahedrally bonded alkane, Smith and Mortenson[23] have shown on the basis of general arguments that the polarizability tensor is proportional to $\Delta\alpha_{\mathrm{CC}} - 2\alpha_{\mathrm{CH}}$, irrespective of the structure of the alkane. If allowance is made for departures from tetrahedral geometry, the proportionality factor appears to be, approximately, $\Delta\alpha_{\mathrm{CC}} - 1.95\Delta\alpha_{\mathrm{CH}}$ in the case of *n*-alkanes.[24] As we have pointed out previously,[24] these quantities display much smaller variations when evaluated from various sets of bond polarizabilities than the wide variations of values assigned individually to $\Delta\alpha_{\mathrm{CC}}$ and to $\Delta\alpha_{\mathrm{CH}}$ by different authors might suggest. A critique of the numerous sets of bond polarizabilities is clearly outside the concerns of the present paper. The Denbigh polarizabilities have been chosen somewhat arbitrarily for the purposes at hand in view of their widespread use. None of the results here presented can be critically dependent on this choice.

(23) R. P. Smith and E. M. Mortenson, *J. Chem. Phys.*, **32**, 502 (1960).

(24) R. L. Jernigan and P. J. Flory, *ibid.*, **47**, 1999 (1967).

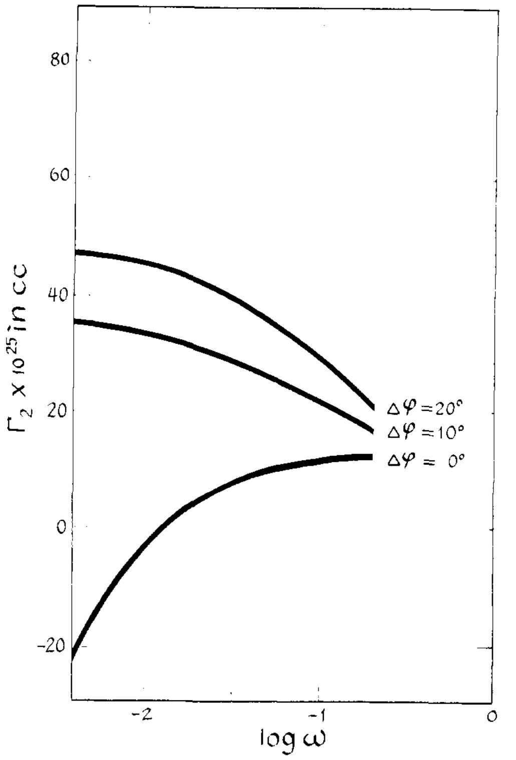

Figure 3. The coefficient Γ_2 for syndiotactic PP plotted against log ω. See legend to Figure 2.

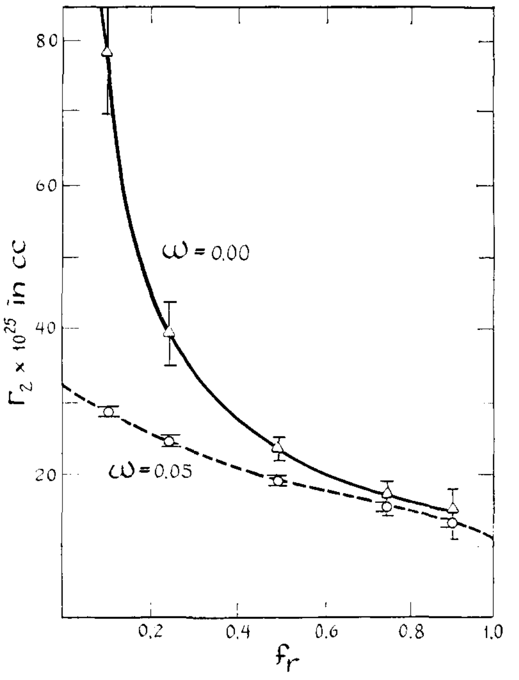

Figure 4. Monte Carlo calculations for PP chains of varying stereochemical composition denoted by the fraction f_r of racemic dyads. Each point represents the average for 15 chains; standard deviations are denoted by vertical bars. Parameters quoted in the legend for Figure 2 were used; $\Delta\phi = 0°$.

apparent for $\Delta\phi = 0°$. Alteration of the rotational states by $\Delta\phi = 10$ and $20°$ reduces the range of correlations of the contributing group tensors, and consequently reduces Γ_2 for small values of ω.

Corresponding calculations for syndiotactic chains are presented in Figure 3. The peculiar behavior of the curve for $\Delta\phi = 0°$ at small values of ω doubtless is related to the suppression of nonplanar conformations with approach of ω toward zero, as discussed previously.[12]

The results of Monte Carlo calculations[12,14] of Γ_2 for PP chains with $\Delta\phi = 0°$ are presented in Figure 4 as a function of the fraction f_r of racemic units. Each point represents the average for 15 Monte Carlo chains consisting of 400 units. Standard deviations are indicated by vertical bars. The calculated coefficient Γ_2 is large for predominantly isotactic chains when $\omega = 0$, and it decreases rapidly with introduction of racemic units. The decrease is monotonic from $f_r = 0$–1.0. The dependence on stereoregularity is moderated markedly by an increase in ω.

Experimental measurements[25] on the stress-optical coefficient for atactic polypropylene have been inconclusive. However, Tsvetkov and coworkers[25] have evaluated the polarizability anisotropy Δa of the segment of the freely jointed chain model from streaming birefringence studies on atactic polypropylene in various solvents. Results in carbon tetrachloride, whose refractive index nearly matches that of the polymer, yielded $\Delta a = 30(\pm 5) \times 10^{-25}$ cc.[25] Calculation of the strain-birefringence coefficient Γ_2 from this result according to eq 4 is fraught with errors attending reliance on this artificial model. However, there is precedent in the work of Tsvetkov and coworkers[25,26] for an approximate correspondence between Δa deduced by the two methods. We thus arrive at $\Gamma_2 = 18(\pm 3) \times 10^{-25}$ cc which agrees satisfactorily with the calculations shown in Figure 4 in the range $f_r = 0.4$–0.8. The value of f_r for the polymer in question is of course unknown, but may be assumed to be within this range.

Numerical Calculations for Polystyrene

The structural parameters and polarizabilities were the same as used for polypropylene, apart from those for the substituent. The polarizability tensor of the phenyl group according to Denbigh[21,27] is

$$\mathrm{diag}(115.2, 57.7, 117.3) \times 10^{-25}\ \mathrm{cc}$$

expressed in the coordinate system x_R, y_R, z_R of Figure 1. Combination of this tensor with the polarizabilities for the C—C bond gives

$$\alpha_{CC_6H_5} = \mathrm{diag}(134.0, 57.9, 117.5) \times 10^{-25}\ \mathrm{cc}$$

or

$$\hat{\alpha}_{CC_6H_5} = \mathrm{diag}(30.9, -45.2, 14.3) \times 10^{-25}\ \mathrm{cc}$$

The preferred conformations *tttt* and *ttgg* for a racemic (*rr*) triad are shown in Figures 5a and 5b, respectively. The conformation *ggtt* which is sterically

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(25) V. N. Tsvetkov, O. V. Kallistov, Ye. V. Korneyeva, and I. K. Nekrasov, *Vysokomol. Soedin.*, **5**, 1538 (1963).

(26) A. Ye. Grishchenko, M. G. Vitovskaya, V. N. Tsvetkov, Ye. P. Vorob'eva, N. N. Saprykina, and L. I. Mezentseva, *ibid.*, **A9**, 1280 (1967).

(27) Since the anisotropy of the polarizability in the polystyrene chain is dominated by the phenyl group whose anisotropy is fairly well established, the particular choice of bond and group polarizabilities is much less vulnerable to referee's criticisms than in the case of polypropylene. We nevertheless include this footnote in acknowledgment thereof.

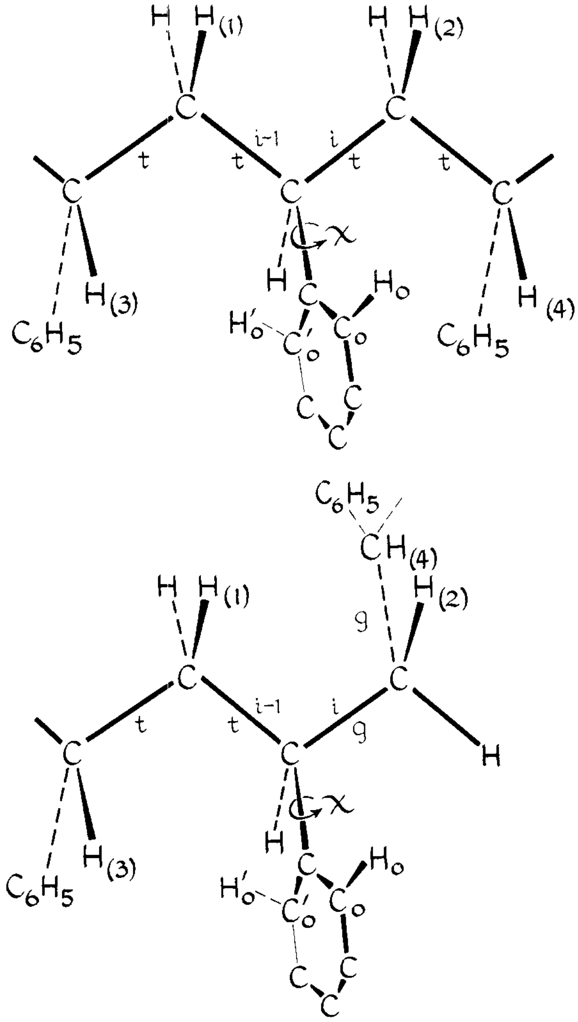

Figure 5. Preferred conformations *tttt* and *ttgg* for a racemic (*rr*) triad of a polystyrene chain. Replacement of the outermost C_6H_5 groups by CH_2 produces the preferred conformations of a *meso* (*mm*) triad: *gttg* in Figure 5a (top), and *gtgt* in Figure 5b (bottom).

equivalent to the latter one is not shown. These diagrams may be used also to illustrate the preferred conformations of a *meso* triad (*mm*), namely, *gttg* and *gtgt*. This further purpose is achieved merely by replacing the outer C_6H_5 substituents by CH_2 groups. The diagrams may also be correlated with the preferred conformations of a heterotactic (*mr*) triad.

It will be immediately apparent from Figure 5a, or by inspection of models, that rotation of the central phenyl group in this planar conformation of the chain skeleton will be symmetric about $\chi = 0$. Further, we may expect χ to be restricted to values near zero (or π) by steric interactions involving atom pairs as follows: (a) the upper *ortho* hydrogen H_0 with either H_1 or H_2, depending on the sign of χ, (b) the *ortho* carbon C_0 with either H_1 or H_2; and (c) both C_0 and C_0' with either H_3 or H_4, depending again on the sign of χ. Interatomic distances for pairs brought closer together by rotations of +10 and +30° are listed in Table I. From the steric overlaps indicated, the rotations about $\chi = 0$ may be assumed to be restricted to a fairly small range, perhaps on the order of ±10 to ±20°.

TABLE I

DEPENDENCES OF INTERATOMIC DISTANCES FOR ATOM PAIRS IN THE *trans* CONFORMATION OF FIGURE 5a ON ROTATION χ. STERIC OVERLAPS[a] ARE GIVEN IN PARENTHESES (ALL VALUES IN ÅNGSTRÖM UNITS)

χ,[b] deg	Interaction (a) $H_0 \cdots H_2$	Interaction (b) $C_0 \cdots H_2$	Interaction (c) $C_0 \cdots H_4$ and $C_0' \cdots H_3$
0	2.43 (−0.03)	2.90 (0.00)	2.96 (−0.06)
10	2.25 (0.15)	2.82 (0.08)	2.77 (0.13)
30	2.04 (0.36)	2.73 (0.17)	2.40 (0.50)

[a] Steric overlaps are calculated assuming van der Waals radii of 1.2 and 1.7 Å for H and for aromatic C, respectively. Values of the steric overlaps are given to the second decimal for purposes of comparison only. [b] For corresponding negative values of χ, H_1 replaces H_2 and the roles of C_0 and C_0' are reversed.

In the conformation shown in Figure 5b, repulsions of kinds (a) and (b) remain but those of class (c) that involve H_4 in Figure 5a are eliminated; those involving H_3 are retained, however. In the approximation that all bonds are tetrahedral and that the rotational states occur precisely at 0° and ±120° (*i.e.*, that $\Delta\phi = 0$), we again have $\chi = 0$ (or π) as the preferred orientation of the phenyl group. The acknowledged small departures from tetrahedral angles, etc., do not vitiate this deduction appreciably. These deductions will be found to hold for the preferred conformations of the heterotactic triad as well. We conclude therefore that $\chi = 0$ represents the orientation of the phenyl group of lowest energy in each of the preferred skeletal conformations for all stereochemical configurations.

Amongst nonpreferred skeletal conformations, the one of greatest prominence is the *gg* state for bond pair $i - 1,i$. In this conformation both of the pendant CH groups are behind the plane of this bond pair (compare Figure 5b). Steric constraints of the kind (c) on the phenyl group are then eliminated; symmetry about $\chi = 0$ obtains but the range of χ may be presumed to be increased somewhat. Other nonpreferred conformations for the racemic triad, *e.g.*, *tttg* or *ttt$\bar{g}$* in which the central phenyl group is apposed to CH_2 or to C_6H_5, respectively, involve such large steric overlaps that their occurrence may be ignored altogether.

We thus arrive at the conclusion that the potential associated with rotation of the phenyl group is symmetric about $\chi = 0$ for all significant conformations, and that the allowed range of χ is fairly small. This conclusion applies to all stereochemical configurations. Through use of eq 33, with $\hat{\alpha}'(\chi = 0)$ given by eq 27 (with $\boldsymbol{\Omega}$ replaced therein by $\boldsymbol{\Omega}_0$; see above), we obtain

$$\hat{\alpha}' = \begin{bmatrix} -12.40 & -31.32 & 4.07 \\ -31.32 & -5.70 & -6.03 \\ 4.07 & -6.03 & 18.10 \end{bmatrix} + \langle \sin^2 \chi \rangle \begin{bmatrix} 29.81 & 41.64 & 16.10 \\ 41.64 & -3.83 & -23.87 \\ 16.10 & -23.87 & -25.98 \end{bmatrix} \quad (37)$$

in units of 10^{-25} cc. The anisotropy of the polarizability of the phenyl group dominates $\hat{\alpha}'$. Equation

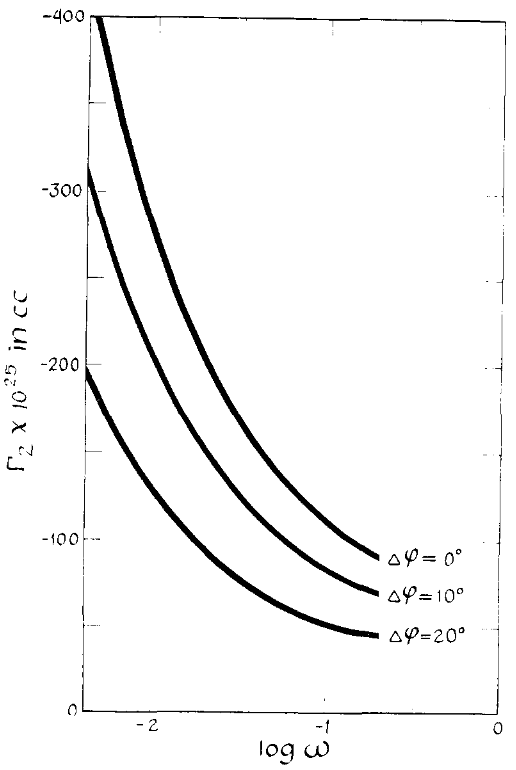

Figure 6. Γ_2 plotted against log ω for isotactic PS chains. Curves calculated for chains of 400 units with $\chi = 0$, $\langle \sin^2 \chi \rangle = 0$, $\tau^* = 1.00$, $\tau = 0.50$, $\eta = 1.5$, and the values of $\Delta\phi$ indicated.

36 for $\hat{\alpha}''$ is applicable also to the CH_2C group of polystyrene.

Results of calculations of Γ_2 for PS chains carried out in the same manner as for PP are presented in Figures 6–8. The group tensor $\hat{\alpha}'$ was represented by the first term only of eq 37; *i.e.*, the phenyl group was treated as if rigidly fixed in all calculations presented in these figures. The effects of nonzero values of $\langle \sin^2 \chi \rangle$ are discussed at the close of this section. Values of the statistical weight parameters used for the calculations shown in Figures 6–8 are: $\tau^* = 1.00$, $\tau = 0.50$, and $\eta = 1.5$,[16] with ω and $\Delta\phi$ taking on various values as indicated.

The sign of Γ_2 for PS is consistently negative.[7] This is an obvious consequence of the direction of the phenyl group with respect to the axis of the chain skeleton and hence the greater polarizability transverse to the chain axis. Apart from the sign of Γ_2, Figure 6 for isotactic PS resembles Figure 2 for isotactic PP. The behavior of Γ_2 for syndiotactic PS, shown in Figure 7 as a function of log ω, differs markedly from that for syndiotactic PP shown in Figure 3. The divergence of Γ_2 with decrease in ω for syndiotactic PS when $\Delta\phi = 0°$ is again attributable to the suppression of nonplanar conformations as $\omega \rightarrow 0$.[12]

According to the Monte Carlo calculations presented in Figure 8, $-\Gamma_2$ for PS passes through a minimum with change in stereochemical composition, at least for $\omega \leq 0.05$. In contrast to PP, the curves rise steeply as the chain becomes predominantly syndiotactic (*i.e.*, as $f_r \rightarrow 1$).

As we have pointed out in conjunction with eq 33, the value of Γ_2 must be linearly dependent upon $\langle \sin^2 \chi \rangle$. Thus, we may let

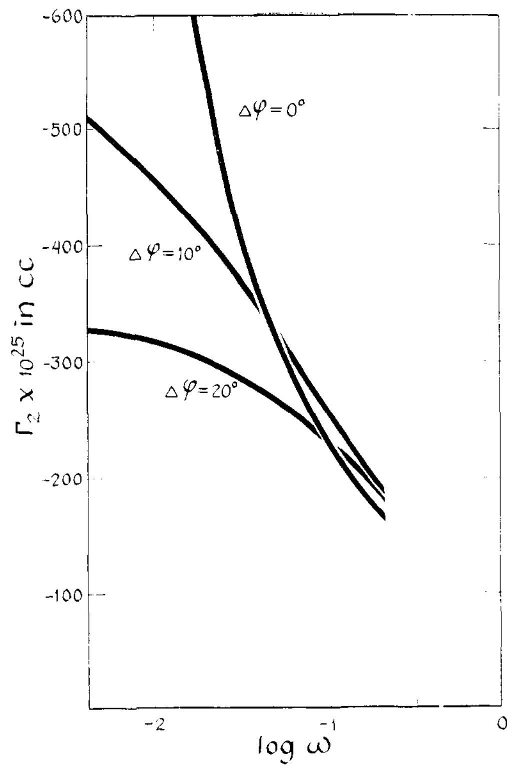

Figure 7. Γ_2 plotted against log ω for syndiotactic PS. Calculations carried out for the parameters given in the legend for Figure 6.

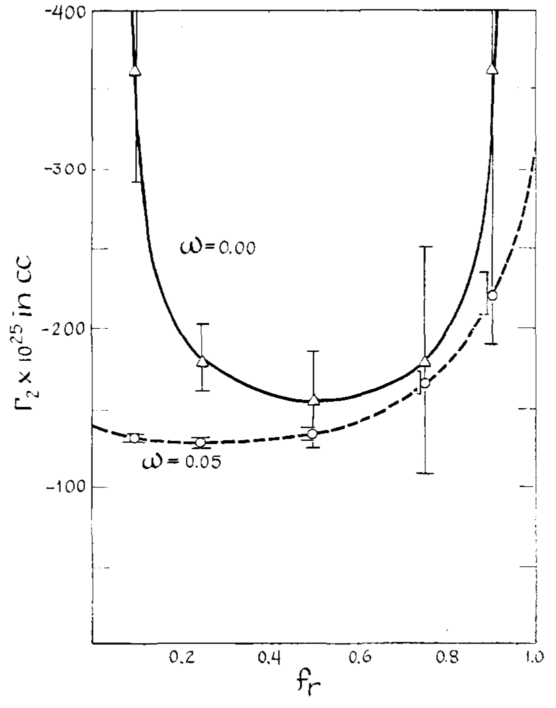

Figure 8. Monte Carlo calculations of Γ_2 for PS chains of various stereochemical compositions specified by f_r. Each point is the average for 15 chains. $\Delta\phi = 0°$. Other parameters are as given in the legend for Figure 6.

$$\Gamma_2 = \Gamma_2(\chi = 0)[1 + a\langle \sin^2 \chi \rangle] \qquad (38)$$

where $\Gamma_2(\chi = 0)$ is the value of Γ_2 calculated above, Γ_2 is the value corrected for fluctuations of χ (assumed to be symmetric about $\chi = 0$), and a is a numerical constant. Computations of the contribution to Γ_2

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 cross-linked 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.

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

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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.