The Effect of the Internal Field on Birefringence in Oriented Polymers

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ABSTRACT: In view of the increasing use of optical techniques to characterize the changes which occur in polymers when they are deformed, we have developed an approximate theory of the effect of deformation on the internal field. It is found that swelling with isotropic liquids should be capable of separating inter- and intramolecular field effects.

The effect of the internal field on the principal bond polarizabilities of molecules in unoriented systems has been presented by several investigators.[1-3] No adequate treatment has been presented for the case or oriented noncrystalline polymers. The major problem is that in the case of liquids or amorphous polymers with random orientation a volume element is chosen in such a way that the internal field from the molecules with the element cancel. However, for oriented systems this field cannot be neglected and it is this field which requires evaluation for a true understanding of the strain or stress birefringence behavior. It is the purpose of this article to present a simple theory of the effect of the internal field in oriented polymers on the birefringence.

Theory

When an electric field of intensity $\mathbf{E}$ is applied to a nonpolar molecule, the induced moment will be

$$\mathbf{m} = \boldsymbol{\alpha}\mathbf{E} \qquad (1)$$

where α represents the polarizability tensor of the molecule. The field E is the local field at the molecule. For gases at sufficiently low pressures, the field E is equal to the applied field E°.

However, when the distances between neighboring molecules become comparable to molecular dimensions, the field at the ith molecule is no longer just the applied field, but has an appreciable fraction contributed by the electric field of other molecules

$$\mathbf{E} = \mathbf{E}_\text{o} + \mathbf{E}_\text{p} \qquad (2)$$

The best known method of attempting to evaluate E_p is that of Lorentz.[4,5] Lorentz showed that under specific conditions $\mathbf{E}_\text{p} = {}^1\!/_3\gamma\mathbf{P}$. In general

$$\mathbf{E} = \mathbf{E}_\text{o} + {}^1\!/_3\gamma\mathbf{P} + \mathbf{E}^* \qquad (3)$$

where $\mathbf{E}^*$ represents the field intensity of molecules within a distance R of any selected molecule. If the moment $\mathbf{m}$ is the same for each dipole, then it can be shown that $\mathbf{E}^*$ will be zero if the system of dipoles has either cubic or tetrahedral symmetry. In the case of deformed rubbers, wide- and small-angle X-ray scattering show no detectable change in the inter- and intramolecular distances, *per se*, but do show a change in their orientational distribution as a function of strain. It is apparent that this field will be dependent on the orientation of the polymer molecules and, therefore, would be affected by any deformation such as uniaxial deformation or swelling with low molecular weight organic fluids.

Stein in a recent paper has evaluated the internal field of a *n*-paraffin crystal.[3] The results of his calculation indicate that the effective bond polarizabilities are affected by the internal field arising from the polarization of the rest of the molecules, and their values will depend upon molecular configuration.

We propose the following alternate theory for long-chain molecules. Following the theories of Zimm and Rouse, we represent the molecule as a chain of N identical segments joining $N + 1$ identical beads with complete flexibility at each bead.[6,7] The segment is assumed to have a Guassian probability function for the distribution of the components of the length of the segment. We further assume that the optical properties of the chain can be represented by a chain of spheres of radius $(\overline{b^2})^{1/2}$, whose centers correspond to the center of mass of the segments and b^2 is the root mean square end-to-end distance of a segment. We let α_1 and α_2 be the polarizabilities of the sphere parallel and perpendicular to the segment axis, respectively. The polarizabilities of the molecule, π_1, π_2, can then be calculated from the interactions between the point dipoles induced at the center of each sphere.

The moment induced at the ith sphere is

$$\mathbf{P}_i = \boldsymbol{\alpha}_i\mathbf{E} \qquad (4)$$

where α is the polarizability tensor of the ith sphere and

$$\mathbf{E} = \mathbf{E}_\text{o} + 2\sum_{m=1}^{N}\mathbf{E}_{ij} \qquad (5)$$

The field $\mathbf{E}$ is a sum of the externally applied field $\mathbf{E}_\text{o}$ and internal field $\mathbf{E}_{ij}$ due to the moments in all other spheres

$$\mathbf{E}_{ij} = (\nabla\nabla + K^2U)e^{-iKR_{ij}}\mathbf{P}_j/\mathbf{R}_{ij} \qquad (6)$$

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(1) K. Pitzer, *Advan. Chem. Phys.*, **2**, 74 (1959).

(2) R. P. Smith and E. M. Mortensen, *J. Chem. Phys.*, **35**, 714 (1961).

(3) R. S. Stein, ONR Technical Report No. 71, Polymer Research Institute, University of Massachusetts, Contract WOWR 3357(01), Project WR 056-378, Amherst, Mass., 1964; *J. Polym. Sci., Part A-2*, **7**, 1021 (1969).

(4) H. A. Lorentz, "The Theory of Electrons, Dover Publications, New York, N. Y., 1952.

(5) P. Debye, "Polar Molecules," Dover Publications, New York, N. Y., 1952.

(6) P. E. Rouse, *J. Chem. Phys.*, **21**, 1272 (1953).

(7) B. H. Zimm, *ibid.*, **24**, 269 (1956).

$K = 2\pi/\lambda$, ∇ gradient operation, U is the unit tensor, and $\mathbf{R}_{ij}$ is the distance from i to j. We examine only the case where $R_{ij} \ll \lambda$, which neglects the radiation field and evaluates only the effect of the electrostatic field and thus eq 6 becomes

$$\mathbf{E}_{ij} = -\frac{3\mathbf{P}_j\mathbf{R}_{ij}}{R_{ij}^5}\mathbf{R}_{ij} + \frac{\mathbf{P}_j}{R_{ij}^3} \tag{7}$$

The solutions of this equation for the field parallel and perpendicular to a perfectly oriented chain where the spheres lie on a straight line along the z axis can be obtained by a series of successive approximations or by solving a set of simultaneous equations. To a first approximation the fields parallel and perpendicular to the chain at the ith sphere are given as

$$\mathbf{E}_{\parallel}{}^{i} \cong \frac{\mathbf{E}_0}{1 - \left[\alpha_i/2(b^2)^{3/2}\left(\sum_1^{\infty}\left(\frac{1}{k^3}\right)\right)\right]} \tag{8}$$

and

$$\mathbf{E}_{\perp}{}^{i} \cong \frac{\mathbf{E}_0}{1 + \left[(\alpha_i/4(\bar{b}^2)^{3/2}\left(\sum_1^{\infty}\left(\frac{1}{k^3}\right)\right)\right]} \tag{9}$$

and the polarizability parallel and perpendicular to the z axis for the ith sphere will be respectively

$$\alpha_{\parallel i} \cong \alpha_1\left[1 + \frac{0.61\alpha_1}{(\bar{b}^2)^{3/2}}\right] \tag{10}$$

$$\alpha_{\perp i} \cong \alpha_2\left[1 - \frac{0.61\alpha_2}{2(\bar{b}^2)^{3/2}}\right] \tag{11}$$

The average polarizability $\overline{\alpha_i}$ is

$$\overline{\alpha_i} = \frac{\alpha_{\parallel i} + 2\alpha_{\perp i}}{3} = \frac{\alpha_1 + 2\alpha_2}{3} - \frac{0.61}{(b^2)^{3/2}}(\alpha_1{}^2 - \alpha_2{}^2) \tag{12}$$

while the anisotropy $\Delta\alpha_i$ is

$$\Delta\alpha_i = \alpha_{\parallel i} - \alpha_{\perp i} = (\alpha_1 - \alpha_2) + \left(\alpha_1{}^2 + \frac{\alpha_2{}^2}{2}\right)\frac{0.61}{(\bar{b}^2)^{3/2}} \tag{13}$$

For the case of an unoriented polymer, as shown by Lorentz, $\overline{\alpha_i}$ and $\overline{\Delta\alpha_i}$ should become

$$\overline{\alpha_i} = \frac{\alpha_1 + 2\alpha_2}{3} \tag{14}$$

and

$$\overline{\Delta\alpha_1} = \alpha_1 - \alpha_2 \tag{15}$$

For intermediate cases, we introduce an orientation function g(cos θ), where

$$g(\cos\theta) = \frac{3\,\overline{\cos^2\theta_i} - 1}{2} \tag{16}$$

and $\overline{\cos^2\theta_i}$ is a measure of the average orientation of our segments.

We assume that the orientation of the ith sphere with respect to the spheres which surround it can be represented by an average value, because in rubbers, the configurations are constantly changing due to Brownian motion. Thus, in the absence of stress or optical relaxation effects, the average value of $\overline{\cos^2\theta_i}$ remains constant.

We further assume that this average value is independent of r_{ij}. A more realistic approach would require a correlation function, $g(r_{ij}, \cos\theta_{ij})$, which was a function of both r_{ij} and θ_{ij}. Since we are restricting $r_{ij} \ll \lambda$, we assume that to a first approximation

$$g(r_{ij}, \cos\theta_{ij}) = g(\cos\theta_{ij}) \tag{17}$$

Thus

$$\alpha_i = \frac{\alpha_1 + 2\alpha_2}{3} - \frac{0.67g(\cos\theta)}{(b^2)^{3/2}}(\alpha_1{}^2 - \alpha_2{}^2) \tag{18}$$

and

$$\Delta\alpha_i = (\alpha_1 - \alpha_2) + \frac{0.67g(\cos\theta)}{(b^2)^{3/2}}\left(\alpha_1{}^2 + \frac{\alpha_2{}^2}{2}\right) \tag{19}$$

For an affine deformation with a deformation ratio of λ_z along the z axis

$$g(\cos\theta) =$$

$$\left[\frac{3\left\langle\frac{\lambda_z{}^3}{\lambda_z{}^3 - 1}\left(1 - \frac{\tan^{-1}(\lambda_z{}^3 - 1)^{1/2}}{\lambda_z{}^3 - 1}\right)\right\rangle - 1}{2}\right] \tag{20}$$

which for small strains reduces to

$$g(\cos\theta) \simeq (\lambda_z{}^3 - 1) \tag{21}$$

It has been shown by several investigators[8] that the polarizabilities of a chain parallel and perpendicular to a deformation axis are given as

$$\pi_{11} = \frac{j}{3}(\alpha_{11_i} + 2\alpha_{1_i}) + \frac{2}{5}j(\alpha_{11_i} - \alpha_{1_i})\left(\frac{R}{ja}\right)^2 \tag{22}$$

and

$$\pi_1 = \frac{j}{3}(\alpha_{11} + 2\alpha_{1_i}) - \frac{1}{5}j(\alpha_{11_i} - \alpha_{1_i})\left(\frac{R}{ja}\right)^2 \tag{23}$$

where j is the number of links, each of length a in our chain, and R is the end-to-end distance, while for the sample

$$P_{11} = N\left[\frac{j}{3}(\alpha_{11_i} + 2\alpha_{1_i}) + \frac{2}{15}(\alpha_{11_i} - \alpha_{1_i})\left(\lambda_z{}^2 - \frac{1}{\lambda_z}\right)\right] \tag{24}$$

$$P_1 = N\left[\frac{j}{3}(\alpha_{11_i} + 2\alpha_{1_i}) + \frac{1}{15}(\alpha_{11_i} - \alpha_{1_i})\left(\lambda_z{}^2 - \frac{1}{\lambda_z}\right)\right] \tag{25}$$

Utilizing the differential of the Lorenz–Lorentz equation, we obtain on substitution

$$\Delta n = C[\alpha_{11} - \alpha_{1_i}]\left[\lambda_z{}^2 - \frac{1}{\lambda_z}\right] \tag{26}$$

where C is a constant.

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[8] L. R. G. Treloar, "Physics of Rubber Elasticity," Oxford University Press, London, 1958.

On substituting eq 10 and 11 into eq 26, we obtain

$$\Delta n = C\left[(\alpha_{11_0} - \alpha_{1_0})\left(\lambda_z^{2} - \frac{1}{\lambda_z}\right) + \frac{0.67(\lambda_z^{3} - 1)}{(b^2)^{3/2}}\left(\alpha_1^{2} + \frac{\alpha_2^{2}}{2}\right)\left(\lambda_z^{2} - \frac{1}{\lambda_z}\right)\right] \quad (27)$$

But

$$b^2 = \left(\lambda_z^{2} + \frac{2}{\lambda_z}\right)b_0^{2} \quad (28)$$

and substitution of eq 28 into eq 27 gives

$$\Delta n = C\left[A\left(\lambda_z^{2} - \frac{1}{\lambda_z}\right) + B\frac{(\lambda_z^{3} - 1)\left(\lambda_z^{2} - \frac{1}{\lambda_z}\right)}{\left(\lambda_z^{2} + \frac{2}{\lambda_z}\right)}\right] \quad (29)$$

where $A = (\alpha_{11_0} - \alpha_{\perp_0})$ and $B = [0.67/(b_0^{2})]^{3/2}[\alpha_{11_0}^{2} + (\alpha \perp ^2/2)]$. Rewriting eq 29, we obtain

$$\frac{\Delta n}{\lambda_z^{2} - \frac{1}{\lambda_z}} = CA + CB\frac{(\lambda_z^{3} - 1)}{\left(\lambda_z^{2} + \frac{2}{\lambda_z}\right)} \quad (30)$$

which is similar to the Mooney–Rivlin equation for mechanical properties of rubbers and to an equation presented by Smith and Puett for optical properties of deformed polymers.[8–10] I have been informed by Professor R. S. Stein that these results are equivalent to an extension of the type of calculation which he and Rowell had made for some very small molecules.[11]

Equation 30 has been obtained assuming that the field contributions due to intermolecular effects are negligible in composition to intramolecular effects. In order to take into account intermolecular effects we assume that the spheres are located on a deformed lattice and their centers of mass have moved in an affine manner; then the effective polarizabilities parallel and perpendicular to the deformation axis are given by

$$\alpha_{\parallel i} = \frac{\alpha_{\parallel}}{1 + 4\alpha_{\parallel}\left(\frac{1}{r_{\parallel}^{3}} - \frac{1}{r_{\perp}^{3}}\right)} \quad (31)$$

and

$$\alpha_{\perp i} = \frac{\alpha_{\perp}}{1 - 2\alpha_{\perp}\left(\frac{1}{r_{\parallel}^{3}} - \frac{1}{r_{\perp}^{3}}\right)} \quad (32)$$

where r_i is the distance between the centers of mass parallel and perpendicular to the deformation axis. If we let

$$r_{\parallel}^{3} = \lambda_z^{3}(\bar{b}_0^{2})^{3/2} \quad (33)$$

and

$$r_{\perp}^{3} = \lambda_z^{-3/2}(\bar{b}_0^{2})^{3/2} \quad (34)$$

then substitution into eq 31 and 32 yields

$$\alpha_{\parallel i} = \frac{\alpha_{\parallel}}{1 + \frac{4\alpha_{\parallel}}{(\bar{b}_0^{2})^{3/2}}\left[\frac{1}{\lambda_z^{3}} - \lambda_z^{-3/2}\right]} \quad (35)$$

and

$$\alpha_{\perp i} = \frac{\alpha_{\perp}}{1 - \frac{2\alpha_{\perp}}{(\bar{b}_0^{2})^{3/2}}\left[\frac{1}{\lambda_z^{3}} - \lambda_z^{-3/2}\right]} \quad (36)$$

which when substituted into eq 24 and 25 and performing the same mathematical operations as in eq 27, 28, and 29 will yield

$$\frac{\Delta n}{\lambda_z^{2} - \frac{1}{\lambda_z}} = CA + CB'\left[\frac{1}{\lambda_z^{3}} - \lambda_z^{3/2}\right] \quad (37)$$

Data by Gent and Vickroy with polyethylene, Blokland with polyurethans, and Smith and Puett with fluoroelastomers appear to fit equations of these forms.[12,13] Blokland has suggested the presence of rodlike bundles in his samples to account for this behavior. It has also been suggested that the reason for this behavior is a reflection of the inadequacy of the statistical model of rubber elasticity.[14]

However, as shown recently by Gent, there are examples where the birefringence and stress–strain behavior are not linearly correlated.[15] This comment was based on observations of the stress birefringence behavior of swollen samples. They pointed out that this arose because of the asymmetry of the swelling liquids. If one were to use an isotropic swelling liquid, then eq 30 and 37 would predict a change in slope, as we swell the material. This technique should, therefore, enable us to evaluate the inter- and intramolecular contributions to the internal field effect.

We believe that our model offers not only a reasonable alternative to both suggestions but a mechanism whereby the Mooney–Rivlin equation may be understood. Since in molecular solids all of the binding is believed to originate in attractive van der Waals forces, which in turn are related to local dipole interactions, it would seem that forces of this magnitude in polymers could contribute to their mechanical behavior and would be a function of the nature of the interacting species as well as their orientation with respect to one another.

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(9) L. R. G. Treloar, *Trans. Faraday Soc.*, **50**, 881 (1954).

(10) K. J. Smith, Jr., and D. Puett, *J. Appl. Phys.*, **37**, 346 (1966).

(11) R. L. Rowell and R. S. Stein, *J. Chem. Phys.*, **47**, 2985 (1967).

(12) A. W. Gent and V. V. Vickroy, Jr., *J. Polym. Sci., Part A-2*, **5**, 47 (1967).

(13) R. Blokland, "Elasticity and Structure of Polyurethane Networks," Rotterdam University Press, Rotherdam, 1968.

(14) D. W. Saunders, private communication.

(15) A. N. Gent, *Macromolecules*, **2**, 262 (1969).