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**Abstract**

**Full Text**

**PHYSICS**

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## **ON THE QUESTION OF CALCULATING THE PHOTOELASTIC COEFFICIENT FOR POLYMERS**

*(Presented by Academician A. F. Ioffe, 23 XI 1956)*

The calculation of the photoelastic coefficient for rubber-like polymers was carried out in works <sup>(1-3)</sup> and others. The indicated authors used a model of a Gaussian polymer network composed of freely jointed chains, with the internal nodes of the network assumed to be fixed in their most probable positions. In the region of small uniaxial deformations the photoelastic coefficient  $B = \Delta n/t$  proves to be equal to

$$B = \frac{2\pi}{27} \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \Delta A, \quad (1)$$

where  $\Delta n = n_1 - n_2$ ;  $n_1$  and  $n_2$  are the refractive indices for light polarized in the direction of deformation and in the plane perpendicular to this direction;  $\bar{n} = \frac{1}{2}(n_1 + n_2)$ ;  $\Delta A$  is the mean anisotropy of the polymer chain in the coordinate system associated with the chain itself;  $t$  is the stress referred to a unit of the actual cross section of the specimen.

In the present note we shall show that expression (1) is applicable to an arbitrary polydisperse Gaussian network composed of chains with hindered internal rotation, and with allowance for fluctuations of the internal nodes of the network. We shall rely on the theory of the mechanical properties of Gaussian networks developed by Guth and James and proceeding from the same assumptions <sup>(4-6)</sup>.

Let us consider the magnitude of the birefringence in a unit cube of a block polymer, whose sides are parallel to the axes of the laboratory Cartesian coordinate system  $X, Y, Z$ . The dimensions of the specimen after deformation are  $L_x, L_y, L_z$ , and from the condition of constancy of volume under deformation  $L_x L_y L_z = 1$ . The coordinates of the points of the network lying on the surface of the specimen ("fixed" points, cf. <sup>(5,6)</sup>) will be denoted by the Greek indices  $\alpha, \beta, \gamma, \dots$ ; the coordinates of all points (fixed and internal, the so-called free nodes) will be denoted by the Latin indices  $m, n, \dots$

For uniaxial deformation of the specimen along the  $Z$  axis ( $L_y = L_x$ ), for Gaussian networks of chains with hindered internal rotation <sup>(4,6)</sup>, the following

relation is obtained between the stress  $t_z = t$ , referred to a unit of actual cross section normal to the axis of deformation, and the relative deformation  $L_z$ :

$$t_z = kKT \left( L_z^2 - \frac{1}{L_z} \right), \quad (2)$$

where  $k$  is Boltzmann's constant;  $T$  is the absolute temperature;  $K$  is a constant which for an isotropic network has the form

$$K = \frac{1}{l_{\text{eff}}^2} \sum_{\alpha > \beta} \sum \frac{(\mathbf{r}_{\alpha}^{(0)} - \mathbf{r}_{\beta}^{(0)})^2}{N'_{\alpha\beta}} = \frac{3}{l_{\text{eff}}^2} \sum_{\alpha > \beta} \sum \frac{(u_{\alpha}^{(0)} - u_{\beta}^{(0)})^2}{N'_{\alpha\beta}}; \quad u_{\alpha} = x_{\alpha}, y_{\alpha}, z_{\alpha}; \quad (3)$$

$\mathbf{r}_{\alpha}^{(0)}$  and  $\mathbf{r}_{\beta}^{(0)}$  are the radius vectors of fixed points in the undeformed specimen;  $N'_{\alpha\beta}$  are certain complicated functions of all  $N_m$ , i.e., of the numbers of links in all chains of the specimen. The mean square length  $\overline{h^2}$  of a Gaussian chain consisting of  $N_{mn}$  links is expressed in terms of the parameter  $l_{\text{eff}}^2$  as follows:

$$\overline{h_{mn}^2} = N_{mn} l_{\text{eff}}^2 + g + o(\lambda^{N_{mn}}), \quad |\lambda| < 1, \quad g \sim 1. \quad (4)$$

The value of  $l_{\text{eff}}^2$  is determined by the internal structure of the chains<sup>(7,8)</sup>. The length and position of the chain connecting two neighboring nodes  $m$  and  $n$  is specified in the laboratory coordinate system by the vector  $\mathbf{h}_{mn}$ .

We introduce an auxiliary molecular coordinate system  $X', Y', Z'$ , in which the  $Z'$  axis is directed along the vector  $\mathbf{h}_{mn}$ , while the  $X'$  and  $Y'$  axes are arranged in the plane normal to  $\mathbf{h}_{mn}$  in an arbitrary manner, since all directions perpendicular to  $\mathbf{h}_{mn}$  are physically equivalent.

For a given  $h_{mn}$ , a chain may assume many configurations, each of which corresponds to its own value of the polarizability. We shall consider the mean value of the polarizability tensor of the chain  $A_{u'v'}$  for a given  $h_{mn} = h(u', v' - x', y', z')$ . In the Gaussian region one may expand the components of the polarizability tensor in powers of the ratio  $(h/h_{\text{max}})$ , just as for freely jointed chains (cf. (1,2,4,9)). Instead of  $h_{\text{max}}$  it is convenient to take the contour length of the chain  $h'_{\text{max}} = N_{mn}l$ , where  $N_{mn}$  is the number of links;  $l$  is the length of the C-C bond. For the present we restrict ourselves to chains of the type  $(-\text{CH}_2 - \text{CHR}-)_n$ .

The indicated expansion of the components of the chain polarizability tensor in the molecular coordinate system  $X', Y', Z'$  at fixed  $h$  has the form:

$$A_{u'u'} = A_{00} + \Gamma_{u'u'} \left( \frac{h}{N_{mn}l} \right)^2 + \dots; \quad u' = x', y', z'. \quad (5)$$

Owing to the axial symmetry of the tensor  $A_{ik}$ , one may write that  $A_{x'x'} = A_{y'y'} = A_{\perp}$ ;  $\Gamma_{x'x'} = \Gamma_{y'y'} = \Gamma_{\perp}$ ;  $A_{z'z'} = A_{\parallel}$  and  $\Gamma_{z'z'} = \Gamma_{\parallel}$ . The nondiagonal components of the averaged polarizability tensor vanish upon averaging over all angles of rotation of the chain about the  $Z'$  axis. Since the polarizability tensor of a chain is an additive quantity, the coefficients  $\Gamma_{\parallel}$  and  $\Gamma_{\perp}$  may be represented in the form  $\Gamma_{\parallel} = N_{mn}\gamma_{\parallel}$  and  $\Gamma_{\perp} = N_{mn}\gamma_{\perp}$ , where  $\gamma_{\parallel}$  and  $\gamma_{\perp}$  characterize the contribution of one monomer unit. We now write the expression for the averaged polarizability tensor of the given chain in the laboratory coordinate system:

$$P^{(mn)} = A_{00}^{(mn)} \cdot I + (A_{\parallel}^{(mn)} - A_{\perp}^{(mn)}) \cdot S, \quad (6)$$

where  $I$  is the unit tensor;  $S_{uu} = \cos^2(z', u) - 1/3$ ;  $S_{uv} = \cos(z', u)\cos(z', v)$ ,  $u, v = X, Y, Z$ .

Substituting (5) into (6) and summing over all chains in a unit volume, we obtain the expression for the tensor of the mean polarizability of a unit volume for given positions of all internal nodes and external fixed points:

$$P = P_{00} + (\gamma_{\parallel} - \gamma_{\perp})R, \quad (7)$$

where

$$R_{uv} = \sum_{m>n} \sum \frac{(u_m - u_n)(v_m - v_n)}{N_{mn}l^2} - \frac{1}{3}\delta_{uv} \sum_{m>n} \sum \frac{(\mathbf{r}_m - \mathbf{r}_n)^2}{N_{mn}l^2};$$

$$u_m, v_m = x_m, y_m, z_m.$$

In obtaining (7) we use the fact that  $h_{mn} \cos(z', u) = u_m - u_n$ . Expression (7) must be averaged over all positions of the inter-

internal junctions. The probability of a specified distribution of all the junctions of the Gaussian network is given by the expression <sup>(6)</sup>

$$W(\dots \mathbf{r}_m, \mathbf{r}_n \dots) = C \exp \left\{ - (3/2l_{\text{eff}}^2) \sum_{m>n} \sum [(\mathbf{r}_m - \mathbf{r}_n)^2 / N_{mn}] \right\}. \quad (8)$$

Then averaging the sum  $\sum_{m>n} \sum [(u_m - u_n)^2 / N_{mn}l^2] \equiv \sum_{uu}$  over all positions of the internal junctions with the aid of the distribution function (8) gives:

$$\sum_{uu} = (l_{\text{eff}}^2/l^2) \left[ \int \sum_{uu} \cdot w d\gamma_{\text{intern}} \right] / \left[ \int w d\gamma_{\text{intern}} \right]. \quad (9)$$

The integration in (9) is carried out over all positions of the internal junctions. In (5) it was shown that

$$\int \dots \int \exp \left\{ -\frac{3}{2l_{\text{eff}}^2} \sum_{m>n} \sum \frac{(u_m - u_n)^2}{N_{mn}} \right\} d\gamma_{\text{intern}} = C_u \exp \left\{ -\frac{3}{2l_{\text{eff}}^2} \sum_{\alpha>\beta} \sum \frac{(u_\alpha - u_\beta)^2}{N'_{\alpha\beta}} \right\}. \quad (10)$$

Here  $u_\alpha$  and  $u_\beta$  are the coordinates of the external fixed points in the deformed specimen;  $N'_{\alpha\beta}$  are the same constants that enter expression (3);  $C_u$  is a certain complicated function of all  $N_{mn}$  and  $l_{\text{eff}}^2$ .

Introduce the auxiliary parameter  $\tau$ ; then

$$\overline{\sum}_{uu} = -\frac{2}{3} \frac{l_{\text{eff}}^2}{l^2} \lim_{\tau \rightarrow 1} \left\{ \frac{d}{d\tau} \ln \left[ \int \exp \left( -\frac{3}{2l_{\text{eff}}^2} \tau \sum_{m>n} \sum \frac{(u_m - u_n)^2}{N_{mn}} \right) d\gamma_{\text{intern}} \right] \right\}. \quad (11)$$

If the specimen is deformed in the direction  $u$  by a factor  $L_u$ , then  $u_\alpha = u_\alpha^{(0)} L_u$ , and, using (10) and (11), we obtain

$$\overline{\sum}_{uu} = \frac{l_{\text{eff}}^2}{l^2} \left\{ \lim_{\tau \rightarrow 1} \ln C_u(\tau) + \frac{1}{3} L_u^2 K \right\}, \quad u = x, y, z. \quad (12)$$

The quantity  $C_u$  does not depend on the coordinates of the external fixed points or on the degree of deformation  $L_x = L_y$  and  $L_z$ . Owing to the isotropy of the network before deformation,

$$C_x = C_y = C_z. \quad (13)$$

To calculate  $\Delta n$  we use the condition  $L_y^2 L_z = 1$ , the Lorentz-Lorenz equation for the refractive indices  $n_1$  and  $n_2$ , and the smallness of  $\Delta n = n_1 - n_2$  in comparison with  $n_1$  and  $n_2$ . The light beam is incident along the direction of the  $X$  axis. The Lorentz-Lorenz equation gives

$$\frac{4}{3} \pi P_{yy} = \frac{n_2^2 - 1}{n_2^2 + 2} \quad \text{and} \quad \frac{4}{3} \pi P_{zz} = \frac{n_1^2 - 1}{n_1^2 + 2}.$$

After simple transformations we obtain the following expressions for  $\Delta n$  and  $B$ :

$$\Delta n = n_1 - n_2 = \frac{2\pi}{27} \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \frac{l_{\text{eff}}^2}{l^2} K \left( L_z^2 - \frac{1}{L_z} \right) (\gamma_{\parallel} - \gamma_{\perp}), \quad (14)$$

$$B = \frac{\Delta n}{t'_z} = \frac{2\pi (\bar{n}^2 + 2)^2 l_{\text{eff}}^2}{27 \bar{n} kT l^2} (\gamma_{\parallel} - \gamma_{\perp}). \quad (15)$$

Expression (15) reflects a very important result for what follows: the photoelastic coefficient of an arbitrary isotropic Gaussian network does not depend on the structure of the network itself (on functionality and polydispersity), i.e., on the choice of  $N_{mn}$ ,  $r_{\alpha}^{(0)}$ , and  $r_{\beta}^{(0)}$ , but is determined only by the anisotropy and structure of the individual polymer chains (through the parameters  $l_{\text{eff}}^2$  and  $\gamma_{\parallel} - \gamma_{\perp}$ ).

Let us express the photoelastic coefficient (15) in terms of the mean anisotropy of an individual chain. The mean anisotropy  $\Delta A$  of an individual Gaussian polymer chain is determined from (4) and (5) as follows:

$$\Delta A = \bar{A}_{\parallel}(h) - \bar{A}_{\perp}(h) = \frac{l_{\text{eff}}^2}{l^2} (\gamma_{\parallel} - \gamma_{\perp}) + O\left(\frac{1}{N}\right). \quad (16)$$

Substituting (16) into (15), we obtain for the photoelastic coefficient  $B$  the required expression (1).

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*Note: Figure translations are in progress. See original paper for figures.*

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