population of an excimer site is no longer dictated by the number of chromophoric pairs. This implies that the energy is delocalized over an average about 35 styrene units and is limited to this extent by energy trapping at excimer sites. Similar considerations will apply to the dependence of I_D/I_M upon molecular weight studied in steady-state excitation.[13-15]

Conclusions

The studies described in this paper have led to the following conclusions.

(1) There is no justification for the proposal[6,7] that excited monomeric styrene residues may be kinetically distinguishable as a consequence of their location within –SSS– as opposed to –SSB– triads.

(2) The kinetics of intramolecular excimer formation in polystyrenes show a molecular weight dependence that is characterized by two distinct regions. This behavior is best explained by implication of energy migration within chromophore sequences.

(3) In agreement with conclusions from steady-state excitation analyses,[14,18] there is no evidence for long-range interactions in excimer formation in polystyrenes.

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Theory of Strain Birefringence of Amorphous Polymer Networks

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ABSTRACT: Recent rubber elasticity theory, according to which departures from relationships derived for phantom networks originate in constraints on the fluctuations of network junctions, is applied to the treatment of strain birefringence. The strain birefringence of phantom networks is first considered. It is smaller than for networks in which the transformation of chain vectors is affine in the macroscopic strain, as assumed in all previous treatments of strain birefringence in rubber elastic systems. The relationship of birefringence to the stress is the same, however. Real networks, in which the constraints on fluctuations impart a pattern of behavior intermediate between the extremes of phantom and affine networks, are treated in detail by extension of rubber elasticity theory. Illustrative numerical calculations are presented. Contributions of the constraints to the birefringence Δn are somewhat larger, relatively, than their contributions to the stress τ. In contrast to theories of phantom and of affine networks, Δn for the real network is predicted to be nonlinear with τ for uniaxial extension; i.e., the stress-optical coefficient $\Delta n/\tau$ should decrease with elongation.

Introduction

The birefringence of an amorphous polymer network under strain reflects the orientation of the structural units comprising the chains of the network. More precisely, it depends directly on the mean orientations of the optical polarizability tensors associated with the structural units.[1,2] Analysis of the strain-induced birefringence rests on establishment of connections between orientation at a molecular level and the macroscopic state of strain. Close parallels with molecular theories of rubber elasticity have long been recognized.[1,3,4]

Heretofore, the theory of strain birefringence of elastomeric polymer networks[1-6] has been formulated on the basis of the affine network model, according to which the transformation of the chain vectors (i.e., the vectors spanning the chains between network junctions) is linear in the macroscopic strain. This model has been discredited by recent investigations, both theoretical[7-10] and experimental.[1,11] The distribution of chain vectors that characterizes the system at a molecular level undergoes a

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smaller alteration[7-9] than the earlier postulate of affine transformation would require. The departure is generally substantial at large strains; the chain vector distribution may be altered by as little as half, or even less, of the macroscopic displacement gradient.[8,12] Reformulation of the theory of strain birefringence of amorphous networks in keeping with recent advances in the theory of rubber elasticity is therefore overdue.

We begin with analysis of strain birefringence according to the theory of Gaussian phantom networks,[8] the foundations of which were set forth in the classic work of James and Guth.[12] In these hypothetical networks the physical effects of the chains are confined to their actions on the junctions to which their ends are connected, the chains being otherwise devoid of material properties. As James and Guth[12] showed, the *mean* positions of the junctions in a Gaussian phantom network are affine in the strain, but *fluctuations* about these positions are invariant with strain. It follows that the chain vector distribution, being the convolution of the distribution of mean vectors and fluctuations therefrom, is not affine in the strain, as was pointed out subsequently.[8] The phantom network represents an extreme in the departure from affine behavior at the molecular level. Although real networks generally depart considerably from their hypothetical phantom analogues at small strains, their elastic properties converge to those of phantom networks at high elongations and/or degrees of dilation.[7,9,10]

Adaptation of recent advances in the theory of rubber elasticity of real networks to strain birefringence is the main concern of the present paper. In addition to the contribution to the stress from affine displacement of mean values of the chain vectors by the strain, as in the corresponding phantom network, this theory takes account of the further distortions arising from restrictions on fluctuations in a real network. In interests of simplification, these restraints may be assumed to be incident on the network junctions; they arise from constraints on the relocation of junctions in the surrounding medium due to the interspersion of chains and junctions in the network consisting of real, space-filling chains. This theory has been strikingly successful in accounting for the relationship of stress to strain for all varieties of strains of typical elastomers throughout ranges accessible to experiment.[11,13-15] It serves also to relate the stress, or modulus, quantitatively to the network structure.[11,16-18] The treatment of strain birefringence elaborated below on the basis of this theory of real networks is compared with experiments in the following paper.[19]

Birefringence of Phantom Networks

General Theory for Homogeneous Strain. The instantaneous end-to-end vector $\mathbf{r}_i$ for chain i of a network at equilibrium under a fixed strain can be resolved into a time-averaged part $\bar{\mathbf{r}}_i$ and a fluctuation $\delta\mathbf{r}_i$ therefrom at the given instant; i.e.

$$\mathbf{r}_i = \bar{\mathbf{r}}_i + \delta\mathbf{r}_i \tag{1}$$

In the case of a Gaussian phantom network, $\bar{\mathbf{r}}_i$ is affine in the macroscopic strain and the probability of a fluctuation $\delta\mathbf{r}_i$ is independent of strain.[12] Hence

$$\mathbf{r}_i = \boldsymbol{\lambda}\bar{\mathbf{r}}_{i,0} + \delta\mathbf{r}_i \tag{2}$$

where $\boldsymbol{\lambda}$ is the macroscopic displacement gradient tensor and $\bar{\mathbf{r}}_{i,0}$ denotes the mean (i.e., time averaged) chain vector in the state of reference defined as usual as the isotropic state in which the mean-square, $\langle r^2\rangle$, of the magnitudes of the chain vectors coincides with the value $\langle r^2\rangle_0$ for a free, unperturbed chain.[8] Inasmuch as the fluctuations and the means are uncorrelated, the ensemble average for the ν chains comprising the network under the strain defined by $\boldsymbol{\lambda}$ follows as

$$\langle r^2\rangle = \langle \bar{\mathbf{r}}_0{}^{\mathrm{T}}\boldsymbol{\lambda}^{\mathrm{T}}\boldsymbol{\lambda}\bar{\mathbf{r}}_0\rangle + \langle(\delta r)^2\rangle \tag{3}$$

where the superscript T denotes the transpose. Choosing the principal axes of $\boldsymbol{\lambda}^{\mathrm{T}}\boldsymbol{\lambda}$ as coordinate axes, one obtains for the mean-square of the x components of the chain vectors

$$\langle x^2\rangle = \lambda_x{}^2\langle \bar{x}_{\mathrm{ph}}{}^2\rangle_0 + \langle(\delta x)^2\rangle \tag{4}$$

with corresponding expressions for the y and z components; λ_x, λ_y, and λ_z are the principal components of the macroscopic deformation gradient tensor.

For a perfect phantom network (i.e., a phantom network free of chains attached at one end only) whose junctions are φ-functional[8]

$$\langle \bar{r}_{\mathrm{ph}}{}^2\rangle_0 = (1 - 2/\varphi)\langle r^2\rangle_0 \tag{5}$$

and

$$\langle (\delta r)_{\mathrm{ph}}{}^2\rangle = (2/\varphi)\langle r^2\rangle_0 \tag{6}$$

The mean-square fluctuation is substantial; for a tetrafunctional phantom network it amounts to half of $\langle r^2\rangle_0$.

Isotropy of the state of reference requires that

$$\langle x^2\rangle_0 = \langle y^2\rangle_0 = \langle z^2\rangle_0 = \langle r^2\rangle_0/3 \tag{7}$$

and hence that

$$\langle (\delta x)_{\mathrm{ph}}{}^2\rangle = (2/\varphi)\langle x^2\rangle_0 = (2/3\varphi)\langle r^2\rangle_0 \tag{8}$$

with corresponding expressions for $\langle(\delta y)_{\mathrm{ph}}{}^2\rangle$ and $\langle(\delta z)_{\mathrm{ph}}{}^2\rangle$. Substitution in eq 4 of the analogues of eq 5 and 6 for the x component together with eq 7 yields

$$\langle x^2\rangle = [(1 - 2/\varphi)\lambda_x{}^2 + 2/\varphi]\langle x^2\rangle_0 \tag{9}$$

for the mean-square of component x at extension λ_x, with corresponding relations for $\langle y^2\rangle$ and $\langle z^2\rangle$. A molecular deformation tensor for the perfect phantom network can therefore be defined whose principal components are given by

$$\Lambda_{t,\mathrm{ph}}{}^2 = (1 - 2/\varphi)\lambda_t{}^2 + 2/\varphi, \qquad t = x, y, z \tag{10}$$

It relates the mean deformation of the chains of the network to the macroscopic deformation.

We consider next the polarizability tensor $\boldsymbol{\alpha}_{\mathbf{r}}$ of a chain averaged over all configurations subject to restriction of the chain vector to the value $\mathbf{r}$. The difference between components of the averaged tensor along arbitrarily chosen Cartesian axes is given in adequate approximation by the first term of a series,[4-6] i.e., by

$$(\alpha_{xx} - \alpha_{yy})_{\mathbf{r}} = \Gamma_2(x^2 - y^2)/\langle r^2\rangle_0 \tag{11}$$

x and y being the components of $\mathbf{r}$ along the respective axes. The quantity Γ_2 is defined by[2,6]

$$\Gamma_2 = (9/10)\sum_i \langle \mathbf{r}^{\mathrm{T}}\hat{\boldsymbol{\alpha}}_i\mathbf{r}\rangle_0/\langle r^2\rangle_0 \tag{12}$$

where $\hat{\boldsymbol{\alpha}}_i$ is the anisotropic part of the polarizability tensor contributed by the structural unit, or group, indexed by i; the angle brackets and subscript 0 denote the average over all configurations of the free chain.

Let the axes of the arbitrary reference frame introduced above be identified with the principal axes of the strain and therefore of $\boldsymbol{\Lambda}^2$. Then the mean difference between the polarizabilities of a chain along axes x and y, taken as the average over the ν chains of the network, is

$$\bar{\alpha}_{xx} - \bar{\alpha}_{yy} = \nu^{-1}\sum_{i=1}^{\nu}(\alpha_{xx} - \alpha_{yy})_i$$
$$= \Gamma_2(\langle x^2\rangle - \langle y^2\rangle)/\langle r^2\rangle_0 \quad (13)$$
$$= (\Gamma_2/3)(\Lambda_x^2 - \Lambda_y^2) \quad (14)$$

According to the Lorentz–Lorenz relation the refractive index difference along the two principal axes is

$$\Delta n_{xy} \equiv n_x - n_y = (2\pi/9)(\nu/V)[(n^2+2)^2/n](\bar{\alpha}_{xx} - \bar{\alpha}_{yy})$$

where n is the mean refractive index and n_t is the refractive index along axis t. Hence

$$\Delta n_{xy} = (2\pi/27)(\nu/V)[(n^2+2)^2\Gamma_2/n](\Lambda_x^2 - \Lambda_y^2) \quad (15)$$

For a perfect phantom network therefore (see eq 10)

$$\Delta n_{xy} = (2\pi\nu/27V)(1 - 2/\varphi)[(n^2+2)^2\Gamma_2/n](\lambda_x^2 - \lambda_y^2) \quad (16)$$

This relation differs by the factor $(1 - \varphi/2)$ from the result obtained in previous treatments[1-4] based on the assumption that the transformation of the chain vectors is affine in λ. For a tetrafunctional network, this factor is $^1/_2$.

Generalization of this result to an imperfect network may be achieved through characterization of the network structure by the cycle rank ξ of the network instead of the number of chains. This may be accomplished through substitution of

$$\nu = \xi/(1 - 2/\varphi) \quad (17)$$

which holds also for imperfect networks if ν is replaced by the effective number ν_{eff} of chains. We thus obtain for the difference in refractive indices along principal axes x and y

$$\Delta n_{xy} = (\xi/V)kTC(\lambda_x^2 - \lambda_y^2) \quad (18)$$

where k is the Boltzmann constant and

$$C = 2\pi(n^2+2)^2\Gamma_2/27nkT \quad (19)$$

Presented in this form, the relation expressed by eq 18 should be applicable to imperfect as well as perfect networks, ξ being defined unambiguously for either.

The true stress along principal axis t is given by

$$\tau_t = (\xi/V)kT\lambda_t^2 \quad (20)$$

from which it follows that

$$\tau_x - \tau_y = (\xi/V)kT(\lambda_x^2 - \lambda_y^2) \quad (21)$$

for a Gaussian phantom network. Hence, the difference between refractive indices along axes x and y is proportional to the difference between the true stresses along the same axes; i.e.

$$\Delta n_{xy}/(\tau_x - \tau_y) = C \quad (22)$$

and C emerges as the stress-optical coefficient.[20] This relationship between birefringence and stress, obtained here for a phantom network, is identical with the result derived previously for an affine network.[1-4]

Uniaxial Deformations. The displacement gradient is conveniently separated into dilational and deviatory factors. For uniaxial deformation the elements of λ parallel and perpendicular to the strain axis are expressed on this basis by

$$\lambda_\parallel = \lambda = (V/V_0)^{1/3}\alpha_e \quad (23a)$$
$$\lambda_\perp = \lambda^{-1/2}(V/V_0)^{1/2} = (V/V_0)^{1/3}\alpha_e^{-1/2} \quad (23b)$$

where λ and α_e are the axial extension ratios relative to the state of reference and to the isotropic state of volume V, respectively, V being the volume in the state of strain.[21] Replacement of $\lambda_x^2 - \lambda_y^2$ in eq 18 and 21 by $(V/V_0)^{2/3}(\alpha_e^2 - \alpha_e^{-1})$ in accordance with these relations yields

$$\Delta n \equiv n_\parallel - n_\perp = C(\xi kT/V_0)(V/V_0)^{-1/3}(\alpha_e^2 - \alpha_e^{-1}) \quad (24)$$

and

$$\tau = \tau_\parallel - \tau_\perp = (\xi kT/V_0)(V/V_0)^{-1/3}(\alpha_e^2 - \alpha_e^{-1}) \quad (25)$$

for the birefringence parallel vs. perpendicular to the axis of cylindrical symmetry. Hence

$$\Delta n/\tau = C \quad (26)$$

as follows directly from eq 22. Equation 26 holds also for an affine network.[1-4] The stresses and the birefringences differ for the affine and phantom networks, but by the same factor.

Birefringence of Real Networks

Relationship of Birefringence to Strain. Owing to constraints resulting from the copious interpenetration of chains in the network, the mean chain vectors $\mathbf{r}$ are increased and the fluctuations $\delta\mathbf{r}$ are decreased. These effects must depend on the state of strain as Ronca and Allegra[7] first pointed out. They may be taken into account by replacing eq 2 with

$$\mathbf{r}_i = \lambda\bar{\mathbf{r}}_{i,ph,0} + \Delta\bar{\mathbf{r}}_i + \delta\mathbf{r}_i \quad (27)$$

where the first term is the time-averaged mean vector that would represent chain i in the state of reference if the network could be reduced to the phantom condition through suppression of the material properties of the chains, $\Delta\bar{\mathbf{r}}_i$ is the alteration of this mean vector due to the effect of these constraints, and $\delta\mathbf{r}_i$ is the fluctuation from the mean, with the mean given by the sum of the first two terms in eq 27. Both $\Delta\bar{\mathbf{r}}_i$ and the distribution of the fluctuations $\delta\mathbf{r}_i$ depend on the strain specified by λ.[7-9] Taking coordinates along the principal axes of λ, we have

$$x_i = \lambda_x\bar{x}_{i,ph,0} + \Delta\bar{x}_i + \delta x_i \quad (28)$$

etc. Since the quantities on the right-hand side are statistically independent for the ν chains of the network, the averages of their squares are related according to

$$\langle x^2\rangle = \lambda_x^2\langle\bar{x}_{ph}^2\rangle_0 + \langle(\Delta\bar{x}^2)\rangle + \langle(\delta x)^2\rangle \quad (29)$$
$$= \lambda_x^2(1 - 2/\varphi)\langle x^2\rangle_0 + \langle(\Delta x)^2\rangle \quad (29')$$

where $\langle x^2\rangle_0$ is the x component of the chain vector for the free chain (see eq 7) and the last two terms in eq 29 have been combined in eq 29′ through use of the quantity

$$\Delta x_i \equiv \Delta\bar{x}_i + \delta x_i \quad (30)$$

For a phantom network $\Delta\bar{x}_i = 0$; hence $\langle(\Delta x)_{ph}^2\rangle = \langle(\delta x)_{ph}^2\rangle$. For a perfect phantom network $\langle(\delta x)_{ph}^2\rangle$ is related to $\langle x^2\rangle_0$, the average for the free chain, according to eq 8. Equation 29′ for the real network may therefore be written

$$\langle x^2\rangle = [\lambda_x^2(1 - 2/\varphi) + (2/\varphi)\langle(\Delta x)^2\rangle/\langle(\Delta x)_{ph}^2\rangle]\langle x^2\rangle_0 \quad (31)$$

The effects of mutual constraints on the configurations of the dense interspersion of chains in polymer networks have been incorporated in the theory of rubber elasticity through analysis of their effects on the locations and fluctuations of junctions of the network.[9,10] The displacements $\Delta\mathbf{R}$ of junctions from their mean positions in the corresponding phantom network were treated and their

mean squares $\langle(\Delta R)^2\rangle$ and components $\langle(\Delta X)^2\rangle$, etc., were deduced as functions of the strain and the severity of the constraints. The mean square of the junction fluctuations $\langle(\Delta X)_{ph}^2\rangle$ in the phantom network can be related to the corresponding quantity $\langle(\Delta x)_{ph}^2\rangle$ for the chain, but the connection is obscure for the constrained network. However, it may be asserted with confidence that

$$\langle(\Delta x)^2\rangle/\langle(\Delta x)_{ph}^2\rangle = \langle(\Delta X)^2\rangle/\langle(\Delta X)_{ph}^2\rangle \quad (32)$$

where $\langle(\Delta X)_{ph}^2\rangle = \langle(\delta X)_{ph}^2\rangle$ measures the strain-independent fluctuations in the phantom network analogously to $\langle(\delta x)^2\rangle$. The ratio on the right-hand side of eq 32 was shown previously[9,10] to be given by $1 + B_x$, where B_x is a function of λ_x and of two parameters, κ and ζ, according to

$$B_t = (\lambda_t - 1)(\lambda_t + 1 - \zeta\lambda_t^2)/(1 + g_t)^2 \quad (33)$$

with $t = x, y, z$ and

$$g_t = \lambda_t^2[\kappa^{-1} + \zeta(\lambda_t - 1)] \quad (34)$$

Hence

$$\langle(\Delta x)^2\rangle/\langle(\Delta x)_{ph}^2\rangle = 1 + B_x \quad (35)$$

The principal parameter κ is defined as the ratio of the mean-square radius of the fluctuations of the junctions in the phantom network to the mean-square radius $\langle(\Delta s)_0$ of the Gaussian domain of constraint in the undistorted network; i.e.

$$\kappa = \langle(\Delta R)_{ph}^2\rangle/\langle(\Delta s)^2\rangle_0 \quad (36)$$

where ΔR measures the magnitude of the fluctuation from its mean position; the subscript 0 denotes that $\lambda = \mathbf{E}$, the matrix identity. The parameter κ has been postulated[9,11] to depend on the degree of interpenetration in the network, a conjecture well supported by experiments.[11] The secondary parameter ζ is proportional to the coefficient of λ_t^3 in the series expansion of Δs_t in powers of λ_t commencing with λ_t^2. It is believed to reflect inhomogeneities in the network topology. It is of marginal importance and usually can be equated to zero with only minor sacrifice of accuracy in the representation of elasticity measurements.

According to eq 31 and 35 the elements of the molecular deformation tensor Λ^2 can be expressed as the sum of contributions from the phantom network and from the constraints; i.e.

$$\Lambda_t^2 = \Lambda_{t,ph}^2 + \Lambda_{t,c}^2 \quad (37)$$

where $\Lambda_{t,ph}^2$ is given by eq 10, and

$$\Lambda_{t,c}^2 = (2/\varphi)B_t \quad (38)$$

The contribution to the birefringence from the molecular deformation due to the constraints is therefore (compare eq 15)

$$\begin{aligned}\Delta n'_{xy,c} &= (\nu/V)kTC(\Lambda_{x,c}^2 - \Lambda_{y,c}^2)\\ &= (2/\varphi)(\nu/V)kTC(B_x - B_y)\end{aligned} \quad (39)$$

where C is defined by eq 19.

In addition to the deformation of the chains associated with the alteration of their chain vectors under strain, it is necessary to consider the action of the junctions on the domains of constraint surrounding them. The junction and its domain are coupled elastic elements and their mutual interaction induces effects on each which contribute to the elastic free energy and, hence, to the stress. Compliances on the part of the domain may be presumed to entail orientational effects which contribute to the birefringence. It is important to distinguish these effects from the relocation and distortion of the domains of constraint under strain that are direct consequences of the distortion of the surrounding medium considered as a continuum. The latter make no contribution to the stress or the orientation beyond the effects of the molecular distortion considered above and embodied in the tensor Λ_c^2. Our present concern is with the further orientations in the domains in response to the relocation of the junction within each of them. (The displacement of the junction is not affine in the distortion of the surrounding medium.) The model does not identify molecular mechanisms responsible for the constraints. They may be assumed, however, to involve interferences with the movements of junctions by comparatively short sequences of chain units. We return later to the matter of the mechanism of response of the constraints.

For immediate purposes it suffices to observe that the constraints within the domains may be characterized by the tensor of second moments of the fluctuations of the captive junctions that would obtain in the absence of the restraining effects of the chains connected to them. If we let $\Delta\mathbf{s}$ denote the displacement of the hypothetical "free" junction from the center of its domain of constraint, then the components of this tensor along principal axes of the strain are given by $\langle(\Delta s_t)^2\rangle_{\lambda_t}$ with $t = x$, y, and z, the averages being taken over all junctions of the network. The subscript λ_t acknowledges distortion of the domain by the strain. Owing to the connectivity of the network and the resulting forces on the junctions, the actual moments of the displacements $\Delta\mathbf{s}$ differ from those for "free" junctions. We represent them by $\langle(\Delta s_{*t})\rangle_{\lambda_t}$. The quantity that measures the reaction of the constraint domain to the action of the junction, averaged over all junctions, is the ratio $\langle(\Delta s_{*t})^2\rangle_{\lambda_t}/\langle(\Delta s_t)^2\rangle_{\lambda_t}$. This ratio is given by[9,10]

$$\langle(\Delta s_{*t})^2\rangle_{\lambda_t}/\langle(\Delta s_t)^2\rangle_{\lambda_t} = 1 + g_tB_t = \Theta_t^2 \quad (40)[22]$$

with B_t and g_t defined by eq 33 and 34. A domain deformation tensor Θ^2 can be introduced in analogy to Λ^2. Its elements are defined by the second equality in eq 40.

The reaction of chains, or chain sequences, to relocation of junctions in the domains of constraint may be assumed to be qualitatively akin to the orienting effect of alteration of the chain vectors spanning each chain as a whole. That is, at the molecular level, reconfiguring of chains, or portions thereof, must be involved, and this may be presumed to provide the primary mechanism of response of the constraints to action of the relative displacements of network junctions. Preferential orientation of chain units resembling that induced by alteration of the chain vectors may be assumed to occur as well. Hence, this effect (generally minor) on the birefringence should likewise be proportional to Γ_2 defined by eq 12 and incorporated in the stress-optical coefficient according to eq 19. The further contribution of the constraints to the birefringence, arising from this source, may therefore be expressed by (see eq 18, 39 and 40)

$$\begin{aligned}\Delta n''_{xy,c} &= b(\mu/V)kTC(\Theta_x^2 - \Theta_y^2)\\ &= b(\mu/V)kTC(g_xB_x - g_yB_y)\end{aligned} \quad (41)$$

where μ is the number of junctions (or the number affected by constraints in an imperfect network) and b is an arbitrary parameter introduced in acknowledgment of obscurities pertaining to the reactions of the constraints and the associated contribution to the birefringence. This parameter should occur in the range $0 \le b \le 1$.

Combination of eq 39 and 41 for the two contributions of the constraints to the birefringence yields

$$\Delta n_{xy,c} = \Delta n'_{xy,c} + \Delta n''_{xy,c} = (\xi/V)kTC(\varphi/2 - 1)^{-1}[(B_x - B_y) + b(g_xB_x - g_yB_y)] \quad (42)$$

where the substitutions

$$\nu/\xi \text{ (or } \nu_{eff}/\xi) = (1 - 2/\varphi)^{-1} \quad (43)$$

$$\mu/\xi \text{ (or } \mu_{eff}/\xi) = (\varphi/2 - 1)^{-1} \quad (44)$$

have been introduced. The total birefringence Δn_{xy} is the sum of the contribution $\Delta n_{xy,ph}$ of the phantom network and of the constraints; i.e.

$$\Delta n_{xy} = \Delta n_{xy,ph}(1 + \Delta n_{xy,c}/\Delta n_{xy,ph}) \quad (45)$$

where $\Delta n_{xy,ph}$ is given by eq 18. According to eq 18 and 42, the ratio appearing in the parenthetic expression in eq 45 is

$$\Delta n_{xy,c}/\Delta n_{xy,ph} = [(B_x - B_y) + b(g_xB_x - g_yB_y)]/(\varphi/2 - 1)(\lambda_x^2 - \lambda_y^2) \quad (46)$$

Relationship of Birefringence to Stress. The stress likewise comprises the sum of contributions for the corresponding phantom network and from the constraints, the latter consisting of contributions, corresponding to $\Delta n'_{xy,c}$ and $\Delta n''_{xy,c}$, from the deformation of the distribution of chain vectors and from the compliances of the domains of constraint, respectively. Its principal components are given by[9,10]

$$\tau_t = (\xi/V)kT\lambda_t^2[1 + (\varphi/2 - 1)^{-1}K(\lambda_t^2)] \quad (47)$$

where

$$K(\lambda^2) = B[\dot{B}(B + 1)^{-1} + g(\dot{g}B + g\dot{B})(gB + 1)^{-1}] \quad (48)$$

with

$$\dot{B} = \partial B/\partial\lambda^2$$

$$\dot{g} = \partial g/\partial\lambda^2$$

The difference between the components of the stress along principal axes x and y is therefore

$$\tau_x - \tau_y = (\xi/V)kT\{\lambda_x^2 - \lambda_y^2 + [\lambda_x^2K(\lambda_x^2) - \lambda_y^2K(\lambda_y^2)]/(\varphi/2 - 1)\} \quad (49)$$

or

$$\tau_x - \tau_y = (\tau_x - \tau_y)_{ph}[1 + (\tau_x - \tau_y)_c/(\tau_x - \tau_y)_{ph}] \quad (50)$$

where $(\tau_x - \tau_y)_{ph}$ is given by eq 21 and

$$(\tau_x - \tau_y)_c/(\tau_x - \tau_y)_{ph} = [\lambda_x^2K(\lambda_x^2) - \lambda_y^2K(\lambda_y^2)]/(\varphi/2 - 1)(\lambda_x^2 - \lambda_y^2) \quad (51)$$

The ratio of the birefringence for principal axes x and y to the difference between the corresponding stresses is

$$\Delta n_{xy}/\tau_x - \tau_y = C\{1 + [(B_x - B_y) + b(g_xB_x - g_yB_y)]/(\varphi/2 - 1)(\lambda_x^2 - \lambda_y^2)\}/\{1 + [\lambda_x^2K(\lambda_x^2) - \lambda_y^2K(\lambda_y^2)]/(\varphi/2 - 1)(\lambda_x^2 - \lambda_y^2)\} \quad (52)$$

according to eq 18, 21, 45, 46, and 49.

In the limit of vanishing constraints where $\kappa \to 0$, physical considerations require[10] that $\kappa\zeta \to 0$ also. It follows that B, gB, and the derivatives $\dot{B}$ and $\dot{g}$ must vanish in this limit. Hence, $K(\lambda^2) = 0$, $\Delta n_{xy,c}$ and $(\tau_x - \tau_y)_c$ vanish, and eq 52 reduces to eq 22, and the result for a phantom network as required in this limit.

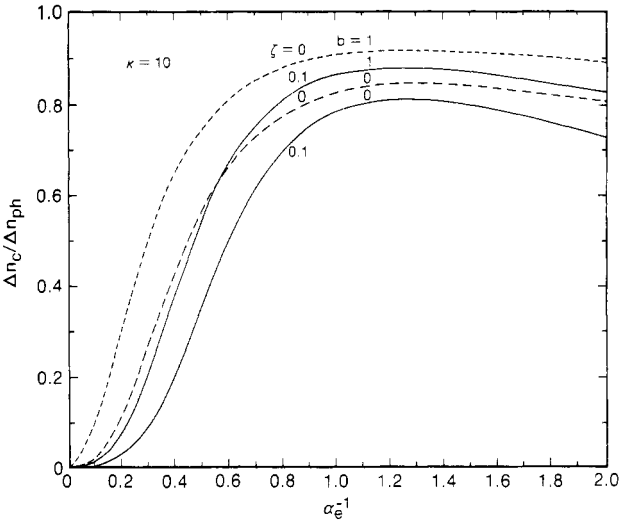

Figure 1. The ratio $\Delta n_c/\Delta n_{ph}$, expressing the birefringence due to the constraints relative to the birefringence for the phantom network, plotted as a function of the reciprocal of the extension ratio α_e. Curves calculated according to eq 53 with $\varphi = 4$, $\kappa = 10$, $\zeta = 0$ (solid curves) or 0.1 (dashed curves), and $b = 0$ or 1 as indicated.

In the opposite extreme, constraints suppress fluctuations altogether and the transformation of the distribution of chain vectors becomes affine. This condition is reached in the limit $\kappa \to \infty$; consistency requires that $\zeta \to 0$ simultaneously.[10] In this limit $g = 0$, $B = \lambda^2 - 1$, $\dot{B} = 1$, and $K(\lambda^2) = 1 - \lambda^{-2}$. Hence $\Delta n_{xy,c}/\Delta n_{xy,ph} = (\tau_x - \tau_y)_c/(\tau_x - \tau_y)_{ph} = (\varphi/2 - 1)^{-1}$, and eq 52 again reduces to eq 22 as required for an affine network. Whereas both the birefringences and the stresses for the phantom network differ from those for the affine network, their ratio is the same at these extremes. At intermediate values of κ the ratio of birefringence to strain varies with values of the parameters κ and ζ according to eq 52, and with the strain as well, as shown by calculations presented below.

Uniaxial Deformation. Particularization of eq 46 and 51 to uniaxial deformations through introduction of the quantities defined in eq 23 yields

$$\Delta n_c/\Delta n_{ph} = \{(B_\parallel - B_\perp) + b[(gB)_\parallel - (gB)_\perp]\}/(\varphi/2 - 1)(V/V_0)^{2/3}(\alpha_e^2 - \alpha_e^{-1}) \quad (53)$$

and

$$\tau_c/\tau_{ph} = [\lambda_\parallel^2K(\lambda_\parallel^2) - \lambda_\perp^2K(\lambda_\perp^2)]/(\varphi/2 - 1)(V/V_0)^{2/3}(\alpha_e^2 - \alpha_e^{-1}) \quad (54)$$

for the contributions of the constraints to the birefringence and stress, respectively, relative to the values for the phantom network; see eq 24 and 25. From eq 52 one likewise obtains

$$\Delta n/\tau = C\{1 + [(B_\parallel - B_\perp + b(gB)_\parallel - b(gB)_\perp]/(\varphi/2 - 1)(V/V_0)^{2/3}(\alpha_e^2 - \alpha_e^{-1})\}/\{1 + [\lambda_\parallel^2K(\lambda_\parallel^2) - \lambda_\perp^2K(\lambda_\perp^2)]/(\varphi/2 - 1)(V/V_0)^{2/3}(\alpha_e^2 - \alpha_e^{-1})\} \quad (55)$$

For a phantom network or for an affine network the ratio of the quantities in braces in eq 55 is unity and this equation reduces to eq 26.

Numerical Calculations

In Figure 1 the contribution Δn_c to the birefringence from the constraints under uniaxial deformation relative to the birefringence Δn_{ph} of the phantom network is plotted against α_e^{-1}. The curves were calculated according to eq 53 for a tetrafunctional network ($\varphi = 4$) with $\kappa = 10$,

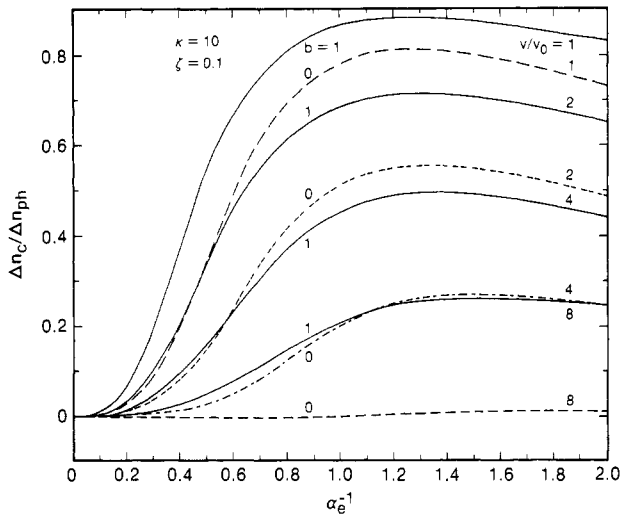

Figure 2. Effect of dilation on the relative contribution of the constraints to the birefringence. Curves calculated according to eq 53 with $\varphi = 4$, $\kappa = 10$, $\zeta = 0.1$, and $b = 1$ (solid curves) or $b = 0$ (dashed curves) for the degrees of dilation V/V_0 indicated with each curve.

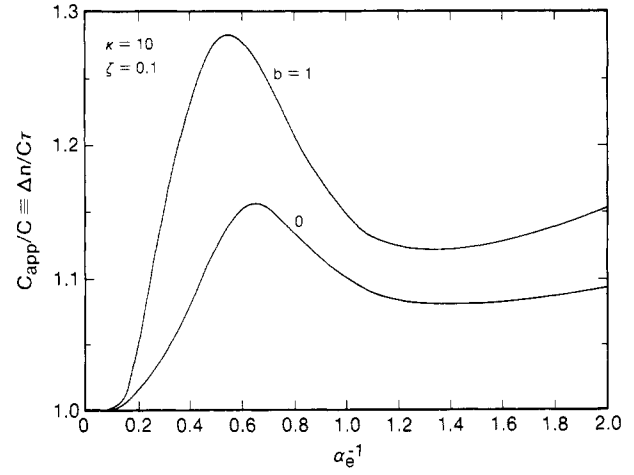

Figure 3. Birefringence–stress ratio $\Delta n/\tau$ relative to its value, C, for the phantom network as a function of reciprocal extension. Curves calculated according to eq 55 with the same parameters as those used in Figure 2.

$\zeta = 0$ and 0.1, and $b = 0$ and 1, as indicated in the figure. The contribution of the reaction of the domains of constraint ($\Delta n''_{xy,c}$ given by eq 41) is zero for $b = 0$. Even for $b = 1$ it is small, as is evident from comparison of the corresponding curves. The combined effect of the constraints manifested in Δn_c relative to the birefringence Δn_{ph} for the phantom is greatest for $\alpha_e \approx 1$, i.e., at small strains. The ratio decreases with extension, vanishing at $\alpha_e^{-1} = 0$. The curves decrease gradually with compression, i.e., with increase in α_e^{-1} for $\alpha_e^{-1} > 1$.

The effect of dilation (swelling) on the ratio $\Delta n_c/\Delta n_{ph}$ is shown in Figure 2. The calculations, like those in Figure 1, were carried out for a tetrafunctional network using eq 53, with V/V_0 being varied from 1 to 8 as indicated. Values of κ and ζ were fixed at 10 and 0.1, respectively. The solid curves were calculated with $b = 1$ and the dashed ones with $b = 0$. The effects of the constraints on Δn diminish with dilation. For $b = 0$ they very nearly vanish at $V/V_0 = 8$. The contribution from the compliances of the constraint domains becomes dominant at high dilations.

The dependence of $\Delta n_c/\Delta n_{ph}$ on strain, on dilation, and on ζ resembles, qualitatively, the dependence of the corresponding stress ratio τ_c/τ_{ph} (usually expressed in terms of the ratio of reduced forces $[f^*]$).[9,10] Quantitative comparisons show the effects on $\Delta n_c/\Delta n_{ph}$ to be appreciably larger, however. This comparison is presented explicitly in Figure 3, where $\Delta n/\Delta n_{ph} = \Delta n/\tau C$, the birefringence–stress ratio relative to its value, C, for the phantom network, is plotted against α_e^{-1} for $b = 0$ and 1. The curves were calculated according to eq 55 with the same values of the other parameters as those used in Figure 2. The nonlinear dependence of the ordinate on strain denotes departure from Brewster's law, according to which the birefringence should be proportional to the stress. The theory leads to the conclusion, therefore, that the birefringence and the stress are not quantitatively equivalent as indices of molecular orientation in real networks.

References and Notes

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(20) The symbol B previously used[2] for the stress-optical coefficient is here replaced by C in order to avoid confusion with the parameter B_f defined by eq 33 and appearing in the following equations. The present notation agrees with that used by Treloar.[1]
(21) The subscript e is appended to the extension ratio α_e in order to distinguish it from the optical polarizability.
(22) The result expressed by eq 40 was identified previously[9,10] with the inverse ratio of the parameters governing, respectively, the Gaussian distribution of the components Δs_i for hypothetical junctions disembodied from the restraining influences of their associated chains and the distribution for the junctions in the actual network. These parameters were denoted by σ_λ and $\sigma_{*\lambda}$, respectively. Their ratio, $\sigma_\lambda/\sigma_{*\lambda}$, is identical with the quantity given on the left-hand side of eq 40.