

## EFFECT OF THE REFERENCE CHAIN DIMENSIONS ON THE VISCOELASTIC BIREFRINGENCE OF POLYMER NETWORKS

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Received December 21st, 1972

In analogy to the molecular theory of mechanical viscoelastic behaviour, the effect of the reference chain dimensions on the deformation birefringence of polymer networks was specified. This enabled the effects connected with the change of the internal energy of chains with temperature and with the strain effect of the solvent to be introduced into the final relationships describing both the linear viscoelastic and nonlinear equilibrium birefringence.

In an earlier paper<sup>1</sup> we discussed the effect of introduction of the reference chain dimensions into the molecular theory of the viscoelastic behaviour of polymer networks which permitted to include into viscoelastic functions the effects connected with a change in the internal energy of chains with temperature and the deformation effect of the diluent. Since the birefringence caused by deformation of amorphous polymers is related to the same motions of macromolecules which are also responsible for the viscoelastic behaviour, this paper will mainly report the consequences of introduction of the reference state of the polymer chain on its value.

Similarly to an earlier example<sup>1</sup>, we shall consider the model of a freely-jointed chain containing  $N$  free submolecules, each of which consists of  $z$  statistical segments having a length  $a$  and allowing the end-to-end distribution of the submolecule to be Gaussian. If a sample is deformed in the isotropic state (which generally differs from the reference one), to the dimensions corresponding to the deformation ratios  $\lambda_x$ ,  $\lambda_y$ ,  $\lambda_z$  ( $\lambda = l/l_0$ , where  $l$  or  $l_0$  respectively is the deformed or initial length in the isotropic state), the molecules are departed from their equilibrium positions and gradually approach new equilibrium positions by a diffusional motion described by the Fokker-Planck equation. For the distribution function of end-to-end chain distances in a deformed isotropic state  $\overline{P_{i,\lambda}^N}$  in the system of normal coordinates  $u_1, v_1, w_1 \dots u_N, v_N, w_N$  it holds<sup>1</sup>

$$\overline{P_{i,\lambda}^N} du_1 \dots dw_N = \left(\frac{b_{i,s}}{\pi}\right)^{3N/2} \exp \left\{ b_{i,s} \sum_{n=1}^N \left[ \frac{u_n^2}{\beta_{x,n}^2} + \frac{v_n^2}{\beta_{y,n}^2} + \frac{w_n^2}{\beta_{z,n}^2} \right] \right\} \frac{du_1 \dots dw_N}{\prod_{n=1}^N \beta_{x,n} \beta_{y,n} \beta_{z,n}}, \quad (1)$$

where  $b_{i,s} = b_0 \langle \alpha_{i,s}^2 \rangle^{-1}$ ,  $b_0 = 3/2za^2 = 3/2\overline{r_0^2}$ ,  $\overline{r_0^2}$

is the mean square end-to-end distance of the submolecule in the reference state,  $\langle \alpha_{i,s}^2 \rangle = \overline{r_{i,s}^2}/\overline{r_0^2}$  is the dilatation factor,  $\overline{r_{i,s}^2}$  is the mean square end-to-end distance of the submolecule in the isotropic state,  $\beta_{x,n}$  is the time-dependent value of the deformation ratio  $\beta_{x,n}^2(t) = 1 + (\lambda_x^2 - 1) \exp(-t/\tau_n)$  (similar relationships hold also for  $\beta_{y,n}^2$  and  $\beta_{z,n}^2$ ),  $\tau_n = 1/\{16b_{i,s}k\mu T \sin^2[(n-1)\pi/2N]\}$  is the relaxation time for a chain whose both ends are bonded in the network,  $\mu$  is the mobility of the junction point of two submolecules,  $k$  is Boltzmann's constant and  $T$  is absolute temperature.

The total polarization anisotropy of the sample  $P_1 - P_2$ , in the deformed isotropic state is given by

$$P_1 - P_2 = \nu \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} (p_l - p_t) \overline{P_{i,\lambda}^N} du_1 \dots dw_N, \quad (2)$$

where  $\nu$  is the number of chains in the sample. For anisotropy of a submolecule in the reference state it can be written<sup>2,3</sup>

$$p_l - p_t = \frac{2}{3}(\alpha_l - \alpha_t) b_0 \sum_{n=1}^N [u_n^2 - \frac{1}{2}(v_n^2 + w_n^2)], \quad (3)$$

where  $\alpha_l$  or  $\alpha_t$  respectively denotes the polarization of light with an electric vector parallel or vertical to the direction of the statistical segment. By using the Lorentz-Lorentz relationship between the refractive index  $n$  and polarization  $P$ , Eqs (2) and (3) give for the birefringence  $\Delta n = n_l - n_t$  in the case of a unidirectional elongation

$$\Delta n(\lambda, t) = \frac{(\bar{n} + 2)^2}{\bar{n}} \frac{2\pi\nu_{i,s}}{45} (\alpha_l - \alpha_t) (\lambda^2 - \lambda^{-1}) \langle \alpha_{i,s}^2 \rangle (1 + \sum_{n=2}^N e^{-t/\tau_n}), \quad (4)$$

where  $\bar{n}$  is the mean refractive index and  $\nu_{i,s} = \nu/V_{i,s}$  is concentration of chains in the isotropic state having the volume  $V_{i,s}$ . The equilibrium part of birefringence from Eq. (4) coincides with the earlier expression<sup>4</sup>. By analogy with the linear viscoelastic behaviour it can be written for the linear viscoelastic birefringence  $\Delta n_1(t)$

$$\Delta n_1(t) = B(t) \cdot \varepsilon = (B_c + \int_{-\infty}^{+\infty} H^{(0)} e^{-t/\tau} d \ln \tau) \varepsilon, \quad (5)$$

where  $\varepsilon = \lambda - 1$ ,  $B(t)$  is the optical relaxation function and  $H^{(0)}$  is the optical relaxation spectrum, for which it can be found from Eq. (4)

$$H^{(0)} = \frac{(\bar{n}^2 + 2)^2}{\bar{n}} (\alpha_l - \alpha_t) \frac{\nu_{i,s} \langle \alpha_{i,s}^2 \rangle^{3/2}}{15} \left( \frac{Z \xi_a \overline{R_0^2}}{6kT} \right)^{1/2} \tau^{-1/2}, \quad (6)$$

where  $Z = zN$  is the total number of statistical segments in the chain,  $\xi_a = N/\mu Z$  is the frictional factor per a statistical segment, and  $\bar{R}_0^2 = N\bar{r}_0^2$ .

When calculating molecular characteristics from birefringence by means of Eqs (4) and (6), the change in the reference state with temperature and dilution during formation of the network must be taken into account similarly to the case of the mechanical relaxation spectrum<sup>1</sup>. Assuming that the reference state is identical with the state of network formation, it holds for the dilatation factor of the isotropic swollen state (characterized by the temperature  $T$  and the volume fraction of the polymer  $v$ )<sup>1</sup>

$$\langle \alpha_{i,s}^2 \rangle_{T,v} = \left( \frac{\bar{r}_{i,s}^2}{r_0^2} \right)_{T,v} = \left( \frac{\bar{R}_{i,s}^2}{R_0^2} \right)_{T,v} = \frac{\langle \alpha_{i,d}^2 \rangle_T}{\langle \alpha_{i,d}^2 \rangle_{T_0}} \left( \frac{v^0}{v} \right)^{2/3}, \quad (7)$$

where  $\langle \alpha_{i,d}^2 \rangle = \bar{R}_{i,d}^2/\bar{R}_0^2$ ;  $\bar{R}_{i,s}^2$  or  $\bar{R}_{i,d}^2$  respectively is the mean square end-to-end distance of a chain in the isotropic swollen or dry state and  $T^0$ ,  $v^0$  are conditions at network formation. By combining Eqs (7) and (4), it is possible to analyze in detail the effect of external conditions on both the equilibrium and viscoelastic birefringence. Comparison of an earlier relationship for stress relaxation<sup>1</sup>  $\sigma(\lambda, t)$  with Eq. (4) gives for the stress-optical coefficient  $C$  the expression

$$C = \frac{\Delta n(\lambda, t)}{\sigma(\lambda, t)} = \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \frac{2\pi}{45kT} (\alpha_1 - \alpha_t), \quad (8)$$

independent of time, the content of crosslinks and the reference state; as a consequence, it can also be deduced that  $H^{(0)}/H^{(m)} = C$ , where  $H^{(m)}$  is the mechanical relaxation spectrum<sup>1</sup>.

The basic condition for the above approach consists in the entropic nature of deformation; in other words, all configurations realized by a chain subject to the action of an external force at a constant temperature and pressure are isoenergetic. On the other hand, the introduction of the reference state of the network enabled us to take into account the change in the internal energy with temperature; as a consequence, the temperature dependence  $\bar{R}_0^2$  differs from  $\bar{R}_{i,d}^2$  and  $\langle \alpha_{i,d}^2 \rangle_T \neq 1$ . For a much more realistic model of the polymer network — that is, for segments with constant valence angles and with hindered rotations<sup>4,5</sup> — this means that the participation of different rotational isomers changes with temperature (while no changes can be observed with deformation). In this way, the participation of the individual rotational isomers in the statistical segment also changes with temperature, which in turn can lead to a pronounced temperature dependence of the difference of the segment polarization,  $\Delta\alpha = \alpha_1 - \alpha_t$ , and thus also of the stress-optical coefficient  $C$ . The procedure outlined above can be used only for the orientational part of the total birefringence, not reflecting the distortional (given by the change in the valency angles) and the shape (given particularly by the specific interaction of the solvent with the chain) birefringence. This predetermines the application of the above relationships in the first place to the end of the main transition region in the proximity of the rubberlike behaviour of amorphous polymers, which is the only region where the orientational birefringence can be expected to determine the total behaviour.

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Translated by L. Kopecská.