EFFECT OF A TEMPERATURE DEPENDENCE OF THE CHAIN DIMENSIONS ON THE VISCOELASTIC AND EQUILIBRIUM RHEOOPTICAL BEHAVIOUR OF A POLYURETHANE NETWORK

M.ILAVSKÝ and K.DUŠEK

Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6

The linear viscoelastic and equilibrium rheooptical behaviour of the polyurethane network (poly(2-methyloxirane), terminated with 4,4'-methylenebis(phenyl isocyanate) and crosslinked with 2,2-bis(hydroxymethyl)-1,4-butanediol) was investigated in the main transition and rubber-like region within the temperature range from -30 to $+90°C$. The temperature dependences of the chain dimensions, $d \ln \overline{r_0^2}/dT = -0.3 \cdot 10^{-3} \, K^{-1}$, and of the optical anisotropy of a statistical segment, $d \ln \Delta\alpha/dT = -0.5 \cdot 10^{-3} \, K^{-1}$, in the rubberlike region were determined; these values are independent of deformation. A continuous dependence of superimposed mechanical and optical curves on time, especially in the proximity and inside the rubberlike region, can be obtained by introducing a correction for the change in the dimensions and in the optical anisotropy with temperature into the method of reduced variables, in accordance with the theory of the viscoelastic rheooptical behaviour of polymeric networks suggested earlier. In the rubberlike region a further decrease with time is observed in the superimposed curves, or in the optical and mechanical relaxation spectrum; the temperature dependence of the shift factor exhibits a change in the slope above $75°C$.

The deformational birefringence of amorphous polymers is determined by the same motions of macromolecules or their parts which are also responsible for the respective viscoelastic behaviour. Since the birefringence determines the measure of molecular orientation, simultaneous measurement of the mechanical and optical relaxation processes leads to a better understanding of the respective molecular mechanisms. The time–temperature superposition principle, commonly in use in the treatment of deformation data[1], has also been applied to the birefringence data in the case of both amorphous[2–5] and semicrystalline[6–8] polymers. Only in a few cases, however, a vertical shift of the experimental data was used when applying the principle of superposition to optical data[2–4,8], similarly to the treatment of mechanical measurements.

The ideal network theory does not consider intermolecular interactions, but by introducing the reference state it was possible to express the effect of intramolecular interactions determined by non-zero rotational energy. In our preceding paper we generalized the molecular theory of the mechanical[9] and optical[10] viscoelastic behaviour of ideal networks for a case when the external force is applied in the isotropic state differing from the state of network formation. The generalization included in the rheooptical functions effects connected with a change in the internal energy of chains and the deformational effect of the solvent. One of the consequences of such modification is the prediction of the magnitude of the vertical shift of rheooptical functions in the super-

position, which depends on the temperature dependence of the chain dimensions. This effect was experimentally verified on the mechanical behaviour of poly(n-butyl methacrylate) networks[11].

This paper reports an experimental investigation of the effect of the temperature dependence of the chain dimensions on the viscoelastic rheooptical behaviour of chains using as an example a polyurethane network consisting of poly(2-methyl-oxirane), 4,4′-methylenebis(phenyl isocyanate) and 2,2-bis(hydroxymethyl)-1,4-butanediol. A special attention is devoted to the effect of the magnitude of the vertical mechanical and optical shift on the detailed form of superimposed curves obtained by the time–temperature superposition.

THEORETICAL

Phenomenological Theory

If a sample in the isotropic dry state is stretched to a constant relative deformation $\varepsilon = (l_\lambda - l_{id})/l_{id}$, then in the linear viscoelastic region the relaxation of stress (related to a deformed cross-section S_λ) and of the birefringence $\Delta n(t) = \bar{n}_\parallel - \bar{n}_\perp$ (related to a deformed thickness d_λ) is given by

$$\sigma(t) = E(t) . \varepsilon, \quad \text{resp.} \quad \Delta n(t) = B(t) . \varepsilon, \tag{1}$$

where l_λ and l_{id} respectively are the deformed and the initial length of the sample, $\bar{n}_\parallel$ and $\bar{n}_\perp$ respectively are the refractive indices in a direction parallel or perpendicular respectively to the direction of elongation, and $E(t)$ and $B(t)$ respectively are the Young modulus or the optical relaxation function (deformational-optical function). The functions $E(t)$ and $B(t)$ can be transformed into rheooptical viscoelastic spectra by using the equations[12] (for crosslinked systems)

$$E(t) = E_e + \int_{-\infty}^{+\infty} H^{(m)} e^{-t/\tau} \, d\log \tau, \tag{2}$$

and

$$B(t) = B_e + \int_{-\infty}^{+\infty} H^{(0)} e^{-t/\tau} \, d\log \tau,$$

where $H^{(m)}$ and $H^{(0)}$ respectively are the mechanical and optical tensile spectrum, E_e and B_e respectively are the equilibrium values of the mechanical and optical relaxation functions, and τ is the relaxation time. Using Eq. (1), it is possible to define the stress-optical function $C(t) = \Delta n(t)/\sigma(t)$, which can also be expressed by means of the stress-optical retardation spectrum $L^{(0)}$ in the form

$$C(t) = C_g + \int_{-\infty}^{+\infty} L^{(0)} (1 - e^{-t/\tau}) \, d\log \tau = C_e - \int_{-\infty}^{+\infty} L^{(0)} e^{-t/\tau} \, d\log \tau, \tag{3}$$

where C_g and C_e respectively are the values of the stress-optical coefficient characteristic of the glass and rubberlike state.

Molecular Theory

The introduction of reference chain dimensions into the molecular theory of the viscoelastic rheooptical behaviour led to the following equations relating the stress, σ, and the birefringence, Δn, of a dry network[9,10]

$$\sigma(\lambda, t) = f/S_\lambda = v_{i,d} kT\langle\alpha_{i,d}^2\rangle[\lambda^2 - (V_\lambda/V_{i,d})\lambda^{-1}]\left(1 + \sum_{n=2}^{N} e^{-t/\tau_n}\right) \qquad (4a)$$

$$\Delta n(\lambda, t) = \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \frac{2\pi v_{i,d}}{45} \Delta\alpha\langle\alpha_{i,d}^2\rangle\left[\lambda^2 - (V/V_{i,d})\lambda^{-1}\right]$$

$$\left(1 + \sum_{n=2}^{N} e^{-t/\tau_n}\right) \qquad (4b)$$

where f is force, λ is relative elongation, $v_{i,d}$ is the number of chains in a dry isotropic volume, V_λ and $V_{i,d}$ respectively are volumes of the sample in the deformed and in the isotropic state, k is the Boltzmann constant, T is temperature, N is the number of submolecules in the chain, $\Delta\alpha = \alpha_1 - \alpha_t$ is the difference between the main polarizabilities of the statistical segment, τ_n is the relaxation time, t is time and $\langle\alpha_{i,d}^2\rangle = \overline{r_{i,d}^2}/\overline{r_0^2}$ is the dilatation factor ($\overline{r_{i,d}^2}$ and $\overline{r_0^2}$ respectively are mean square end-to-end distances in the isotropic and reference states). The temperature dependence of $\overline{r_0^2}$ differs from the temperature dependence of $\overline{r_{i,d}^2}$, and $\Delta\alpha$ is also temperature-dependent. Eqs $(4a)$ and $(4b)$ predict for the stress-optical function that

$$C(t) = \frac{\Delta n(\lambda, t)}{\sigma(\lambda, t)} = \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \frac{2\pi}{45kT} \Delta\alpha = C_e ; \qquad (5)$$

hence, $C(t)$ is independent of time, of the content of the crosslinks and of the reference state of the network.

By comparing Eqs $(4a)$ and $(4b)$ with (1), one obtains the following equations for the functions $E(t)$ and $B(t)$ at small deformations $(\lambda \rightarrow 1)$:

$$E(t) = 3v_{i,d}kT\langle\alpha_{i,d}^2\rangle\left(1 + \sum_{n=2}^{N} e^{-t/\tau_n}\right), \qquad (6a)$$

$$B(t) = 3v_{i,d} \frac{(\bar{n}^2 + 2)^2}{n} \frac{2\pi}{45} \Delta\alpha\langle\alpha_{i,d}^2\rangle\left(1 + \sum_{n=2}^{N} e^{-t/\tau_n}\right), \qquad (6b)$$

from which the rheooptical spectra can be calculated using Eq. (2):

$$H^{(m)} = (1/2) \, v_{i,d} \langle \alpha_{i,d}^2 \rangle^{3/2} / \pi) \, (P \xi_M^0 \overline{r_0^2} kT/6)^{1/2} \, \tau^{-1/2} , \qquad (7a)$$

$$H^{(0)} = C_e H^{(m)} , \qquad (7b)$$

where P is the degree of polymerization of the chain, and ξ_M^0 is the monomeric frictional coefficient. It follows from Eq. (7b) that the theory predicts the same time dependence for the mechanical and optical relaxation spectra. Since the proportionality constant of Eq. (7b) is the same as in Eq. (5), the spectrum $L^{(0)}$ from Eq. (3) must be zero within the whole time interval.

The change in the internal energy of the chain with temperature in the rubber-like region can be quantitatively characterized by the factor $k^{(m)} = \mathrm{d} \ln \overline{r_0^2}/\mathrm{d}T$ (which as a rule is constant for the given polymer), for which it holds, using the constant length 1 and pressure p from Eq. (4a):

$$k^{(m)} = \left[\frac{-\mathrm{d} \ln (f_e/T)}{\mathrm{d}T} \right]_{p,1} - \frac{\beta}{\lambda^3 V_{i,d}/V_\lambda - 1} ; \qquad (8)$$

here, β is the temperature volume expansion coefficient of the sample, f is the equilibrium force value. Under the same conditions and using the temperature dependence of the equilibrium birefringence value Δn_e (Eq. (4b)), we have for the factor $k^{(0)} = \mathrm{d} \ln |\Delta \alpha|/\mathrm{d}T$

$$k^{(0)} = \left[\frac{\mathrm{d} \ln |\Delta n_e|}{\mathrm{d}T} \right]_{p,1} + k^{(m)} + \frac{\beta \lambda^3}{\lambda^3 - V_\lambda/V_{i,d}} - \gamma \frac{3\bar{n}^2 + 2}{\bar{n}^2 + 2} , \qquad (9)$$

$\gamma = (1/\bar{n}) \, (\mathrm{d}\bar{n}/\mathrm{d}T)$ being the coefficient of the temperature change of the refractive index.

From Eqs (6a) and (6b), the theory predicts the following reduced variables in the time–temperature superposition of the rheooptical functions measured at a temperature T and reduced to the temperature T_0:

$$E_p(t) = E(t) \, (T_0/T) \, (\varrho_{T_0}/\varrho_T)^{1/3} \exp \left[k^{(m)}(T - T_0) \right] \quad \text{against} \quad t/a(T_0, T) , \quad (10)$$

$$B_p(t) = B(t) \, (\varrho_{T_0}/\varrho_T)^{1/3} \, (X_0/X) \exp \left[(k^{(m)} - k^{(0)}) \, (T - T_0) \right] \quad \text{against} \quad t/a(T_0, T) , \qquad (11)$$

$$C_p(t) = C(t) \, (T/T_0) \, (X_0/X) \exp \left[-k^{(0)}(T - T_0) \right] \quad \text{against} \quad t/a(T_0, T) , \qquad (12)$$

where the index p stands for the functions reduced to T_0 and $a(T_0, T)$ is the shift factor, ϱ is density, $X = [(\bar{n}^2 + 2)^2/\bar{n}]_T$ and $X_0 = [(\bar{n}^2 + 2)^2/\bar{n}]_{T_0}$.

EXPERIMENTAL

Sample Preparation

The polyurethane network was prepared from a prepolymer obtained by reacting 1 mol of OH-terminated poly(2-methyloxirane) ($M_n = 1\,200$) with 2 mol of 4,4'-methylene-bis(phenyl isocyanate) and from 2,2-bis(hydroxymethyl)-1,4-butanediol as a crosslinking agent. The reaction occurred between teflon plates in the bulk state at 70°C for 10 h; the ratio of the NCO/OH groups was 1 : 1. Purification of the starting compounds and the network preparation have been described in detail elsewhere[13]. After completion of the polymerization the network was extracted with benzene and dried to constant weight at reduced pressure. Samples $5 \times 1 \times 0.1$ cm^3 were used in the measurements.

Photoelastic Characteristics

The photoelastic characteristics were measured by using an apparatus described earlier[13]; the force was measured with a force inductive transducer connected with a bridge (Hottinger Baldwin Messtechnik, FRG) and recorded with a recorder. The birefringence Δn was determined from the optical retardation, δ, in de-Senarmont's arrangement, $\delta = -\phi/2 = 2\pi\,\Delta nd/\lambda_0$ where λ_0 is the wavelength (546·1 nm), ϕ is the extinction angle, and d is the sample tickness. ϕ was determined from the minimum of the intensity of the passing light recorded with a photomultiplier connected with a recorder. The deformation was determined by a centesimal indicator. The measurements were carried out in nitrogen in a thermostated cylinder; the temperature was maintained with an accuracy of ± 0.2°C. Two types of photoelastic measurements were performed:

a) *Dependence of force and of the extinction angle on temperature*: The sample was deformed to a constant length ($\lambda = 1.0\text{--}1.4$) at room temperature; after that its temperature was raised to 75°C. The sample was maintained at constant temperature until the force and intensity of light had reached constant values (time interval c. 1 h), after which f_e (force) and ϕ_e (extinction angle) were determined. The temperature was reduced (by c. 7°) and the whole procedure repeated up to $T = 20$°C. After that a reverse temperature cycle from 20°C to 75°C was examined. The temperature dependences of the equilibrium force values f_e (T) and of the extinction angle values $\phi_e(T)$ or the $\phi_e/(f_e/T)$ values were used in the determination of the coefficients $k^{(m)}$ and $k^{(0)}$. Eq. (9) in our arrangement gives

$$k^{(0)} = k^{(m)} + [\mathrm{d}\ln|\phi_e|/\mathrm{d}T]_{p,1} + [(\beta/2)\,(\lambda^3 + 1)/(\lambda^3 - 1)] - \gamma[(3\bar{n}^2 + 2)/(\bar{n}^2 + 2)]. \quad (13)$$

By combining Eqs (8) and (13) we also obtain

$$k^{(0)} = [\mathrm{d}\ln\{|\phi_e|/(f_e/T)\}/\mathrm{d}T]_{p,1} + \beta/2 - \gamma(3n^{-2} + 2)/(n^{-2} + 2). \quad (14)$$

Eqs (13), (14) together with Eq. (8) were used to obtain $k^{(m)}$ and $k^{(0)}$.

b) *Linear viscoelastic behaviour*: Stress and birefringence relaxation were measured within the time interval 5—600 s and at temperatures from −30° to 90°C. The constant deformations (ε) used were 0·002 in the low-temperature region and 0·02 in the rubberlike region. The Young modulus was determined from the equation $E(t) = \lambda f(t)/\varepsilon\; S_{i,d}$; the optical relaxation function

$B(t) = (\lambda_0/\pi)(\lambda^{1/2}/d_{i,d}\dot{\varepsilon})$ arc sin $(I(t)/K)^{1/2}$, where $I(t)$ is the time dependence of light intensity, $S_{i,d}$ is the initial cross-section, and K is the proportionality constant determined from $I(t')$ and the extinction angle $\phi(t)'$ at the end of the experiment[12] at a time $t' = 600$ s at each constant temperature. In calculating $E(t)$ and $B(t)$ correction was taken for the deformation of the force transducer alone and for the device used in applying the deformation; these corrections were important mainly at low temperatures in the range of high $E(t)$ values. The time dependence of the stress-optical function $C(t) = B(t)/E(t)$ was also determined using the functions $E(t)$ and $B(t)$.

Characterization of Volume Changes of the Refractive Index

The volume expansion coefficient of the sample in the rubberlike state β $(7 \cdot 8 \cdot 10^{-4}\ \mathrm{K}^{-1})$ was determined from the linear expansion $(\beta = 3\omega)$; ω was determined experimentally in the photoelastic apparatus so that at each temperature within the interval $20-80°C$ the length of the sample corresponding to zero force was determined. The measurements were carried out in the directions of increasing and decreasing temperatures. The refractive index $\bar{n} = 1·510$ at $20°C$ was determined with an Abbe refractometer. The thermal expansion coefficient of the refractive index was determined using an approximative equation[14] $(\bar{n} - 1)_{T_0} = (\bar{n} - 1)_T [1 + \beta(T - T_0)]$, which in our case gives $\gamma \approx -\beta/3$.

RESULTS AND DISCUSSION

Temperature Dependence of the Chain Dimensions and of the Optical Anisotropy of the Statistical Segment

Fig. 1, in which the temperature dependence of viscoelastic rheooptical functions measured at a constant time $t' = 600$ s has been plotted, shows that in the rubberlike region at $T > 80°C$ there is a decrease in the modulus or in the optical relaxa-
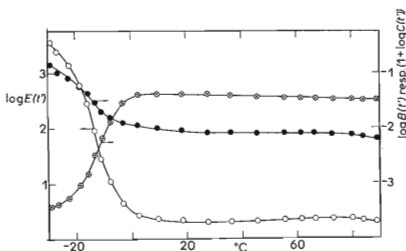

FIG. 1

Dependence of the Modulus $E(t')$ (MPa), Optical Relaxation Function $B(t')$ and Stress-Optical Function $C(t')$ (MPa^{-1}) Measured at $t' = 600$ s on Temperature

○ $E(t')$ values, ● $B(t')$ values, ⊗ $10 \times C(t')$ values.

tion function; the temperature dependence of the chain dimensions and of the optical anisotropy was therefore determined within the interval $20°C < T < 80°C$.

A typical example of the temperature dependence of equilibrium photoelastic characteristics at a constant length corresponding to $\lambda = 1 \cdot 3$ at $T = 50°C$ is given in Fig. 2. The dependences of $\ln f_e/T$ and $\ln \varphi_e$ on T in the region of higher $\lambda(\lambda \geqq 1 \cdot 2)$ were practically linear; in the region of smaller elongations ($1 \cdot 05$ and $1 \cdot 1$) these dependences were curved, as a consequence of a change in the initial length $l_{i,d}$, and thus also in λ with temperature. These dependences were used in the determination of slopes at various λ (corresponding to $50°C$):

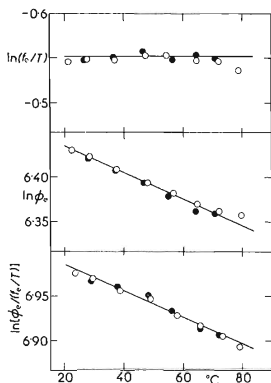| λ:	1·05	1·1	1·2	1·3	1·4
$\mathrm{d}\ln(f_e/T)/\mathrm{d}T$, 10^{-4} K^{-1}:	49·2	19·7	8·9	0	1·3
$\mathrm{d}\ln \Phi_e/\mathrm{d}T$, 10^{-4} K^{-1}:	61·7	31·0	18·7	13·5	12·0
$\mathrm{d}\ln[\Phi_e/(f_e/T)]/\mathrm{d}T$, 10^{-4} K^{-1}:	12·7	11·8	10·3	13·5	11·1

Fig. 2

Example of the Dependences of (f_e/T), Extinction Angle ϕ_e and $[\phi_e/(f_e/T)]$ on Temperature

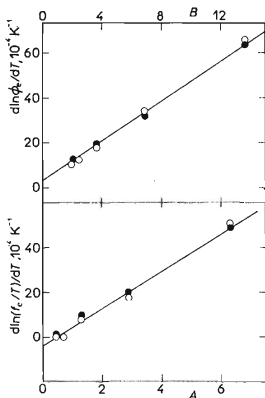$\lambda \approx 1 \cdot 3$, ○ decrease in temperature, ● increase in temperature.

Fig. 3

Dependence of the Temperature Characteristics of Force or of the Extinction Angle on the Deformation Functions A and B

$A = 1/(\lambda^3 - 1)$, $B = (\lambda^3 + 1)/(\lambda^3 - 1)$ (Eqs (8) and (13)); ○ Values read off at decreasing temperature, ● values read off at increasing temperature.

Their dependence on the deformation functions defined by Eqs (8) and (13) is given in Fig. 3. The slopes of linear dependences correspond to the experimentally determined β and $\beta/2$; from the intercept on the y-axis and Eqs (8), and (13) we determined $k^{(m)} = -0.3 \cdot 10^{-3}\ \mathrm{K}^{-1}$ and $k^{(0)} = -0.5 \cdot 10^{-3}\ \mathrm{K}^{-1}$ which already is independent of deformation. The same $k^{(0)}$ can also be obtained from Eq. (14). From $k^{(m)}$ one may estimate the mean value of that part of force which corresponds to the contribution of internal energy, f_u, to the total force, f_e, within the temperature range under investigation, using $f_u/f_e = Tk^{(m)} = -0.1$. f_u determined by us is similar to the f_u values determined for similar polyurethane networks[15].

Time–Temperature Superposition

The time dependences of rheooptical functions in the rubberlike region are given in detail in Figs 4 and 5 after vertical corrections given by Eqs (10) and (11). The reference temperature $T_0 = -3°C$ and the already determined values of the factors $k^{(m)}$ and $k^{(0)}$ were used in the correction. In applying the superposition method to experimental data (Figs 6, 7), one must use a vertical correction given by Eqs (10) through (12), particularly in the treatment of data in the rubberlike region. At the
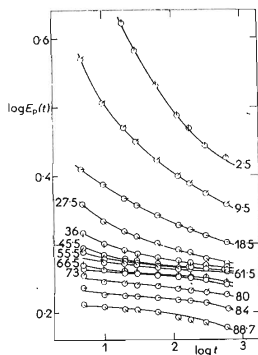

FIG. 4

Dependence of the Reduced Modulus $E_p(t)$ (MPa) in the Rubberlike Region on Time t(s) for $T_0 = -3°C$
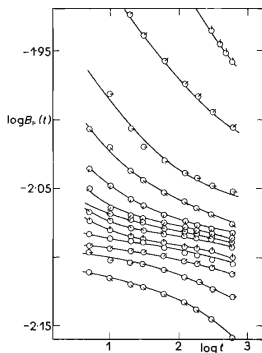
Numbers at curves denote the measurement temperatures in °C.

F·G. 5

Dependence of the Reduced Optical Relaxation Function $B_p(t)$ in the Rubberlike Region on Time t(s) for $T_0 = -3°C$

Temperatures denoted as in Fig. 4.

same time that part of the vertical shift in the reduction of the modulus which is determined by the temperature dependence of the chain dimensions amounts to c. 10% of its total value (vertical shift for $T = 88.7°C$ reduces the total value of $E(t)$ by c. 26%). The temperature dependence of optical anisotropy participates by c. 60% of the total value of the vertical shift of the optical relaxation function $B(t)$ (vertical shift raises the value of the function $B(t)$ at $T = 88.7°C$ by c. 5%). Similarly to the modulus, the factor T/T_0 plays also a decisive role in the vertical correction of the stress-optical function $C(t)$; the temperature dependence of anisotropy represents c. 15% of the total correction which raises $C(t)$ for $T = 88.7°C$ by c. 40%.

The dependence of the shift factor $\log a(T_0, T)$ on temperature is shown in Fig. 8. One can see that the values of the mechanical shift factor (obtained from the shift of the modulus $E_p(t)$) and of the optical shift factor (obtained from $B_p(t)$) are the same within the limits of experimental error. Also the shift factor obtained by the treatment of the stress-optical function $C_p(t)$ has the same values as the preceding two shift factors in the region in which it could be comparatively well determined $(T \leqq 45°C)$. The dependence of the shift factors on temperature within the interval $-30 < T < 75°C$ can be described by the Williams–Landel–Ferry equation with the variable parameter T_s (cf.[1]) assuming that $T_s = 30°C$; in the temperature region $T > 75°C$ the shift factor increases again, and the dependence does not obey the WLF equation any more.

It can be said, therefore, that particularly for the treatment of data in the rubberlike region $(T > 10°C)$ vertical corrections are necessary, and they influence in an im-
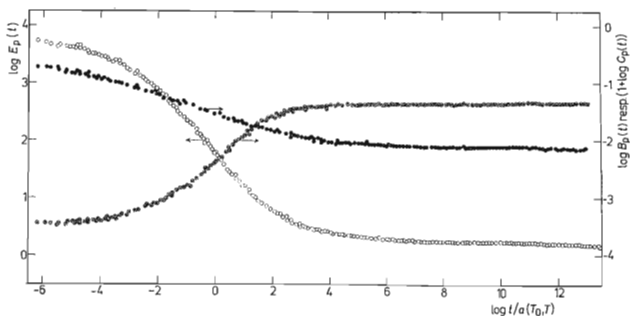

FIG. 6

Superimposed Dependences of the Reduced Modulus $E_p(t)$ (MPa), Reduced Optical Relaxation Function $B_p(t)$ and Reduced Stress-optical Function $10 \times C_p(t)$ (MPa^{-1}) on Time $t/a(T_0, T)$ (s) for $T_0 = -3°C$.

portant manner the shift factors (Figs 4, 5). The inclusion of the temperature change in the chain dimensions and of the temperature dependence of optical anisotropy of the statistical segment in the vertical shift when using the time–temperature superposition leads to a smaller scattering of the superimposed curves.

Viscoelastic Characteristics and the Mechanical and Optical Spectra

The course of the superimposed curve of the Young modulus $E_p(t)$ (Fig. 6) is typical of an amorphous polymer. The limiting value of the modulus in the glassy state (at short times) is usually assigned to distorsional effects, such as a change in the valence angles, or to motions of short parts of the chain. The birefringence originating in this mechanism, called "distorsional birefringence", is positive and leads to positive values of the optical relaxation functions $B_p(t)$ and of the stress-optical function $C_p(t)$. With increasing time there is an onset of motion of longer chain
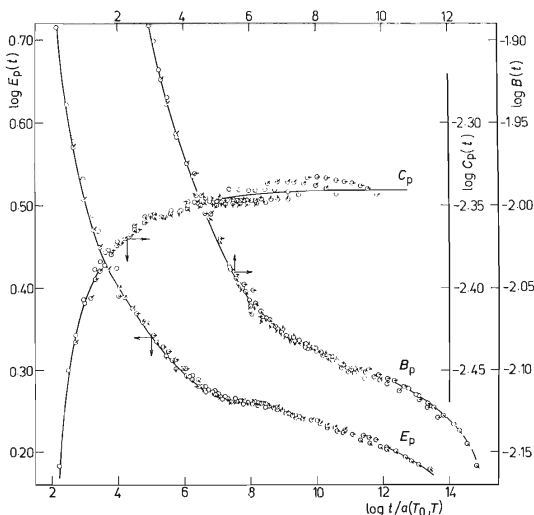

Fig. 7

Dependence (in detail) of Superimposed Curves of the Functions $E_p(t)$ (MPa), $B_p(t)$ and $C_p(t)$ (MPa^{-1}) in the Rubberlike Region on Time $t/a(T_0, T)$ (s) for $T_0 = -3°C$

Points denoted in accordance with temperatures in Fig. 4.

sections, which leads to a pronounced decrease in the modulus in the transition region and also to a decrease in the total birefringence value. The theory predicts a stress-optical function independent of time $\left(\text{Eq. } (5)\right)$, which can actually be observed in Fig. 6 within the time range $t/a(T_0, T) > 10^3$ s. A detailed investigation of the dependence of the modulus $E_p(t)$ on time in the rubberlike region $\left(\text{Fig. } 7\right)$ leads to a conclusion that after the main transition there is only a short time range within which the modulus is constant; after that, another secondary decrease in the modulus with time sets in $\left(\text{for } T > 70^{\circ}C\right)$. The course of the optical relaxation function in this range is similar to that of the modulus $\left(\text{Fig. } 7\right)$; since the velocity at which both functions, $E_p(t)$ and $B_p(t)$, decrease is approximately the same, the stress-optical function $C_p(t)$ is practically independent of time in this region. This indicates the orientational origin of molecular mechanisms, responsible for the secondary decrease in the two functions, $E_p(t)$ and $B_p(t)$. One of possible explanations of the time dependence of $E_p(t)$ and $B_p(t)$ situated deep in the rubberlike region for $t/a(T_0, T) > 10^9$ s can be seen in the sliding of hydrogen bonds between urethane groups under stress[14,16].

The viscoelastic spectra were calculated by the second-approximation method of Schwarzl and Staverman[17] and are given in Fig. 9. At short times the mechanical relaxation spectrum $H^{(m)}$ passes through a maximum; in the time interval $\tau = 10^2 - 10^4$ s it has the theoretically predicted slope $-1/2$ $\left(cf. \text{ Eq. } (7a)\right)$. The slope $-1/2$ can still be observed for the time interval $\tau = 10^6 - 10^8$ s. These two regions are displaced from each other by c. 1·5 decades and their behaviour resembles
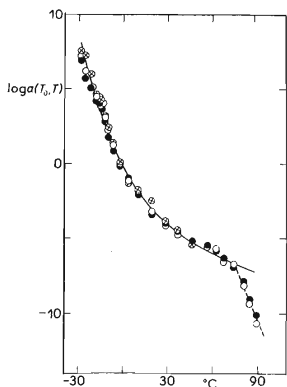
F$_{\text{IG}}$. 8

Dependence of the Shift Factor $\log a(T_0, T)$ on Temperature

○Values obtained by shifting $E_p(t)$, ● values obtained by shifting $B_p(t)$, ⊗ values obtained by shifting $C_p(t)$, ——— Williams–Landel–Ferry equation with the parameter $T_s = 30^{\circ}C$.

that of an amorphous system with entanglements[18]. On the other hand, however, within the whole main transition there is no region long enough to allow the optical spectrum $H^{(0)}$ to possess the slope $-1/2$ as predicted by Eq. (7b), not even in the part in which $C_p(t)$ is practically independent of time. In the range of long times the spectrum $H^{(0)}$ increases, similarly to $H^{(m)}$. The retardation optical spectrum $L^{(0)}$ passes through a maximum approximately in that interval of shorter times in which the slope of the log $H^{(m)}$–log τ dependence is $-1/2$. In the range of longer times, where the slope of log $H^{(m)}$–log τ dependence is still $-1/2$, the spectrum $L^{(0)}$ rapidly decreases. For longer times log $\tau > 8$, $L^{(0)}$ is practically negligible, in accordance with (5). This fact also suggests an orientation origin of the molecular motions responsible for the increase in the spectra $H^{(m)}$ and $H^{(0)}$ in this range of the retardation times.

Using the stress-optical coefficient $C = 0.33 . 10^{-2}$ MPa^{-1} determined at 60°C, one can calculate from Eq. (5) the magnitude of the optical anisotropy of the statistical segment $\Delta\alpha = 8.95 . 10^{-24}$ cm^{-3}. This value is approximately four times higher than for poly(2-methyloxirane) crosslinked with α,α'-dicumyl peroxide and sulphur[19,20] ($M_w = 1.8 . 10^6$), where $\Delta\alpha = 1.99 . 10^{-24}$ cm^{-3}, and for a solution of poly(2-methyloxirane) ($M_w = 0.9 . 10^6$) in cyclohexanone[20], where $\Delta\alpha = 2.5 . 10^{-24}$ cm^{-3}. This could be due to the contribution by urethane groups and/or to strong intermolecular interactions between them[13].
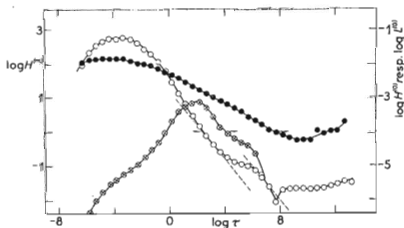

FIG. 9

Dependence of the Mechanical Relaxation Spectrum $H^{(m)}$ (MPa), Optical Relaxation Spectrum $H^{(0)}$ and Optical Retardation Spectrum $L^{(0)}$ (MPa^{-1}) on Time τ(s) for $T_0 = -3°C$

○ $H^{(m)}$ values, ● $H^{(0)}$ values, ⊗ $L^{(0)}$ values, ----- slope $-1/2$.

REFERENCES

1. Ferry J. D.: *Viscoelastic Properties of Polymers,* 2nd Ed., p. 292. Interscience, New York 1970.
2. Read B. E.: J. Polym. Sci., Part C5, 87 (1963).
3. Read B. E.: Polymer 5, 1 (1964).
4. Theocaris P. S.: Rheologica Acta 2, 92 (1962).
5. Theocaris P. S.: Trans. Soc. Rheol. 18, 607 (1974).
6. Fukui Y., Ushirokawa M., Asada T., Onigi S.: J. Polym. Sci., Part A-2, 8, 1195 (1970).
7. Onogi S., Sato T., Asada T., Fukui Y.: J. Polym. Sci., Part A-2, 8, 1211 (1970).
8. Takeuchi A., Stein R. S.: J. Polym. Sci., Part A-2, 5, 1079 (1967).
9. Ilavský M., Hasa J., Havlíček I.: J. Polym. Sci., Part A-2, 10, 1775 (1972).
10. Ilavský M.: This Journal 38, 1771 (1973).
11. Ilavský M., Hasa J.: J. Polym. Sci., Polym. Phys. Ed. 11, 539 (1973).
12. Ilavský M., Prins W.: Macromolecules 3, 415, 425 (1970).
13. Nesterov A. E., Lipatova T. E., Dušek K., Pelzbauer Z., Houska M., Hradil J., Lipatov Yu. S.: Angew. Makromol. Chem 52, 39 (1976).
14. Gent A. N.: Macromolecules 2, 262 (1969).
15. Tanaka T., Yokoyama T.: J. Polym. Sci., Part C 23, 865 (1968).
16. Tanaka T., Yokoyama T., Yamaguchi Y.: J. Polym. Sci., Part A-1, 6, 2153 (1968).
17. Schwarzl F., Staverman A. J.: Physica (Utrecht) 18, 791 (1952).
18. Chömpff A. J., Prins W.: J. Chem. Phys. 48, 235 (1968).
19. Ishikawa T.: Polymer 5, 227 (1973).
20. Cvetkov V. N., Garmonova T. I., Stankevitch R. P.: Vysokomol. Soedin. 8, 980 (1966).