A new kinetic description of the rheo-optical behaviour of polymer melts: 1. The predictions of the kinetic orientation model

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A new kinetic orientation model for the description of the rheo-optical behaviour of polymer melts is presented. According to this model, constraints to deformation are introduced by specific changes in Gibbs free energy. The applicability of the model is demonstrated by using it to calculate the transient birefringence in model fluids occurring upon simple elongation with constant stretch rate and constant derivative of the Hencky strain. For both deformation histories, small and large strain rates are considered.

(Keywords: orientation model; flow birefringence; stress-optical coefficient; simple elongation; polymer melts)

INTRODUCTION

It is often claimed that the streaming birefringence of polymer melts is directly proportional to the appropriate stress difference, if the stresses are below 1 MPa[1,2].

The constancy of the stress-optical coefficient, under equilibrium conditions, for small extensions of crosslinked rubbers (Gaussian networks) is derived from the statistical segment model[3,4] according to which the tensile stress during simple elongation is given by:

$$\sigma = NkT(\lambda^2 - \lambda^{-1}) \tag{1}$$

and the simultaneously occurring birefringence by:

$$\Delta n = (2\pi/45)[(n_0^2+2)^2/n_0]N(\alpha_{S1}-\alpha_{S2})(\lambda^2-\lambda^{-1}) \tag{2}$$

where N is the number of chains between crosslinks per unit volume, k the Boltzmann constant, T the absolute temperature, λ the extension ratio, n_0 the refractive index of the undeformed material, and $(\alpha_{S1}-\alpha_{S2})$ the polarizability anisotropy of one segment. Combining equations (1) and (2) gives the stress-optical coefficient $C = \Delta n/\sigma$ as a material-specific constant:

$$C = (2\pi/45kT)[(n_0^2+2)^2/n_0](\alpha_{S1}-\alpha_{S2}) \tag{3}$$

Almost all subsequent treatments of birefringence in viscoelastic fluids[5–7] culminate in a rederivation of the above expression for C. The essential idea here is to incorporate a mechanism that accounts for relaxation. However, some of the assumptions introduced previously have been retained, i.e. it is supposed that:

(i) the internal energy is not affected by deformation;
(ii) the orientating units are optically uniaxial; and
(iii) the material possesses a temporary network structure.

There is experimental[8] and theoretical[9,10] evidence that a polymer melt may not have a constant stress-optical coefficient. Within the conceptual framework of a simple fluid with fading memory, it has been shown[9] that a simple linear relationship between the deviators of the stress and the refractive-index tensor can only be expected to hold for very slow motion, i.e. in the 'Newtonian' flow region.

This paper presents a microscopic model that describes the kinetics of orientation in polymer melts in which constraints on deformation are introduced by differences in Gibbs free energy. It should be emphasized that this model does not contain any of the assumptions mentioned above, and it is also not assumed that the deformation obeys an affine mechanism. To demonstrate the applicability of the model, it will be used to describe the transient birefringence $\Delta n(t)$ that occurs in model fluids upon simple elongation at constant stretch rate $\dot{\lambda}_0 = \mathrm{d}\lambda/\mathrm{d}t = \text{constant}$ and at constant derivative of the Hencky strain $\dot{\varepsilon}_0 = \mathrm{d}(\ln\lambda)/\mathrm{d}t = \text{constant}$; for both deformation histories, small and large strain rates will be considered. In a further paper the predictions of the model will be evaluated experimentally.

THE KINETIC ORIENTATION MODEL FOR POLYMER MELTS

In the following, deformations taking place under isochoric and isothermal conditions and at constant strain rates will be considered. A polymer melt is taken to be a tangle of three-dimensional macromolecules, each of which has a well defined configuration that is determined by chemical bond lengths and valence angles, and a certain flexibility arising from restricted rotation about the single bonds. It is assumed that the melt consists of a mixture of linear macromolecules that differ only in

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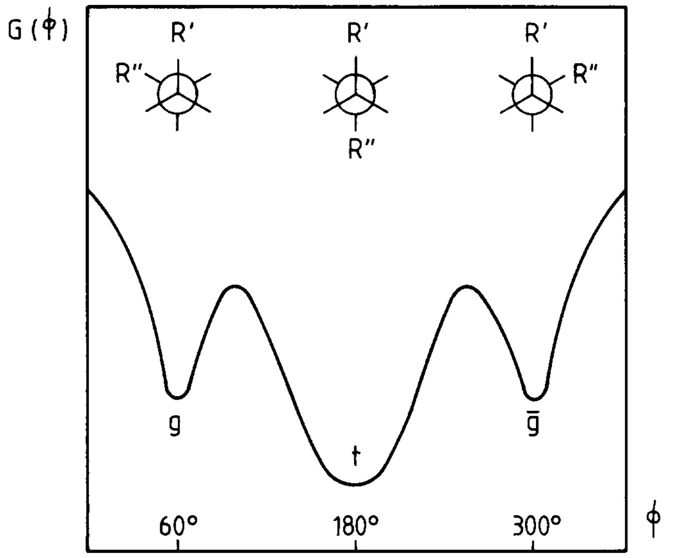

Figure 1 The change in Gibbs free energy during rotation about the central bond of R'–H_2C–CH_2–R''; *g*, *t* and *ḡ* designate the stable conformations, *gauche* ($\phi = +60°$), *trans* ($\phi = 180°$) and *gauche* ($\phi = -60°$)

chain length. If one such molecule contains *n* chain atoms, then there are $(n-1)$ bonds along the chain and $(n-3)$ bonds with the potential of generating different conformations (rotations about the two terminal bonds do not produce additional conformers). The change in Gibbs free energy $G(\phi)$ during rotation about a C–C bond is usually described by a three-well curve as shown in *Figure 1*. If only potentials of this type hold, then there are $3^{(n-3)}$ conformers for an n-alkane.

It should be emphasized that *Figure 1* is based on the assumption that the R' and R'' groups both possess an all-*trans* conformation that can be represented as *tttttttt*.... If this is not the case, i.e. if there are twists (e.g. R' = *ttgttttt*... and R'' = *ḡttttt*...), then an asymmetrical potential, as shown in *Figure 2*, is valid. As illustrated here, the two *gauche* states are no longer energetically equivalent, i.e. $G(+60°) \neq G(-60°)$. In the following treatment it will be assumed that those conformational changes that contribute substantially to the orientational behaviour of the melt take place at bonds having an asymmetric rotational potential (i.e. one conformer has a much higher energy than the other two).

A consideration of *Figure 2* leads to the conclusion that, in this model, to first approximation, only the two states corresponding to $G_i(180°)$ and $G_i(-60°)$ are populated, whereas $G_i(+60°)$ is a quasi-empty state. It is further assumed that there are *N* conformational equilibria in the melt. As they concern different bonds, they will be treated as mutually independent subsystems. Under isothermal conditions the densities of the two populated states, i_d and i_o, which participate in the *i*th equilibrium, are thus:

$$p_i = p_{id} + p_{io} = \text{constant} \qquad i = 1, \ldots, N \tag{4}$$

where the states i_d and i_o are each characterized by an appropriate rotational angle. The population density distribution in the *i*th subsystem:

$$p_{id} \rightleftarrows p_{io} \tag{5}$$

is determined by the difference in the free energies of these two states:

$$G_{io} - G_{id} = -RT\ln(p_{io}/p_{id}) \tag{6}$$

Between the states i_d and i_o there is a transition state i^*, which is characterized by a free-energy maximum:

$$G_{i^*} = H_{i^*} - TS_{i^*} = G_{i,\max} \tag{7}$$

The rate constant for the process $i_d \rightarrow i_o$, which is given by transition-state theory[11–13], is:

$$k_i = (kT/h)\exp[(S_{i^*} - S_{id})/R - (H_{i^*} - H_{id})/RT] \tag{8a}$$

and for the reverse process:

$$\bar{k}_i = (kT/h)\exp[(S_{i^*} - S_{io})/R - (H_{i^*} - H_{io})/RT] \tag{8b}$$

where *k*, *h* and *R* are the Boltzmann, Planck and gas constants, respectively, *T* is the absolute temperature, *S* the entropy and *H* the enthalpy of the state designated. At equilibrium:

$$k_i p^0_{id} = \bar{k}_i p^0_{io} \tag{9}$$

where p^0_{id} and p^0_{io} are the population densities in the undisturbed melt, and as:

$$p^0_{id} = p_i - p^0_{io}$$

we can write:

$$p^0_{io} = p_i / [1 + (\bar{k}_i / k_i)] \tag{10}$$

If a fully relaxed, isotropic melt is subjected to a simple isochoric elongation, for which the principal components of the strain-rate tensor are:

$$\dot{\varepsilon}_{\mathrm{I}}(t) = \dot{\varepsilon}_0 h(t) \qquad \dot{\varepsilon}_{\mathrm{II}}(t) = \dot{\varepsilon}_{\mathrm{III}}(t) = -0.5\dot{\varepsilon}_{\mathrm{I}}(t) \tag{11}$$

where $\dot{\varepsilon}_0$ is a constant and $h(t)$ is the unit step function:

$$h(t) = \begin{cases} 0 & \text{for } t < 0 \\ 1 & \text{for } t > 0 \end{cases} \tag{12}$$

then it is assumed that the free energy of the conformational pair i_d and i_o varies as shown in *Figure 3*. It should be noted that, in this figure, the angle of rotation is considered as a reaction coordinate.

In this model a simple elongation, starting at $t = 0$, will cause the following changes in the free energy in the *i*th

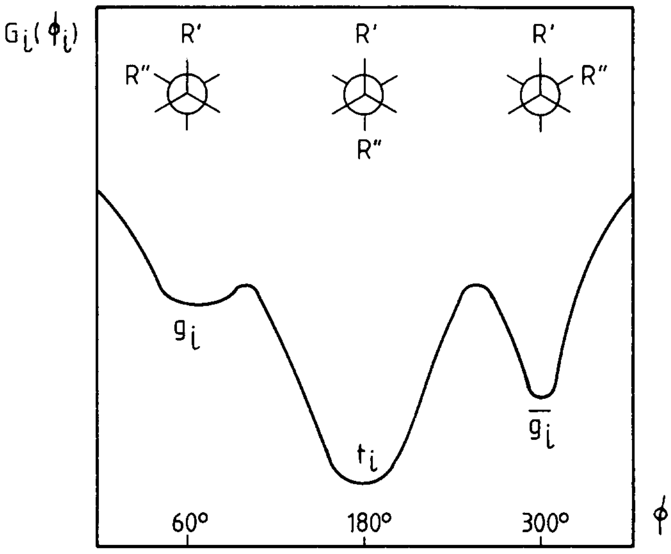

Figure 2 The change in Gibbs free energy during roation about the *i*th bond of a macromolecule

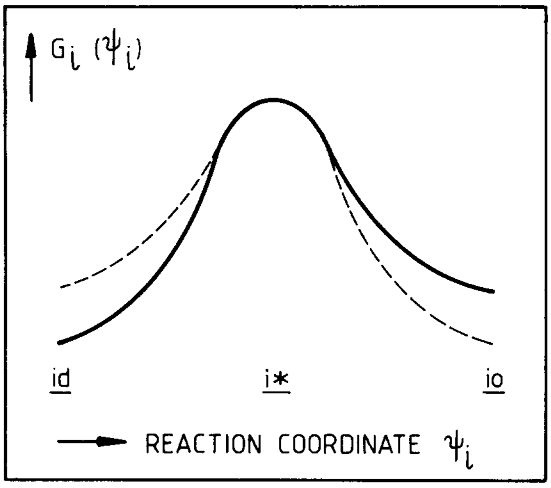

Figure 3 The conformational change in Gibbs free energy along the ith reaction coordinate, ψ_i; i_d and i_o are populated conformations, and i^* is the transition state between them; (———) undisturbed, isotropic melt; (----) anisotropic fluid after the application of a strain rate, $\dot{\varepsilon}_0$ = constant

subsystem:

$$G_{io}(t>0)-G_{io}(t<0)=\Delta_t G_{io}(\dot{\varepsilon}_1)<0 \qquad (13)$$

$$G_{id}(t>0)-G_{id}(t<0)=\Delta_t G_{id}(\dot{\varepsilon}_1)>0 \qquad (14)$$

Furthermore it is assumed that:

$$\Delta_t G_{id}(\dot{\varepsilon}_1)=-\Delta_t G_{io}(\dot{\varepsilon}_1) \qquad (15)$$

and that the transition state i^* does not alter its energy level during deformation:

$$\Delta_t G_{i^*}(\dot{\varepsilon}_1)=0 \qquad (16)$$

where $\Delta_t G$ is the transient change of free energy due to deformation. Since the state i_o is favoured by deformation, it will be termed the oriented conformer, and the state i_d the disoriented conformer, of the ith subsystem.

It should be mentioned that Eyring[14,15] has used a similar procedure for deriving an expression for non-Newtonian steady-state shear viscosity[16]. However, in contradistinction to the model presented here, Eyring's concept was based on the idea that stress causes an alteration of molecular translational jumping processes.

THE STREAMING BIREFRINGENCE IN THE LINEAR VISCOELASTIC RANGE OF DEFORMATION

The change of the population density distribution in the ith subsystem due to an elongational flow field

In the range of deformation in which strains and strain rates are very small — usually called the linear viscoelastic range — $\Delta_t G_{io}(\dot{\varepsilon}_1)$ can be taken to be a linear function of $\dot{\varepsilon}_1=\dot{\varepsilon}_0 h(t)$:

$$\Delta_t G_{io}(\dot{\varepsilon}_0)=-a_i\dot{\varepsilon}_0 \qquad (17)$$

a_i is a positive constant of proportionality with the dimension of action (= energy × time). As the deformation proceeds, the rate constants (equations (8a) and (8b)) become:

$$c_i=k_i\exp(+a_i\dot{\varepsilon}_0/RT) \qquad (18a)$$

$$\bar{c}_i=\bar{k}_i\exp(-a_i\dot{\varepsilon}_0/RT) \qquad (18b)$$

and the population density distribution in the ith subsystem moves towards a new stationary state:

$$\mathrm{d}p_{io}/\mathrm{d}t=c_i p_{id}-\bar{c}_i p_{io} \qquad (19a)$$

where

$$\mathrm{d}p_{io}/\mathrm{d}t=-\mathrm{d}p_{id}/\mathrm{d}t \qquad (19b)$$

Here $\mathrm{d}p_{io}/\mathrm{d}t$ is the growth rate in the population density of state i_o, and $\mathrm{d}p_{id}/\mathrm{d}t$ is the rate of decrease in the population density of state i_d. With the initial value $p_{io}(t=0)=p^0_{io}$, integration of equation (19a) gives:

$$[p_{io}(c_i+\bar{c}_i)-p_i c_i]/[p^0_{io}(c_i+\bar{c}_i)-p_i c_i]=\exp[-(c_i+\bar{c}_i)t] \qquad (20)$$

After rearrangement and the introduction of the expression for p^0_{io} (equation (10)), the time dependence of the increase of the population density of state i_o (the molar number of $i_d \rightarrow i_o$ net transitions per unit volume) can be obtained:

$$\begin{aligned}\Delta p_{io}(t)&=p_{io}(t)-p^0_{io}\\&=p_i[(1+\bar{c}_i/c_i)^{-1}-(1+\bar{k}_i/k_i)^{-1}]\{1-\exp[-(c_i+\bar{c}_i)t]\}\end{aligned} \qquad (21)$$

If the applied $\dot{\varepsilon}_0$ is sufficiently small, i.e. if

$$a_i\dot{\varepsilon}_0/RT \ll 1 \qquad (22)$$

then to a first approximation:

$$(1+\bar{c}_i/c_i)^{-1}-(1+\bar{k}_i/k_i)^{-1}=2a_i\dot{\varepsilon}_0/RT[2+(k_i/\bar{k}_i)+(\bar{k}_i/k_i)] \qquad (23a)$$

Using the relationship $k_i/\bar{k}_i=\exp[-(G_{io}-G_{id})/RT]$, equation (23a) can be simplified to:

$$(1+\bar{c}_i/c_i)^{-1}-(1+\bar{k}_i/k_i)^{-1}=a_i\dot{\varepsilon}_0/RT[1+\cosh(G_{io}-G_{id})/RT] \qquad (23b)$$

The sum $(c_i+\bar{c}_i)$ can be written as:

$$c_i+\bar{c}_i=k_i+\bar{k}_i+(a_i\dot{\varepsilon}_0/RT)(k_i-\bar{k}_i) \qquad (24a)$$

Thus, if k_i is approximately equal to $\bar{k}_i$, then:

$$c_i+\bar{c}_i\approx k_i+\bar{k}_i \qquad (24b)$$

The substitution of equations (23b) and (24b) into equation (21) gives the following expression for $\Delta p_{io}(t)$:

$$\Delta p_{io}(t)=\frac{p_i a_i\dot{\varepsilon}_0/RT}{1+\cosh(\Delta G_i/RT)}\{1-\exp[-(k_i+\bar{k}_i)t]\} \qquad (25)$$

Here ΔG_i designates the usual, time-independent difference in Gibbs free energy, $G_{io}-G_{id}$. It should be noted that equation (25) describes a state of thermodynamic non-equilibrium, which decays as soon as the strain rate is switched off. If the end of deformation is at $t'=0$, then the depopulation of the state i_o is given by:

$$p_{io}(t')=\Delta p_{io}(t'=0)\exp[-(k_i+\bar{k}_i)t']+p^0_{io} \qquad (26)$$

This shows that at $t'=1/(k_i+\bar{k}_i)$ the departure from equilibrium will have become 1/e times its initial value. Evidently the constant $(k_i+\bar{k}_i)$ is the reciprocal value of a relaxation time for the ith subsystem:

$$k_i+\bar{k}_i=1/\tau^*_i \qquad (27)$$

An analogous result has been derived previously for dielectric relaxation processes[17]. Substituting equations

Table 1 The five arbitrary fluids

Fluid	(a)	(b)	(c)	(d)	(e)
τ_m (s)	0.01	0.1	1	10	100
g_m (N m^{-2})	81 500	45 100	31 300	10 000	757
$g_m\tau_m/\sum g_m\tau_m$	0.004	0.021	0.147	0.471	0.357

(8a) and (8b) into equation (27) gives:

$$\tau_i^* = (h/kT)\exp[(G_{i*} - G_{io})/RT][1+\exp(-\Delta G_i/RT)]^{-1} \tag{28}$$

If $\Delta G_i/RT \gg 1$, equation (28) can be approximated by:

$$\tau_i^* \approx (h/kT)\exp[(G_{i*} - G_{io})/RT] \tag{29}$$

which is the usual expression for τ for an activated process in which $G_{i*} - G_{io}$ is the activation energy[18].

The stress-optical coefficient of a linear viscoelastic fluid

In deriving an expression for the transient birefringence $\Delta n(t) = n_\mathrm{I}(t) - n_\mathrm{II}(t)$ that occurs upon simple elongation of the type specified by equation (11), the polarizability of the states i_d and i_o has to be considered. Without making any assumptions about the optical properties of the material, the mean contribution of an i_d and an i_o conformer to the polarizability in the principal direction I (i.e. the direction of the applied stretch) will be designated as:

$$\alpha_{id\mathrm{I}} \quad \text{and} \quad \alpha_{io\mathrm{I}} \tag{30}$$

respectively. If $\Delta\alpha_{i\mathrm{I}}$ is the change in molar polarizability in the direction I:

$$\Delta\alpha_{i\mathrm{I}} = N_\mathrm{A}(\alpha_{io\mathrm{I}} - \alpha_{id\mathrm{I}}) \tag{31}$$

then the complete change of volume polarizability by time t is given by:

$$\beta_\mathrm{I}(t) - \beta_\mathrm{I}(t=0) = \sum_{i=1}^{N} \Delta p_{io}(t)\Delta\alpha_{i\mathrm{I}} \tag{32}$$

Here $\Delta p_{io}(t)$ is the molar number of $i_d \to i_o$ transitions and summation is over N subsystems. Transforming polarizability into refraction by means of the Lorentz–Lorenz formula[19] yields:

$$n_\mathrm{I}(t) - n_\mathrm{I}(t=0) = (2\pi/9n_0)(n_0^2+2)^2[\beta_\mathrm{I}(t) - \beta_\mathrm{I}(t=0)] \tag{33}$$

Substituting equations (25), (27) and (32) into equation (33), and including the initial condition $n_\mathrm{I}(t=0) = n_0$ (which holds for any direction):

$$n_\mathrm{I}(t) = n_0 + 2\dot{\varepsilon}_0[\pi(n_0^2+2)^2/9RTn_0] \sum_{i=1}^{N} p_i a_i \Delta\alpha_{i\mathrm{I}} \times [1+\cosh(\Delta G_i/RT)]^{-1}[1-\exp(-t/\tau_i^*)] \tag{34}$$

The difference $n_\mathrm{I}(t) - n_0$, is the first component of the refractive-index deviator transformed to principal directions. For a simple, isochoric elongation of an originally isotropic fluid, the two remaining components are given by:

$$n_{\mathrm{DII}}(t) = n_{\mathrm{DIII}}(t) = -\tfrac{1}{2}n_{\mathrm{DI}}(t) \tag{35}$$

The transient birefringence $\Delta n(t)$ induced by the strain-rate history (equation (11)) is thus:

$$\begin{aligned}\Delta n(t) &= n_{\mathrm{DI}}(t) - n_{\mathrm{DII}}(t) = n_{\mathrm{DI}}(t) - n_{\mathrm{DIII}}(t)\\ &= 3\dot{\varepsilon}_0[\pi(n_0^2+2)^2/9RTn_0] \sum_{i=1}^{N} p_i a_i \Delta\alpha_{i\mathrm{I}}\\ &\quad \times [1+\cosh(\Delta G_i/RT)]^{-1}[1-\exp(-t/\tau_i^*)]\end{aligned} \tag{36}$$

For the same strain-rate history, the corresponding tensile stress is given by the theory of linear viscoelasticity[16,20] as:

$$\sigma(t) = 3\dot{\varepsilon}_0 \sum_{m=1}^{M} g_m\tau_m[1-\exp(-t/\tau_m)] \tag{37}$$

Here g_m is the intensity and τ_m is the time constant of the mth relaxation process and summation is over M such processes.

A comparison of equations (36) and (37) shows that $\Delta n(t)$ and $\sigma(t)$ are of exactly the same form. From equations (36) and (37) the stress-optical coefficient $\Delta n(t)/\sigma(t)$ is:

$$C(t) = c\sum f_i[1-\exp(-t/\tau_i^*)]/\sum g_m\tau_m[1-\exp(-t/\tau_m)] \tag{38}$$

Here $p_i a_i \Delta\alpha_{i\mathrm{I}}/(1+\cosh(\Delta G_i/RT)]$ has been abbreviated as f_i and $\pi(n_0^2+2)^2/9RTn_0$ as c. For the sake of generality the conditions $\tau_i^* \neq \tau_m$ and $f_i \neq g_m$ have been set. Thus, C is only a constant in two limiting cases and is otherwise a function of time. In the first limiting case, as $t \to \infty$, the steady-state value is given by:

$$\lim_{t\to\infty} C(t) = c\sum f_i/\sum g_m\tau_m = C_{\mathrm{ss}} \tag{39}$$

Analogously, when t is much smaller than the shortest relaxation time, i.e. as $t \to 0$, the short-time limit is:

$$\lim_{t\to 0} C(t) = c\sum (f_i/\tau_i^*)/\sum g_m = C_{\mathrm{in}} \tag{40}$$

In order to illustrate the behaviour of the model, $C(t)$ has been evaluated for five arbitrary fluids (a)–(e), all having the same mechanical relaxation-time spectrum (*Table 1*). The relative weights of these processes are also shown in *Table 1*. For convenience, the optical relaxation times τ_i^* have been set to be identical with the mechanical ones: $\tau_i^* = \tau_m = 10^{-3+m}$, $m = 1, 2, 3, 4, 5$. The constant c has been set to $c = 0.001$ mol J^{-1}. The f_i factors of the five fluids (a)–(e) are shown in *Table 2*. It should be noted that $\sum f_i = 1$ for each of these fluids and that the f_i factors thus reflect the relative weight of the corresponding optical process.

Figure 4 shows the time dependence of $C(t)$ for each of the fluids. $C(t)$ will obviously decrease with time when the optical weighting factors of the fast processes are greater than the corresponding stress weighting factors

Table 2 The f_i factors of the five fluids

f_i (J s mol^{-1})	Fluid (a)	(b)	(c)	(d)	(e)
f_1	0.01	0.005	0.004	0.002	0
f_2	0.02	0.01	0.02	0.02	0
f_3	0.3	0.3	0.158	0.158	0.14
f_4	0.47	0.47	0.5	0.5	0.5
f_5	0.2	0.215	0.318	0.32	0.36

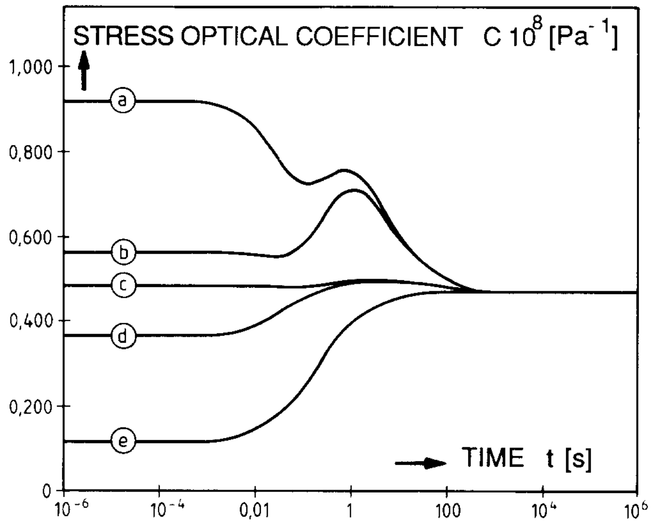

Figure 4 The time dependence of the stress-optical coefficient for five linear viscoelastic fluids that differ only in respect of their optical weighting factors f_i

(curve a); when the opposite is the case (curve e), $C(t)$ will increase with time. The strong optical weighting of the process with $\tau_3^* = 1$ s (curves a and b) causes a local maximum in $C(t)$ at $t \approx \tau_3^*$. It is interesting to note that in all cases $C(t)$ becomes time-independent at $t \approx 2\tau_{\max}^*$, i.e. at $t \approx 200$ s. Furthermore it can be seen that the most pronounced variations in $C(t)$ take place when $t < 1$ s. This fact might be the reason why the time dependence of $C(t)$ has been passed over in most earlier experimental work.

The optical analogue of Trouton's rule

For a simple shear process the shear-rate history is given by:

$$\dot{\varepsilon}_{12}(t) = \dot{\varepsilon}_{21}(t) = \tfrac{1}{2}\dot{\gamma}_0 h(t) \qquad (41)$$

where $\dot{\gamma}_0$ is a constant and $h(t)$ is the unit step function defined in equation (12). If the response of a linear viscoelastic fluid exposed to this history is designated $p_{21}(t)$, then Trouton's rule gives[21]:

$$3[p_{21}(t)/\dot{\gamma}_0] = [\sigma(t)/\dot{\varepsilon}_0] \qquad (42)$$

where $p_{21}(t)/\dot{\gamma}_0$ is the linear viscoelastic shear viscosity, $\hat{\eta}(t)$, and $\sigma(t)/\dot{\varepsilon}_0$ is the linear viscoelastic elongational viscosity, $\hat{\mu}(t)$. For polymer melts the numerical value of the Trouton factor between $\hat{\mu}(t)$ and $\hat{\eta}(t)$ has been found to be 3[21,22].

In order to calculate the optical response to a simple shear process, a transformation to principal strain-rate axes must be performed. This is accomplished by the operation:

$$\boldsymbol{Q} \cdot \dot{\boldsymbol{\varepsilon}} \cdot \boldsymbol{Q}^{\mathrm{T}} \qquad (43)$$

Here $\dot{\boldsymbol{\varepsilon}}$ is the strain-rate tensor, $\boldsymbol{Q}$ is an orthogonal transformation tensor, given by:

$$\boldsymbol{Q} = \begin{bmatrix} \cos\chi & \sin\chi & 0 \\ -\sin\chi & \cos\chi & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad (44)$$

and $\boldsymbol{Q}^{\mathrm{T}}$ is its transpose. For the linear viscoelastic range of deformation the extinction angle χ (the angle between the direction of flow and the nearest principal axis of refraction) is known to be equal to 45°. In this case the principal strain rates (eigenvalues) are:

$$\dot{\varepsilon}_{\mathrm{I}} = \tfrac{1}{2}\dot{\gamma}_0 \qquad \dot{\varepsilon}_{\mathrm{II}} = -\tfrac{1}{2}\dot{\gamma}_0 \qquad \dot{\varepsilon}_{\mathrm{III}} = 0 \qquad (45)$$

A simple shear, with respect to the principal axes of deformation, is thus a planar elongation. The strain rate in direction I is fully compensated by the strain rate in direction II, so that the strain rate in the third direction is zero (i.e. $\dot{\varepsilon}_{\mathrm{III}} = 0$). For the deformation defined in equation (45) the principal components of the deviatoric part of the refractive-index tensor are thus:

$$n_{\mathrm{DI}}(t) = -n_{\mathrm{DII}}(t) \qquad \text{and} \qquad n_{\mathrm{DIII}}(t) = 0 \qquad (46)$$

Applying equation (34) to the strain-rate history given by equation (45), the proposed model gives the following principal indices of refraction:

$$n_{\mathrm{I}}(t) = n_0 + \dot{\gamma}_0[\pi(n_0^2+2)^2/9RTn_0] \sum_{i=1}^{N} p_i a_i \Delta\alpha_i \times [1+\cosh(\Delta G_i/RT)]^{-1}[1-\exp(-t/\tau_i^*)] \qquad (47)$$

$$n_{\mathrm{II}}(t) = n_0 - \dot{\gamma}_0[\pi(n_0^2+2)^2/9RTn_0] \sum_{i=1}^{N} p_i a_i \Delta\alpha_i \times [1+\cosh(\Delta G_i/RT)]^{-1}[1-\exp(-t/\tau_i^*)] \qquad (48)$$

$$n_{\mathrm{III}}(t) = n_0 \qquad (49)$$

Back-transforming to the axes of the original coordinate system by $\boldsymbol{Q}^{\mathrm{T}} \cdot \boldsymbol{n} \cdot \boldsymbol{Q}$ gives:

$$\boldsymbol{n} = \begin{bmatrix} n_0 & n_{12} & 0 \\ n_{21} & n_0 & 0 \\ 0 & 0 & n_0 \end{bmatrix} \qquad (50)$$

where $n_{12} = n_{21} = \tfrac{1}{2}[n_{\mathrm{I}}(t) - n_{\mathrm{II}}(t)]$. From equations (36), (47), (48) and (50) it can readily be seen that, in the linear viscoelastic range of deformation, the optical analogue of Trouton's rule holds:

$$3[n_{21}(t)/\dot{\gamma}_0] = [\Delta n(t)/\dot{\varepsilon}_0] \qquad (51)$$

Were the stress-optical coefficient to be a constant, equation (51) could have been derived directly from Trouton's rule (equation (42)). It is therefore remarkable that equation (51) is derived from a model that postulates a time-dependent stress-optical coefficient.

It should be emphasized that all the relationships given above have been derived without making any assumptions as to the orientating units or to the structure of the material, nor has it been necessary to assume that the internal energy remains unaffected during deformation.

STREAMING BIREFRINGENCE IN THE NON-LINEAR RANGE OF DEFORMATION

The change of the population density distribution in the ith subsystem due to an enlongational flow field

So far only small deformations, in which $\dot{\varepsilon} \approx \dot{\lambda}$, have been considered. While $\dot{\varepsilon}$ is an appropriate strain-rate measure for a fluid without memory (i.e. a Newtonian liquid), $\dot{\lambda}$ is applicable to a material that never forgets its initial state (i.e. a rubber-like solid). Polymer melts are somewhere between these two limiting cases and, to account for this, equation (17) has been extended:

$$\Delta_t G_{io}(\dot{\varepsilon}_0, t) = -a_i \dot{\varepsilon}_0 (1 + m_i \dot{\varepsilon}_0 t)^{1/m_i} \qquad (52)$$

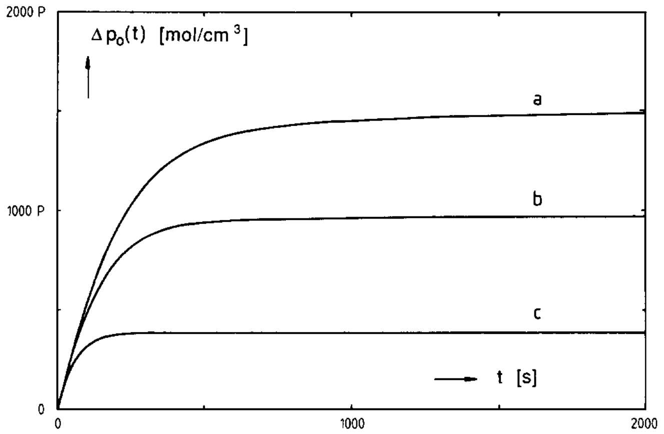

Figure 5 The influence of the ratio $k/\bar{k}$ on $\Delta p_o(t)$ of a fluid with $a/RT = 10$ s, $m = 10$, $p_d^0 + p_o^0 = 2000P$ mol cm^{-3}; the applied strain rate was $\dot{\varepsilon}_0 = \text{constant} = 0.1\ \text{s}^{-1}$: (a) $k = 0.0010\ \text{s}^{-1}$, $\bar{k} = 0.0040\ \text{s}^{-1}$, $t_{\text{inf}} = 32$ s; (b) $k = 0.0016\ \text{s}^{-1}$, $\bar{k} = 0.0016\ \text{s}^{-1}$, $t_{\text{inf}} = 24$ s; (c) $k = 0.0040\ \text{s}^{-1}$, $\bar{k} = 0.0010\ \text{s}^{-1}$, $t_{\text{inf}} = 10$ s

Here a_i is the same constant as in equation (17) and m_i is a dimensionless parameter, which ranges from 0 to ∞ and thereby characterizes the solid–fluid dualism for a given melt. This dualism becomes clear if we consider the two limiting values of equation (52):

$$\lim_{m_i \to 0} \Delta_t G_{io}(\dot{\varepsilon}_0, t) = -a_i \dot{\varepsilon}_0 \exp(\dot{\varepsilon}_0 t) = -a_i \dot{\lambda}_0(t)|_{\dot{\varepsilon}_0} \qquad (53a)$$

and:

$$\lim_{m_i \to \infty} \Delta_t G_{io}(\dot{\varepsilon}_0, t) = -a_i \dot{\varepsilon}_0 \qquad (53b)$$

These equations show that $m_i \to 0$ characterizes a material with a perfect deformation memory, whereas $m_i \to \infty$ characterizes one with a completely fading memory; m_i will therefore be called the memory-loss number for the ith subsystem.

In the following the response of the ith subsystem to simple elongation with $\dot{\varepsilon}_0 = \text{constant}$ and with $\dot{\lambda}_0 = \text{constant}$ will be derived, whereby the strain rates are considered to be large. For the Hencky strain-rate history given by equation (11), the rate constants can be obtained from equation (52):

$$c_i(t) = k_i \exp[(a_i \dot{\varepsilon}_0 / RT)(1 + m_i \dot{\varepsilon}_0 t)^{1/m_i} \qquad (54a)$$

$$\bar{c}_i(t) = \bar{k}_i \exp[(-a_i \dot{\varepsilon}_0 / RT)(1 + m_i \dot{\varepsilon}_0 t)^{1/m_i} \qquad (54b)$$

For the stretch-rate history:

$$\lambda_{\text{I}}(t) = \dot{\lambda}_0 h(t) \qquad \lambda_{\text{II}}(t) = \lambda_{\text{III}}(t) = [\lambda_{\text{I}}(t)]^{-1/2} \qquad (55)$$

where:

$$\dot{\varepsilon}_{\text{I}}(t)|_{\dot{\lambda}_0} = 1/(t + 1/\dot{\lambda}_0) \qquad (56)$$

the rate functions are:

$$c_i(t) = k_i \exp\left[\frac{a_i}{RT(t + 1/\dot{\lambda}_0)}\left(1 + \frac{m_i t}{t + 1/\dot{\lambda}_0}\right)^{1/m_i}\right] \qquad (57a)$$

$$\bar{c}_i(t) = \bar{k}_i \exp\left[\frac{-a_i}{RT(t + 1/\dot{\lambda}_0)}\left(1 + \frac{m_i t}{t + 1/\dot{\lambda}_0}\right)^{1/m_i}\right] \qquad (57b)$$

Since c_i and $\bar{c}_i$ are now functions of time for both strain-rate histories, the change in the population density:

$$\mathrm{d}p_{io}/\mathrm{d}t = c_i(t)p_i - [c_i(t) + \bar{c}_i(t)]p_{io}(t) \qquad (58)$$

and its integrated form[23]:

$$p_{io}(t) = p_{io}^0 \exp\left(-\int_0^t (c_i + \bar{c}_i)\,\mathrm{d}t'\right) + p_i \exp\left(-\int_0^t (c_i + \bar{c}_i)\,\mathrm{d}t'\right) \int_0^t c_i \exp\left(\int_0^{t'} (c_i + \bar{c}_i)\,\mathrm{d}t''\right)\mathrm{d}t' \qquad (59)$$

both have to be computed numerically. From equations (58) and (59) and the expressions above for the rate functions, it can be seen that the shift of the population density distribution in the ith subsystem due to deformation depends on five characteristic quantities: the total population density $p_i = p_{id} + p_{io}$, the two rate constants k_i and $\bar{k}_i$, the action constant a_i and the memory-loss number m_i.

Simulated experimental results for model fluids with N = *1*

The fluids to be considered here contain only one subsystem and, since $N = 1$, the index i is omitted. Under the influence of a strain-rate history of the type defined in equation (11) or (55), the transient birefringence will be given by the equations (31), (33) and (35):

$$\Delta n(t) = A \Delta p_o(t) \qquad (60)$$

Here $A = (\pi/3n_0)(n_0^2 + 2)^2 \Delta\alpha_1$ and $\Delta p_o(t) = p_o(t) - p_o^0$ is the molar number of $d \to o$ net transitions that will have occurred in a unit volume by time t. The subsequently given Δp_o *versus* t plots have been calculated by numerical integration of equation (58). In these figures Δp_o is plotted in units of a constant scaling factor P. Thus each of these curves represents the transient birefringence $\Delta n(t)$ of the corresponding fluid in units of the constant product PA.

Figures 5 and *6* demonstrate the effect of the ratio $k/\bar{k} = p_o^0/p_d^0$ on $\Delta p_o(t)$ for a fluid with $a/RT = 10$ s, $m = 10$ and $p_d^0 + p_o^0 = 2000P$ mol cm^{-3} for both kinds of elongation, i.e. with $\dot{\varepsilon}_0 = \text{constant} = 0.1\ \text{s}^{-1}$ and $\dot{\lambda}_0 = \text{constant} = 0.1\ \text{s}^{-1}$. In all cases $\Delta p_o(t)$ and $\Delta n(t)$ move towards a steady state; however, owing to the kinematical difference between $\dot{\varepsilon}_0 = \text{constant}$ and $\dot{\lambda}_0 = \text{constant}$, the shape of the curves for the two kinds of elongation are very different. With $\dot{\varepsilon}_0 = \text{constant}$, the rate $\mathrm{d}\Delta p_o/\mathrm{d}t$ increases until, after a comparatively short time, it begins to decrease, approaching zero as $t \to \infty$. With $\dot{\lambda}_0 = \text{constant}$, $\mathrm{d}\Delta p_o/\mathrm{d}t$

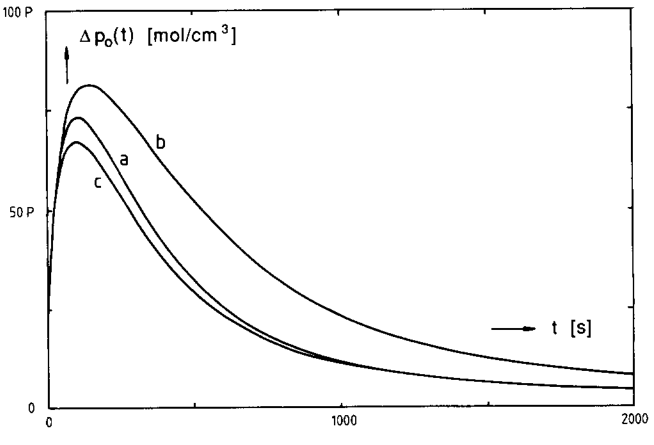

Figure 6 The influence of the ratio $k/\bar{k}$ on $\Delta p_o(t)$ of a fluid with $a/RT = 10$ s, $m = 10$, $p_d^0 + p_o^0 = 2000P$ mol cm^{-3}; the applied stretch rate was $\dot{\lambda}_0 = \text{constant} = 0.1\ \text{s}^{-1}$: (a) $k = 0.0010\ \text{s}^{-1}$, $\bar{k} = 0.0040\ \text{s}^{-1}$, $t_{\text{max}} = 107$ s, $t_{\text{inf}} = 248$ s; (b) $k = 0.0016\ \text{s}^{-1}$, $\bar{k} = 0.0016\ \text{s}^{-1}$, $t_{\text{max}} = 145$ s, $t_{\text{inf}} = 348$ s; (c) $k = 0.0040\ \text{s}^{-1}$, $\bar{k} = 0.0010\ \text{s}^{-1}$, $t_{\text{max}} = 102$ s, $t_{\text{inf}} = 238$ s

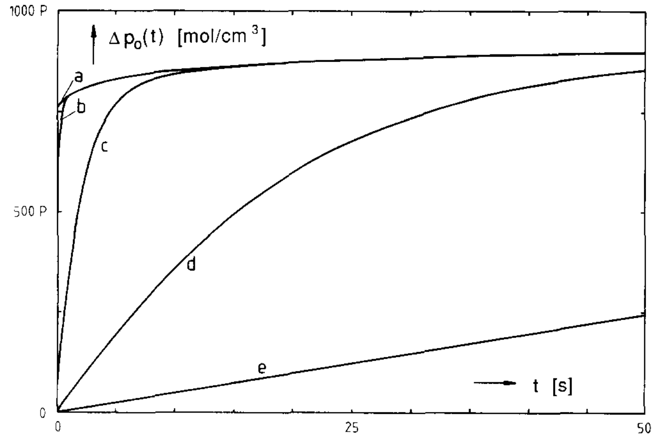

Figure 7 The effect of the relaxation time τ^* on $\Delta p_o(t)$ for a fluid with $a/RT = 10$ s, $m = 10$; strain rate $\dot{\varepsilon}_0 = \text{constant} = 0.1\ \text{s}^{-1}$: (a) $\tau^* = 0.0313$ s, no point of inflection; (b) $\tau^* = 0.3125$ s, no point of inflection; (c) $\tau^* = 3.125$ s, no point of inflection; (d) $\tau^* = 31.25$ s, $t_{\text{inf}} = 1.65$ s; (e) $\tau^* = 312.5$ s, $t_{\text{inf}} = 23.0$ s

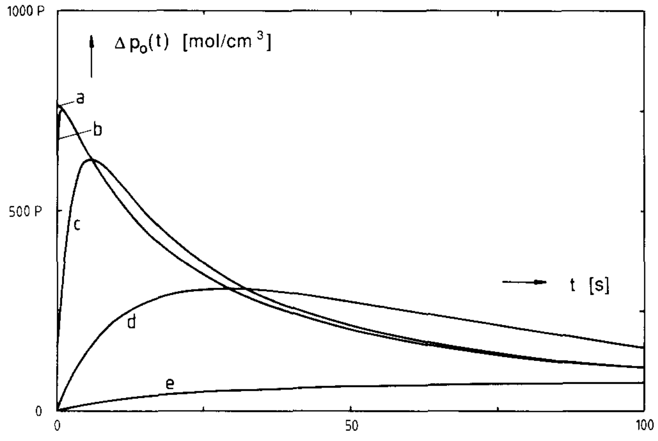

Figure 8 The effect of τ^* on $\Delta p_o(t)$ for a fluid with $a/RT = 10$ s, $m = 10$; stretch rate $\dot{\lambda}_0 = \text{constant} = 0.1\ \text{s}^{-1}$: (a) $\tau^* = 0.0313$ s, $t_{\text{max}} = 0.14$ s, $t_{\text{inf}} = 3.5$ s; (b) $\tau^* = 0.3125$ s, $t_{\text{max}} = 0.8$ s, $t_{\text{inf}} = 3.5$ s; (c) $\tau^* = 3.1250$ s, $t_{\text{max}} = 5.7$ s, $t_{\text{inf}} = 11.5$ s; (d) $\tau^* = 31.250$ s, $t_{\text{max}} = 29.0$ s, $t_{\text{inf}} = 59.8$ s; (e) $\tau^* = 312.5$ s, $t_{\text{max}} = 145$ s, $t_{\text{inf}} = 350$ s

decreases right from the beginning, becomes zero, further decreases ($d\Delta p_o/dt < 0$) until there occurs a point of inflection, and finally it increases to approach zero as $t \to \infty$. In both cases (i.e. with either $\dot{\varepsilon}_0 = \text{constant}$ or $\dot{\lambda}_0 = \text{constant}$), the general shape of the Δp_o *versus* t curve is independent of the value of the ratio $k/\bar{k}$. Therefore it will be assumed that

$$p_d^0 = p_o^0 = 1000P \quad \text{and} \quad k = \bar{k}$$

so that (by means of equation (27)):

$$\tau^* = (2k)^{-1} = (2\bar{k})^{-1}$$

Figures 7 and *8* show how the orientation, $\Delta p_o(t)$, is influenced by the relaxation time τ^*. Here again it is assumed that $a/RT = 10$ s, $m = 10$ and $\dot{\varepsilon}_0 = \text{constant} = 0.1\ \text{s}^{-1}$ or $\dot{\lambda}_0 = \text{constant} = 0.1\ \text{s}^{-1}$, respectively. As can be seen, the smaller the value of τ^* the larger is the initial rate, $d\Delta p_o/dt$, and the shorter is the time taken for the system to reach its final steady state. It is interesting to note that the curves of *Figure 7*, in which $\tau^* \leqslant 3.1$ s, do not exhibit an inflection point. With $\dot{\lambda}_0 = \text{constant}$, increasing the value of τ^* shifts t_{max} and t_{inf}, the times at which $\Delta n(t)$ shows a maximum or inflection point, respectively, to larger values.

Figures 9, *10* and *11* show how the orientation $\Delta p_o(t)$ depends on the parameters a and m for an elongation with $\dot{\varepsilon}_0 = \text{constant} = 0.1\ \text{s}^{-1}$. Here m has been varied from 10^{-6} to 10^6, a/RT has been given the values 10, 20 and

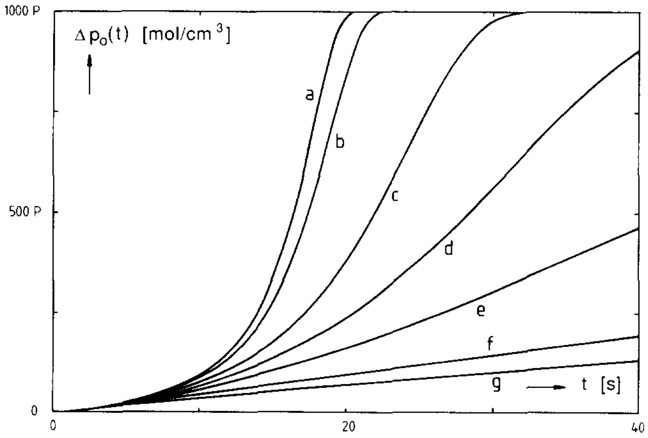

Figure 9 The effect of m on $\Delta p_o(t)$ for a fluid with $a/RT = 10$ s, $\tau^* = 312.5$ s; strain rate $\dot{\varepsilon}_0 = \text{constant} = 0.1\ \text{s}^{-1}$: (a) $m = 10^{-6}$, $t_{\text{inf}} = 17.8$ s; (b) $m = 0.1$, $t_{\text{inf}} = 19.0$ s; (c) $m = 0.5$, $t_{\text{inf}} = 24.5$ s; (d) $m = 1.0$, $t_{\text{inf}} = 31.5$ s; (e) $m = 2.0$, $t_{\text{inf}} = 41.0$ s; (f) $m = 10$, $t_{\text{inf}} = 23.1$ s; (g) $m = 10^6$, no inflection point

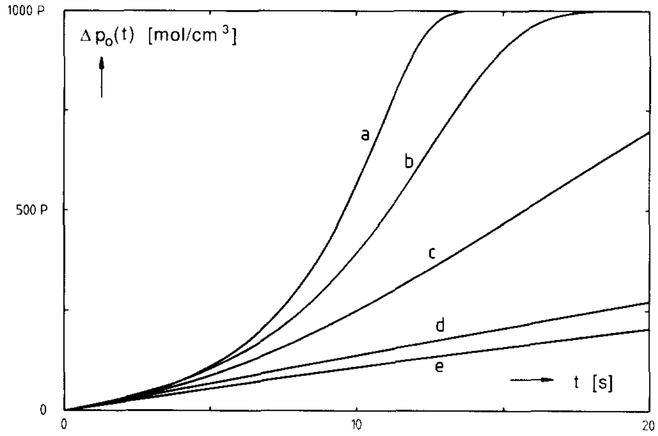

Figure 10 The effect of m on $\Delta p_o(t)$ for a fluid with $a/RT = 20$ s, $\tau^* = 312.5$ s; strain rate $\dot{\varepsilon}_0 = \text{constant} = 0.1\ \text{s}^{-1}$: (a) $m = 10^{-6}$, $t_{\text{inf}} = 10.8$ s; (b) $m = 0.5$, $t_{\text{inf}} = 12.7$ s; (c) $m = 2.0$, $t_{\text{inf}} = 16.2$ s; (d) $m = 20$, $t_{\text{inf}} = 6.9$ s; (e) $m = 10^{-6}$, no inflection point

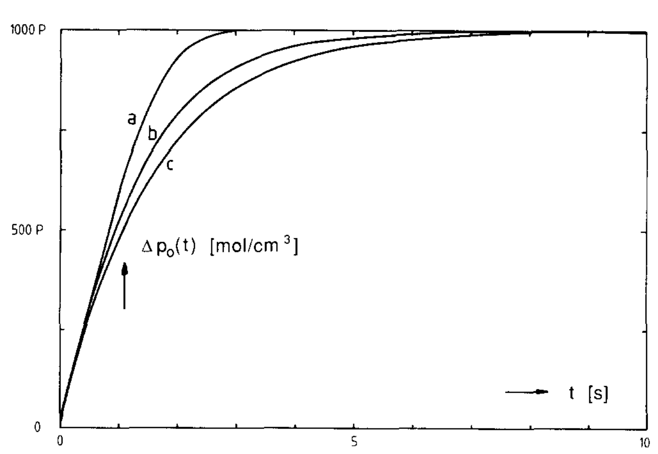

Figure 11 The effect of m on $\Delta p_o(t)$ for a fluid with $a/RT = 60$ s, $\tau^* = 312.5$ s; strain rate $\dot{\varepsilon}_0 = \text{constant} = 0.1\ \text{s}^{-1}$: (a) $m = 10^{-6}$; (b) $m = 60$; (c) $m = 10^6$

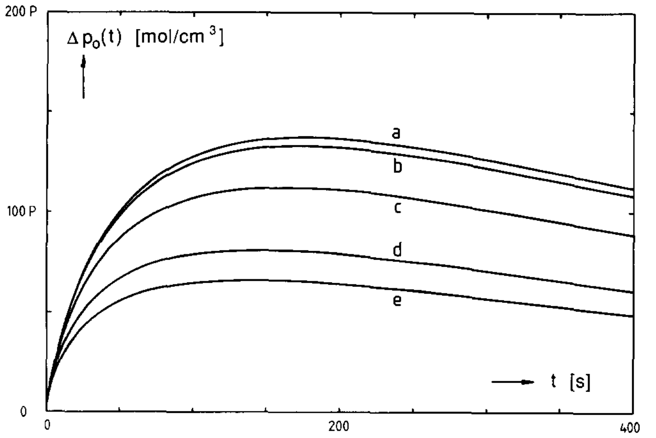

Figure 12 The effect of m on $\Delta p_o(t)$ for a fluid with $a/RT = 10$ s, $\tau^* = 312.5$ s; stretch rate $\dot{\lambda}_0 = \text{constant} = 0.1\ \text{s}^{-1}$: (a) $m = 10^{-6}$, $t_{\max} = 176$ s, $t_{\text{inf}} = 402$ s; (b) $m = 0.1$, $t_{\max} = 175$ s, $t_{\text{inf}} = 396$ s; (c) $m = 1.0$, $t_{\max} = 162$ s, $t_{\text{inf}} = 375$ s; (d) $m = 10$, $t_{\max} = 145$ s, $t_{\text{inf}} = 350$ s; (e) $m = 10^6$, $t_{\max} = 140$ s, $t_{inf} = 340$ s

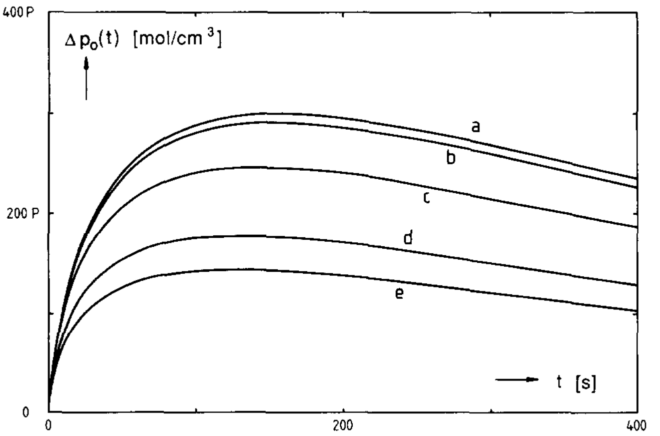

Figure 13 The effect of m on $\Delta p_o(t)$ for a fluid with $a/RT = 20$ s, $\tau^* = 312.5$ s; stretch rate $\dot{\lambda}_0 = \text{constant} = 0.1\ \text{s}^{-1}$: (a) $m = 10^{-6}$, $t_{\max} = 155$ s, $t_{\text{inf}} = 371$ s; (b) $m = 0.1$, $t_{\max} = 154$ s, $t_{\text{inf}} = 368$ s; (c) $m = 1.0$, $t_{\max} = 143$ s, $t_{\text{inf}} = 350$ s; (d) $m = 10$, $t_{\max} = 130$ s, $t_{\text{inf}} = 325$ s; (e) $m = 10^6$, $t_{\max} = 127$ s, $t_{\text{inf}} = 321$ s

60 s, respectively, and the relaxation time has been taken as $\tau^* = 312.5$ s (i.e. $k = \bar{k} = 0.0016\ s^{-1}$). These figures demonstrate that, first, the initial rate $\mathrm{d}\Delta p_o/\mathrm{d}t$ depends only on the action constant a, and, secondly, the effect of the memory-loss number m decreases as the value of a increases. At $a/RT = 10$ s (*Figure 9*) the course of the transient birefringence $\Delta n(t)$ is much more susceptible to the actual value of m than at $a/RT = 60$ s (*Figure 11*). When a is large and m is small, the birefringence increases maximally and reaches saturation (at $1000PA$) after a minimum deformation time and, furthermore, there is no point of inflection if $a/RT = 60$ s or if $m = 10^6$.

Figures 12, 13 and *14*, in which $\dot{\lambda}_0 = \text{constant} = 0.1\ \text{s}^{-1}$, show the counterparts to the preceding examples. A comparison between the two sets of figures shows that the influence of the parameters a and m is much more pronounced for elongations with $\dot{\varepsilon}_0 = \text{constant}$ than for those with $\dot{\lambda}_0 = \text{constant}$. In all of the curves in *Figures 12–14* the value of $\Delta p_o(t_{\max})$ increases as a/RT increases or as m decreases. For either $a/RT = 10$ s (*Figure 12*) or $a/RT = 20$ s (*Figure 13*) the maximum shifts to shorter times as m increases; however, for $a/RT = 60$ s (*Figure 14*), increasing m shifts the maximum to longer times. The time required to reach a point of inflection is shortened as a or m increases. For elongations with $\dot{\lambda}_0 = \text{constant}$ the initial rate $\mathrm{d}\Delta p_o/\mathrm{d}t$ is independent of the actual value of m, just as has been the case with $\dot{\varepsilon}_0 = \text{constant}$.

The effect of the applied strain rate ($\dot{\varepsilon}_0 = \text{constant}$), and the stretch rate ($\dot{\lambda}_0 = \text{constant}$) on the orientation of a fluid with $a/RT = 10$ s, $m = 10$ and $\tau^* = 312.5$ s (i.e. $k = \bar{k} = 0.0016\ s^{-1}$) are shown in *Figures 15* and *16*. Increasing the value of either $\dot{\varepsilon}_0$, or $\dot{\lambda}_0$ increases the initial slope of the curve and shifts $t_{\max}$ and t_{inf} to smaller values. The change of the initial slope is consistent with the results in an earlier section. For sufficiently small t it follows from equation (36) that $\Delta n(t) = 3\dot{\varepsilon}_0 c \sum (f_i/\tau_i^*)t$, where $c = \pi(n_0^2 + 2)^2/9RTn_0$ and $f_i = p_i a_i \Delta\alpha_{i1}/[1 + \cosh(\Delta G_i/RT)]$.

To conclude this section it should be mentioned that a great variety of orientational behaviour, i.e. many different time courses of $\Delta n(t)$, can be modelled by superimposing various subsystems, the contribution of each being weighted differently.

SUMMARY

A microscopic orientation model has been developed, using the methods of chemical kinetics, to describe the

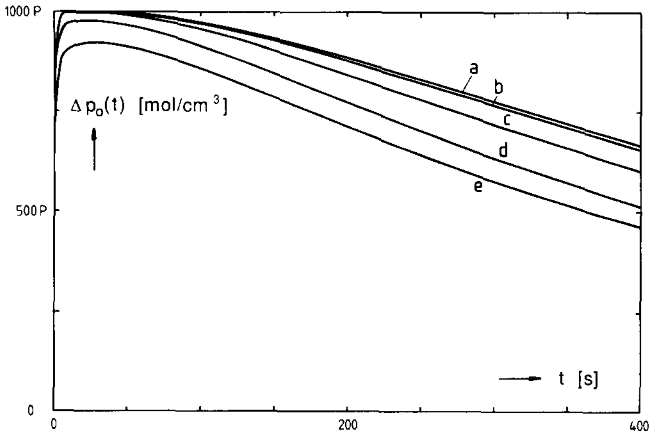

Figure 14 The effect of m on $\Delta p_o(t)$ for a fluid with $a/RT = 60$ s, $\tau^* = 312.5$ s; stretch rate $\dot{\lambda}_0 = \text{constant} = 0.1\ \text{s}^{-1}$: (a) $m = 10^{-6}$, $t_{\max} = 18$ s, $t_{\text{inf}} = 276$ s; (b) $m = 0.1$, $t_{\max} = 18$ s, $t_{\text{inf}} = 269$ s; (c) $m = 1.0$, $t_{\max} = 20$ s, $t_{\text{inf}} = 230$ s; (d) $m = 10$, $t_{\max} = 23$ s, $t_{\text{inf}} = 180$ s; (e) $m = 10^6$, $t_{\max} = 27$ s, $t_{\text{inf}} = 164$ s

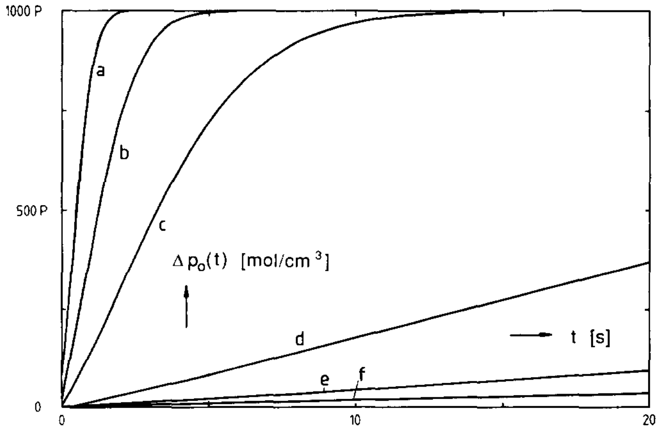

Figure 15 The influence of the magnitude of the strain rate $\dot{\varepsilon}_0$ on $\Delta p_o(t)$ for a fluid with $a/RT = 10$ s, $m = 10$ and $\tau^* = 312.5$ s: (a) $\dot{\varepsilon}_0 = 0.6\ \text{s}^{-1}$, $t_{\text{inf}} = 0.3$ s; (b) $\dot{\varepsilon}_0 = 0.5\ \text{s}^{-1}$, $t_{\text{inf}} = 0.8$ s; (c) $\dot{\varepsilon}_0 = 0.4\ \text{s}^{-1}$, $t_{\text{inf}} = 1.9$ s; (d) $\dot{\varepsilon}_0 = 0.2\ \text{s}^{-1}$, $t_{\text{inf}} = 10.7$ s; (e) $\dot{\varepsilon}_0 = 0.1\ \text{s}^{-1}$, $t_{\text{inf}} = 23.0$ s; (f) $\dot{\varepsilon}_0 = 0.05\ \text{s}^{-1}$, $t_{\text{inf}} = 29.4$ s

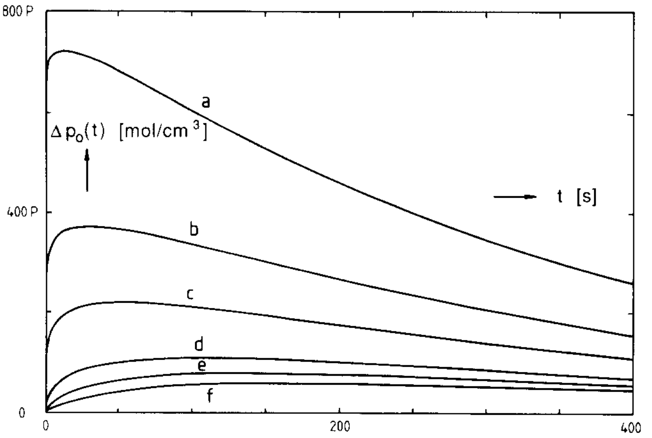

Figure 16 The influence of the magnitude of the stretch rate $\dot{\lambda}_0$ on $\Delta p_o(t)$ for a fluid with $a/RT = 10$ s; $m = 10$, $\tau^* = 312.5$ s: (a) $\dot{\lambda}_0 = 0.6\ \mathrm{s}^{-1}$, $t_{\max} = 12$ s, $t_{\inf} = 84$ s; (b) $\dot{\lambda}_0 = 0.5\ \mathrm{s}^{-1}$, $t_{\max} = 30$ s, $t_{\inf} = 130$ s; (c) $\dot{\lambda}_0 = 0.4\ \mathrm{s}^{-1}$, $t_{\max} = 53$ s, $t_{\inf} = 182$ s; (d) $\dot{\lambda}_0 = 0.2\ \mathrm{s}^{-1}$, $t_{\max} = 108$ s, $t_{\inf} = 286$ s; (e) $\dot{\lambda}_0 = 0.1\ \mathrm{s}^{-1}$, $t_{\max} = 145$ s, $t_{\inf} = 348$ s; (f) $\dot{\lambda}_0 = 0.05\ \mathrm{s}^{-1}$, $t_{\max} = 181$ s, $t_{\inf} = 410$ s

rheo-optical behaviour of polymer melts. The model is based on the assumption that the macromolecules in a polymer melt are capable of continuously changing their conformation. It is further assumed that those conformational changes which contribute to the orientational behaviour of the melt take place at bonds that have an asymmetrical rotational potential that has only two free-energy minima. Only the conformers that correspond to these minima are considered to be populated, while all other conformational states are assumed to be quasi-empty. The pair of conformers generated by rotation at a specific bond is treated as an independent subsystem.

In the undeformed, thermally equilibrated melt, the relative population densities of the two conformers of a subsystem depend on the Gibbs free energies of the corresponding states and on the temperature. In the presence of an elongational flow field, the Gibbs free energy of one conformer decreases by a specific amount, while that of the other increases by the same amount. In the range of small deformations the shift of the population density distribution in the ith subsystem produced in this way depends on the action constant a_i, and on the applied strain rate. In the non-linear range of deformation, an additional constant m_i, the memory-loss number, is important. The transition from linear to non-linear behaviour is governed by the magnitude of the strain rate, the duration of the deformation and the value of the constant m_i.

Each subsystem is characterized by: a total population density $p_i = p_{id} + p_{io}$, two rate constants k_i and $\bar{k}_i$, an action constant a_i and, in the non-linear viscoelastic range, a memory-loss number m_i.

The main predictions of the model can be summarized as follows:

1. The time dependence of the birefringence in the linear viscoelastic range of deformation can be represented (for simple elongation as well as for simple shear) by an expression that is analogous to the corresponding stress expression known from the theory of linear viscoelasticity. However, in the present case, summation is not over M spring–dashpot elements but over N orientational processes.

2. If the theory of linear viscoelasticity is accepted as an adequate description of the rheological behaviour of polymer melts under small strain and small strain rate, then it must be concluded that the so-called stress-optical rule, $\Delta n/\sigma = \text{constant}$, is not valid even in the linear viscoelastic range of deformation. The ratio $C(t)$ is predicted to have a constant value, C_{in}, within short deformation times but a different constant value, C_{ss}, as $t \to \infty$.

3. In addition to the well known mechanical relaxation-time spectrum $\{g_m, \tau_m\}$ there is a stress-optical relaxation-time spectrum $\{(cf_i/\tau_i^*), \tau_i^*\}$.

4. In the linear viscoelastic range of deformation, the optical analogue of Trouton's rule holds, while the stress-optical rule is invalid.

5. In the non-linear range of deformation $\Delta n(t)$ is predicted to depend strongly on the applied deformation history. For two elongations, carried out with $\dot{\varepsilon} = \text{constant}$ and $\dot{\lambda} = \text{constant}$, respectively, $\dot{\varepsilon}$ and $\dot{\lambda}$ both of the same magnitude, the corresponding $\Delta n(t)$ curves have a common initial part of short duration (in the linear viscoelastic range) and then they diverge to different steady state values. For the elongation with $\dot{\varepsilon} = \text{constant}$, $\Delta n(t)$ increases steadily, for the one with $\dot{\lambda} = \text{constant}$, $\Delta n(t)$ passes a maximum and then decreases to a final value which is much smaller than $\Delta n_{\max}$ if $\dot{\lambda}$ is big.

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to Professor Meissner, Dr Garbella and Dr Vansco for valuable discussions, and to the Swiss National Foundation for Scientific Research (Grant No. 2.046-0.86) for financial support.

LIST OF SYMBOLS

a_i	$(\mathrm{J\,s\,mol^{-1}})$	action constant of the ith subsystem
A	$(\mathrm{cm^3\,mol^{-1}})$	constant
c	$(\mathrm{mol\,J^{-1}})$	constant
c_i	$(\mathrm{s^{-1}})$	rate constant for orientation in the ith subsystem
$\bar{c}_i$	$(\mathrm{s^{-1}})$	rate constant for disorientation in the ith subsystem
$c_i(t)$	$(\mathrm{s^{-1}})$	rate function for orientation in the ith subsystem
$\bar{c}_i(t)$	$(\mathrm{s^{-1}})$	rate function for disorientation in the ith subsystem
C	$(\mathrm{Pa^{-1}})$	stress-optical coefficient
C_{in}, C_{ss}	$(\mathrm{Pa^{-1}})$	linear viscoelastic expression for C at short times or for $t \to \infty$, respectively
f_i	$(\mathrm{J\,s\,mol^{-1}})$	weighting factor for transient birefringence under linear viscoelastic condition
G	$(\mathrm{J\,mol^{-1}})$	Gibbs free energy
ΔG_i	$(\mathrm{J\,mol^{-1}})$	molar difference in Gibbs free energy between the oriented and the disoriented conformers of the ith subsystem
$\Delta_t G_{io}(\dot{\varepsilon}_0)$	$(\mathrm{J\,mol^{-1}})$	temporal change of Gibbs free energy in the ith subsystem due to deformation

g_m	(Pa)	weighting factor for stress under linear viscoelastic conditions
h	(J s)	Planck constant
$h(t)$		step function
H	(J mol^{-1})	enthalpy
k	(J K^{-1})	Boltzmann constant
k_i	(s^{-1})	rate constant for orientation in the undisturbed ith subsystem
$\bar{k}_i$	(s^{-1})	rate constant for disorientation in the undisturbed ith subsystem
L, L_0	(m)	sample length at time t and $t=0$, respectively
m_i		memory-loss number of the ith subsystem
n_0		refractive index of undeformed material
$\Delta n(t)$		transient birefringence exhibited upon simple elongation
n_{I}		refractive index in the principal direction I
n_{DI}, n_{DII}, n_{DIII}		principal components of the deviator of the refraction tensor
N	(cm^{-3})	density of chains between crosslinks
N_{A}	(mol^{-1})	Avogadro number
p_{id}	(mol cm^{-3})	population density for disoriented conformer of the ith subsystem
p_{io}	(mol cm^{-3})	population density for oriented conformer of the ith subsystem
p_{io}^0	(mol cm^{-3})	p_{io} in the undeformed melt
P		scaling factor
Q, Q^{T}		orthogonal transformation tensor and its transpose, respectively
R	(J K^{-1} mol^{-1})	gas constant
S	(J K^{-1} mol^{-1})	entropy
t, t', t''	(s)	time
t_{inf}	(s)	time corresponding to a point of inflection in $\Delta n(t)$
t_{max}	(s)	time corresponding to a maximum in $\Delta n(t)$
T	(K)	absolute temperature
$\Delta\alpha_{i\mathrm{I}}$	(cm^3 mol^{-1})	mean change of polarizability in the principal direction I due to N_{A} orientational transitions in the ith subsystem
$\alpha_{id\mathrm{I}}$	(cm^3)	mean contribution of a disoriented conformer of the ith subsystem to the polarizability in the principal direction I
$\alpha_{io\mathrm{I}}$	(cm^3)	mean contribution of an oriented conformer of the ith subsystem to the polarizability in the principal direction I
α_{S1}, α_{S2}	(cm^3)	principal polarizabilities of a segment
β_{I}		volume polarizability in principal direction I
$\dot{\gamma}_0$	(s^{-1})	constant shear rate
$\dot{\varepsilon}_0$	(s^{-1})	constant derivative of the Hencky strain
$\dot{\varepsilon}_{\mathrm{I}}$' $\dot{\varepsilon}_{\mathrm{II}}$' $\dot{\varepsilon}_{\mathrm{III}}$	(s^{-1})	principal components of the Hencky strain-rate tensor
$\hat{\eta}$	(Pa s)	linear viscoelastic shear viscosity
$\dot{\lambda}_0$	(s^{-1})	constant stretch rate
$\dot{\lambda}_{\mathrm{I}}$' $\dot{\lambda}_{\mathrm{II}}$' $\dot{\lambda}_{\mathrm{III}}$	(s^{-1})	principal components of the stretch-rate tensor
$\hat{\mu}$	(Pa s)	linear viscoelastic elongational viscosity
σ	(Pa)	tensile stress
τ	(s)	mechanical relaxation time
τ^*	(s)	optical relaxation time
χ	(deg)	extinction angle

REFERENCES

1 Janeschitz-Kriegl, H. 'Polymer Melt Rheology and Flow Birefringence', Springer-Verlag, Berlin, 1983
2 White, J. L. and Spruiell, J. E. *Polym. Eng. Sci.* 1983, **23**, 247
3 Kuhn, W. and Grün, F. *Kolloid-Z.* 1942, **101**, 248
4 Treloar, L. R. G. 'The Physics of Rubber Elasticity', Clarendon Press, Oxford, 1975
5 Lodge, A. S. *Kolloid-Z.* 1960, **171**, 46
6 Read, B. E. *Polymer* 1962, **3**, 143
7 Janeschitz-Kriegl, H. *Adv. Polym. Sci.* 1969, **6**, 170
8 Read, B. E. *Polymer* 1964, **5**, 1
9 Coleman, B. D., Dill, E. H. and Toupin, R. A. *Arch. Rat. Mech. Anal.* 1970, **39**, 358
10 Dill, E. H. *J. Polym. Sci. (C) Polym. Symp.* 1964, **5**, 67
11 Moore, W. J. 'Physical Chemistry', 5th Edn., Longman, London, 1972
12 Laidler, K. J. 'Chemical Kinetics', 2nd Edn., McGraw-Hill, New York, 1965
13 Glasstone, S., Laidler, K. and Eyring, H. 'The Theory of Rate Processes', McGraw-Hill, New York, 1941
14 Eyring, H. *J. Chem. Phys.* 1936, **4**, 283
15 Ree, T. and Eyring, H. 'Rheology' (ed. F. R. Eirich), Academic Press, New York, 1958, Vol. II
16 Bird, R. B., Armstrong, R. C. and Hassager, O. 'Dynamics of Polymeric Liquids', Vol. I, 'Fluid Mechanics', Wiley, New York, 1977
17 Fröhlich, H. 'Theory of Dielectrics', Clarendon Press, Oxford, 1958
18 McCrum, N. G., Buckley, C. P. and Bucknall, C. B. 'Principles of Polymer Engineering', Oxford University Press, Oxford, 1988
19 Born, M. and Wolf, E. 'Principles of Optics', 6th Edn., Pergamon Press, Oxford, 1983
20 Stavermann, A. J. and Schwarzl, F. 'Die Physik der Hochpolymeren' (ed. H. A. Stuart), Springer-Verlag, Berlin, 1956, Vol. IV
21 Petrie, C. J. S. 'Elongational Flows', Pitman, London, 1979
22 Meissner, J. *Rheol. Acta* 1971, **10**, 230; *J. Appl. Polym. Sci.* 1972, **16**, 2877
23 Margenau, H. and Murphy, G. M. 'The Mathematics of Physics and Chemistry', 2nd Edn., Van Nostrand, Princeton, NJ, 1956