Remarks on the Birefringence in Stress-Controlled Linear Viscoelasticity:

71st Meeting of the Society of Rheology
October 1999

G. C. Berry

Department of Chemistry

Carnegie Mellon University

Lecture Notes available at the web site:
www.chem.cmu.edu/Berry/birefringence.pdf

e-mail: gcberry@andrew.cmu.edu

Linear Viscoelasticity:

$$R(t) = J(t) - t/\eta = J_\infty - [J_\infty - J_o]\alpha(t)$$
$$G(t) = G_e + [G_o - G_e]\varphi(t)$$

Here,

η is the (linear) viscosity, with $1/\eta = 0$ for a fluid,
G_e is the equilibrium modulus, with $G_e = 0$ for a solid,
G_o is the "instantaneous" modulus, with $J_oG_o = 1$, and
J_∞ is the limit of R(t) for large t, with values discussed below

$$1 = \frac{1}{t}\int_0^t du\, G(t-u)\, J(u)$$

$$B(t) = B_e - [B_e - B_o]\beta(t)$$
$$K(t) = K_e + [K_o - K_e]\kappa(t)$$

Incompressible linear elastic solid: $K >> G \approx E/3$ or, equivalently, $B << J \approx 3D$.

$$\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right);$$ **u** is the displacement vector

$$2\varepsilon_{ij}(t) = \int_{-\infty}^{t} ds\left\{J(t-s)\left[\frac{\partial S_{ij}(s)}{\partial s} - \tfrac{1}{3}\,\delta_{ij}\frac{\partial S_{\alpha\alpha}(s)}{\partial s}\right] + (2/9)\delta_{ij}\,B(t-s)\,\frac{\partial S_{\alpha\alpha}(s)}{\partial s}\right\}$$

$$S_{ij}(t) = \int_{-\infty}^{t} ds\left\{2G(t-s)\left[\frac{\partial \varepsilon_{ij}(s)}{\partial s} - \tfrac{1}{3}\,\delta_{ij}\frac{\partial \varepsilon_{\alpha\alpha}(s)}{\partial s}\right] + \delta_{ij}\,K(t-s)\,\frac{\partial \varepsilon_{\alpha\alpha}(s)}{\partial s}\right\}$$

Coleman, B. D.; Dill, E. H.; Toupin, R. A. "A phenomenological theory of streaming birefringence" *Arch. Rational Mech. Anal.* **1970**, *39*, 358-99.

$$n_{ij}(t) = \int_{-\infty}^{t} ds\left\{J_n(t-s)\left[\frac{\partial S_{ij}(s)}{\partial s} - \tfrac{1}{3}\,\delta_{ij}\frac{\partial S_{\alpha\alpha}(s)}{\partial s}\right] + \delta_{ij}\left[n_o + (2/9)B_n(t-s)\,\frac{\partial S_{\alpha\alpha}(s)}{\partial s}\right]\right\}$$

$$n_{ij}(t) = \int_{-\infty}^{t} ds\left\{2G_n(t-s)\left[\frac{\partial \varepsilon_{ij}(s)}{\partial s} - \tfrac{1}{3}\,\delta_{ij}\frac{\partial \varepsilon_{\alpha\alpha}(s)}{\partial s}\right] + \delta_{ij}\left[n_o + K_n(t-s)\,\frac{\partial \varepsilon_{\alpha\alpha}(s)}{\partial s}\right]\right\}$$

$$1 = G(0)J(t) + \int_{0}^{t} du\, J(t-u)\,\frac{\partial G(u)}{\partial u}$$

$$J_n(t) = G_n(0)J(t) + \int_{0}^{t} du\, J(t-u)\,\frac{\partial G_n(u)}{\partial u}$$

NOTE: $J_n(t)$ is a constant if $G_n(t)/G(t)$ is independent of t.

Deviatoric Components:

Strain-defined history:

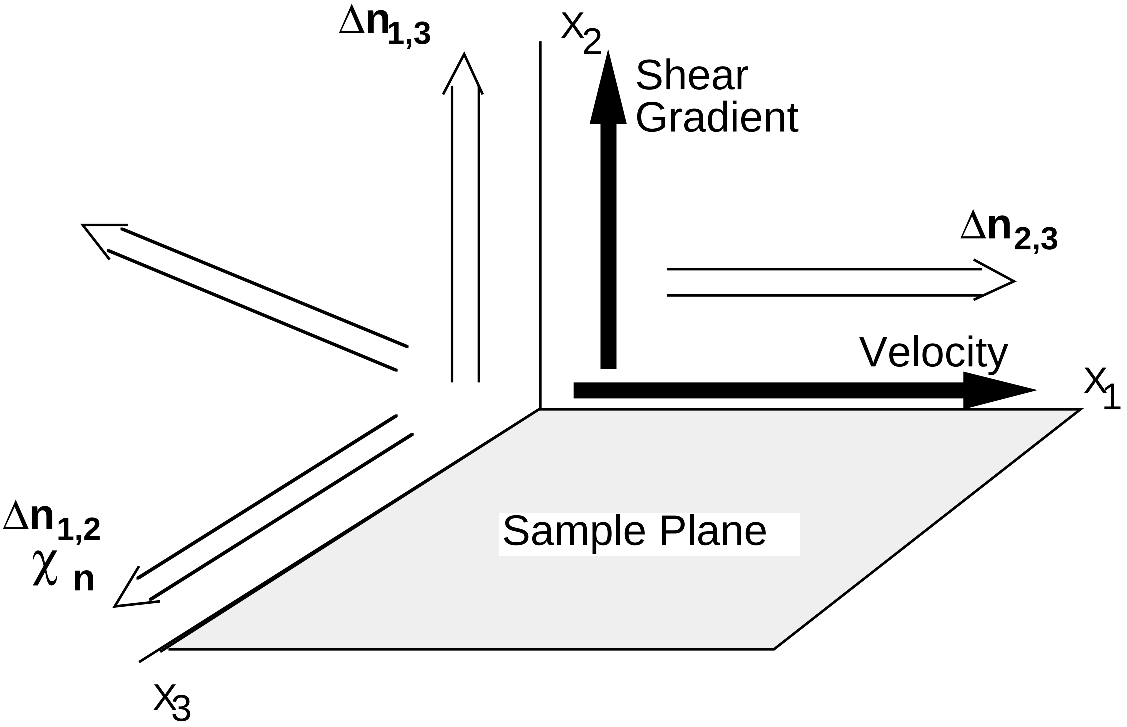
$$n_{12}(t) \;=\; G_n(0)\varepsilon_{12}(t) + \int_0^{\infty} du\; \varepsilon_{12}(t-u)\,\frac{\partial G_n(u)}{\partial u}$$

$$n_{11}(t) - n_{22}(t) \;=\; G_n(0)[\varepsilon_{11}(t) - \varepsilon_{22}(t)] + \int_0^{\infty} du\; [\varepsilon_{11}(t-u) - \varepsilon_{22}(t-u)]\,\frac{\partial G_n(u)}{\partial u}$$

Stress-defined history:

$$n_{12}(t) \;=\; J_n(0)S_{12}(t) \;+\; \int_0^{\infty} du\; S_{12}(t-u)\,\frac{\partial J_n(u)}{\partial u}$$

$$n_{11}(t) - n_{22}(t) \;=\; J_n(0)[S_{11}(t) - S_{22}(t)] + \int_0^{\infty} du\; [S_{11}(t-u) - S_{22}(t-u)]\,\frac{\partial J_n(u)}{\partial u}$$



$$\Delta n_{1,2}(t) = [n_{11}(t) - n_{22}(t)]\cos[2\chi_n(t)] + 2n_{12}(t)\sin[2\chi_n(t)]$$

$$\cot[2\chi_n(t)] = [n_{11}(t) - n_{22}(t)]/2n_{12}(t)$$

Shear deformation along x_1

$$\Delta n_{1,2}(t)\sin[2\chi_n(t)] = 2n_{12}(t); \qquad \pi/4 > \chi_n(t) > 0$$

Uniaxial elongation along x_1

$$\Delta n_{1,2}(t) = n_{11}(t) - n_{22}(t); \qquad \chi_n(t) = 0.$$

Linear elastic solid:

$(\chi_n \approx \pi/4)$

$\partial G_n(t)/\partial t = \partial J_n(t)/\partial t = 0$

Strain-defined:

$$n_{12}(t) \;=\; G_n(0)\varepsilon_{12}(t)$$

Stress-defined:

$$n_{12}(t) \;=\; J_n(0)S_{12}(t) = G_n(0)J(t)S_{12}(t) = G_n(0)\varepsilon_{12}(t)$$

Linear viscoelastic fluid in steady state deformations:

Steady-state shear flow in the linear response ($\chi_n \approx \pi/4$):

Strain-defined:

$\gamma(t) = \dot{\gamma}t$

$$\Delta n_{ss} = 2n_{12}(t) = 2\lim_{t=\infty}\int_0^t du\, G_n(t-u)\frac{\partial\gamma(s)}{\partial s} = 2\dot{\gamma}\int_0^\infty du\, G_n(u)$$

Assume $G_n(t) = C\times G(t)$:

$$\Delta n_{ss}/2C = \dot{\gamma}\int_0^\infty du\, G(u) = \eta\dot{\gamma} = (1/J_s)\hat{\gamma}_R(\dot{\gamma})$$

with $\hat{\gamma}_R(\dot{\gamma})$ the total strain recoil on cessation of steady-state flow at shear rate $\dot{\gamma}$.

Stress-defined:

$\sigma(t) = \sigma_o = \eta\dot{\gamma}_{ss}$ for $t \geq 0$

$$\Delta n_{ss} = 2n_{12}(t) = 2\lim_{t=\infty}\int_0^t du\, J_n(t-u)\frac{\partial\sigma(s)}{\partial s} = 2J_n(\infty)\eta\dot{\gamma}_{ss}$$

$$\lim_{t=\infty}\hat{\gamma}_R(t) = \lim_{t=\infty}\sigma_o\int_0^t du\, R(t-u) = \sigma_o J_s = \eta\dot{\gamma}_{ss}J_s$$

But from above,

$$\Delta n_{ss}/2C = \eta\dot{\gamma}_{ss} = (1/J_s)\hat{\gamma}_R(\dot{\gamma}_{ss})$$

Consequently, for correspondence, $J_n(\infty) = C$

Steady-state oscillatory deformation in the linear response:

$(\chi_n \approx \pi/4)$

Strain-defined:

$$\sigma(t) = \gamma_o\{G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)\}$$

$$G'(\omega) = G_e + \omega[G_o - G_e]\int_0^{\infty} ds\ \varphi(s)\sin(\omega s)$$

$$G''(\omega) = \omega[G_o - G_e]\int_0^{\infty} ds\ \varphi(s)\cos(\omega s)$$

$$n_{12}(t) = \gamma_o\{G_n'(\omega)\sin(\omega t) + G_n''(\omega)\cos(\omega t)\}$$

If $G_n(t) = C\,G(t)$, then

$$G_n'(\omega) = CG'(\omega) \quad \text{and} \quad G_n''(\omega) = CG''(\omega)$$

e.g., for small ω: $G_n'(\omega) \propto G'(\omega) \propto \omega^2$ and $G_n''(\omega) \propto G''(\omega) \propto \omega$.[100]

Stress-defined:

$$\gamma(t) = \sigma_o\{J'(\omega)\sin(\omega t) - J''(\omega)\cos(\omega t)\}$$

$$J'(\omega) = J_\infty - \omega[J_\infty - J_o]\int_0^\infty ds\, \alpha(s)\sin(\omega s)$$

$$J''(\omega) = (1/\omega\eta) + \omega[J_\infty - J_o]\int_0^\infty ds\, \alpha(s)\cos(\omega s)$$

$$n_{12}(t) = \sigma_o\{J_n'(\omega)\sin(\omega t) - J_n''(\omega)\cos(\omega t)\}$$

Since $J_n^*(\omega) = G_n^*(\omega)J^*(\omega)$:

$$J_n'(\omega) = G_n'(\omega)J'(\omega) + G_n''(\omega)J''(\omega)$$

$$J_n''(\omega) = G_n''(\omega)J'(\omega) - G_n'(\omega)J''(\omega)$$

If $G_n(t) = G(t)$:

$$J_n'(\omega)/C = G'(\omega)J'(\omega) + G''(\omega)J''(\omega)$$

$$J_n''(\omega)/C = G''(\omega)J'(\omega) - G'(\omega)J''(\omega)$$

For small ω:

$$J_n'(\omega)/C = (\eta J_s\omega)^2 + 1 \approx 1$$

$$J_n''(\omega)/C = (\eta J_s\omega) - (\eta J_s\omega) = 0$$

For small ω, the birefringence is predicted to be exactly in phase with the oscillating stress, as expected: Note that $J_n''(\omega)$ provides no input on η.

Application of $G_n(t) = C\,G(t)$ for all t would require this same behavior for all ω.

Transient shear flow in the linear response ($\chi_n \approx \pi/4$):

Strain-defined:

Approximation $G_n(t)/G(t) = C$:

$$n_{ij}(t) = 2C\int_0^t ds G(t-s)\left[\frac{\partial\varepsilon_{ij}(s)}{\partial s} - \frac{1}{3}\delta_{ij}\frac{\partial\varepsilon_{\alpha\alpha}(s)}{\partial s}\right]$$

For a shear deformation:

$$\Delta n(t) = 2C\sigma(t) = 2C\int_0^t du\, G(t-u)\frac{\partial\gamma(u)}{\partial u}$$

Stress relaxation following a small step-strain γ_o:

$$\Delta n(t) = 2C\gamma_o G(t)$$

Stress-growth in low shear flow at shear rate $\dot{\gamma}$:

$$\Delta n(t) = 2C\dot{\gamma}\int_0^t du\, G(u)$$

Stress-defined:

$$n_{ij}(t) = (C/J_\infty)\int_0^t ds\, J_n(t-s)\left[\frac{\partial S_{ij}(s)}{\partial s} - \frac{1}{3}\delta_{ij}\frac{\partial S_{\alpha\alpha}(s)}{\partial s}\right]$$

If $J_n(t) = C$, consistent with $G_n(t) = G(t)$, then Δn in creep would step up at creep onset, and the remain constant--this does not seem reasonable.

Suppose $J_n(t) = C\,R(t)/J_s$

$$\Delta n(t) = 2(C/J_\infty)\int_0^t du\, R(t-u)\frac{\partial\sigma(u)}{\partial u}$$

The total recoverable strain $\hat{\gamma}_R(t)$ obtained a long time after the stress is reduced to zero at time t following an arbitrary stress history up to t is given by

$$\hat{\gamma}_R(t) = \int_0^t du\, R(t-u)\frac{\partial\sigma(u)}{\partial u}$$

Consequently,

$$\Delta n(t) = 2(C/J_\infty)\hat{\gamma}_R(t)$$

i.e., the birefringence provides a measure of the recoverable deformation in the chains.

For recovery starting at time T_e during stress relaxation:

$$\hat{\gamma}_R(T_e) = \gamma_o\{1 - \eta^{-1}\int_0^{T_e} du\, G(u)\}$$

Not equal to $\gamma_o G(t)$ unless $G(t) \propto \exp(-t/\tau)$, in which case $R(t) = J_s$

Second-Order Nonlinear Behavior:

$$S_{\alpha\beta}(t) = -\int_0^\infty du\, Q^{o}_{\alpha\beta}(t,u)\,\frac{\partial G(t-u)}{\partial u} - \delta_{\alpha\beta}P$$

Shear deformation along x_1 and shear gradient along x_2:

$$\mathbf{Q}^{\mathbf{o}}_{\mathbf{sh}} = \begin{pmatrix} 1+\gamma(t,u)^2 & \gamma(t,u) & 0 \\ \gamma(t,u) & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \qquad \gamma(t,u) = \int_u^t ds\,\dot{\gamma}(s)$$

Uniaxial elongational deformation with deformation along x_1:

$$\mathbf{Q}^{\mathbf{o}}_{\mathbf{el}} = \begin{pmatrix} \lambda(t,u)^2 & 0 & 0 \\ 0 & \lambda(t,u)^{-1} & 0 \\ 0 & 0 & \lambda(t,u)^{-1} \end{pmatrix}; \quad \ln[\lambda(t,u)] = \int_u^t ds\,\dot{\lambda}(s)$$

for the strain- and stress-defined experiments, respectively, where $G'_n(\omega)$ is defined in terms of $G_n(t)$ in a way analogous to the relation between $G'(\omega)$ and $G(t)$, etc. If it is assumed that $G_n(t)/G(t) = C$ for all t, then for the stress-defined history. Dynamic birefringence measurements in the 1,2-plane with small γ_o appear to be in accord with the stress-optic approximation over limited ranges in ω near the "terminal response" for which Dynamic measurements of $\Delta n_{1,3}(t)$ in the 1,3-plane with small γ_o, for which $\Delta n_{1,3}(t) = C(1-\hat{\psi})N_1(t)$ with $N_1(t)$ given by the expression for nonlinear normal stress in oscillatory shear deformation discussed above using the strain tensor $\mathbf{Q}^{\mathbf{o}}$, have been used to estimate $\hat{\beta}$ on the basis that $\hat{\psi} = \hat{\beta}$, as expected with the stress-optic approximation.[100] Nevertheless, the stress-optic approximation is known to be inadequate in some

Step strain of γ_o:

$$N_1(t,\gamma_o) \approx \gamma\sigma(t,\gamma_o) = \gamma_o^2 G(t)$$

Constant shear rate $\dot{\gamma}$:

$$N_1(t, \dot{\gamma}) \approx 2\dot{\gamma}^2\int_0^t du\, uG(u)$$

$$\sigma(t, \dot{\gamma}) \approx \dot{\gamma}\int_0^t du\, G(u)$$

Steady-state oscillation :

$$N_1(t) = S_{11}(t) - S_{22}(t) = \gamma_o^2\{G'(\omega) + [G''(\omega) - G''(2\omega)/2]\sin(2\omega t) - [G'(\omega) - G'(2\omega)/2]\cos(2\omega t)\}$$

$$N_3(t) = S_{11}(t) - S_{33}(t) = (1 - \hat{\beta})[S_{11}(t) - S_{22}(t)]$$

$\hat{\beta} = -N_2/N_1$, with $N_2 = N_3 - N_1$

If $G_n(t) = C\,G(t)$:

Step strain of γ_o:

$$\begin{aligned}
\Delta n \sin[2\chi_n((t, \gamma_o))] &= 2C\sigma(t; \gamma_o) = 2C\gamma_o G(t) \\
\Delta n \cos[2\chi_n((t, \gamma_o))] &= CN_1(t; \gamma_o) = C\gamma_o^2 G(t) \\
\cot[2\chi_n((t, \gamma_o))] &= N_1(t, \gamma_o)/2\sigma(t; \gamma_o) = \gamma_o/2
\end{aligned}$$

Constant shear rate $\dot{\gamma}$:

$$\begin{aligned}
\Delta n \sin[2\chi_n(t, \dot{\gamma})] &= 2C\sigma(t, \dot{\gamma}) = 2C\dot{\gamma}\int_0^t du\, G(u) \\
\Delta n \cos[2\chi_n(t, \dot{\gamma})] &= CN_1(t, \dot{\gamma}) = C\dot{\gamma}^2 \int_0^t du\, uG(u) \\
\cot[2\chi_n(t, \dot{\gamma})] &= N_1(t, \dot{\gamma})/2\sigma(t; \dot{\gamma}) = \dot{\gamma}\int_0^t du\, uG(u)/2\int_0^t du\, G(u)
\end{aligned}$$

elongation, respectively,[17g]

$$\mathbf{F_{sh}} = \begin{pmatrix} F_1[\gamma(t,u)] & 0 & 0 \\ 0 & F_1[\gamma(t,u)] & 0 \\ 0 & 0 & F_2[\gamma(t,u)] \end{pmatrix}$$

$$\mathbf{F_{el}} = \begin{pmatrix} F_3[\lambda(t,u)] & 0 & 0 \\ 0 & F_3[\lambda(t,u)] & 0 \\ 0 & 0 & F_3[\lambda(t,u)] \end{pmatrix}$$

$$\sigma(t) = \int_0^t du \frac{\partial G(u)}{\partial u}\gamma(t - u)F_1[\gamma(t - u)] \tag{88a}$$

$$N_1(t) = \int_0^t du \frac{\partial G(u)}{\partial u}\gamma(t - u)^2 F_1[\gamma(t - u)] \tag{88b}$$

$$\sigma(t,\dot{\gamma}) = -\int_0^t du\, \Delta\gamma(t,u)F_1[\Delta\gamma(t,u)]\frac{\partial G(u)}{\partial u} \tag{89}$$

$$N_1(t,\dot{\gamma}) = -\int_0^t du\, [\Delta\gamma(t,u)]^2 F_1[\Delta\gamma(t,u)]\frac{\partial G(u)}{\partial u} \tag{90}$$

$$\tau(t,\dot{\varepsilon}) = -\int_0^t du\, \Delta\varepsilon(t,u)F_3[\Delta\varepsilon(t,u)]\frac{\partial E(u)}{\partial u} \tag{91}$$

for incompressible fluids, where $\Delta\gamma(t,u) = (t - u)\dot{\gamma}$, etc.

shear-rate dependent functions in steady-state flow given information on the linear viscoelastic shear relaxation modulus G(t):[18; 43]

$$
\begin{aligned}
\eta(\dot{\gamma}) &= \eta H(\tilde{\beta}\tau_c\dot{\gamma}) \\
S^{(1)}(\dot{\gamma}) &= J_s S(\tilde{\beta}\tau_c\dot{\gamma}) \\
J_s(\dot{\gamma}) &= J_s P(\tilde{\beta}\tau_c\dot{\gamma})
\end{aligned}
$$

8. Strain-induced birefringence for concentrated and undiluted polymeric fluids.

Rheo-optical measurements have long been used in conjunction with rheological measurements. Examples include strain-induced birefringence, optical dichroism and light scattering.[16; 17h; 24c; 27; 97; 99; 115-120] Here only birefringence measurements will be discussed. The increasing availability of commercially available rheo-optical equipment afford enhanced opportunities for the use of birefringence techniques. For an isotropic material, the principal components (proper vectors) n_1, n_2 and n_3 of the refractive index tensor are equal, but this symmetry is usually lost under deformation. Thus, in the shear and elongational deformations discussed above, with deformation in the 1,3-plane (in Cartesian coordinates), the birefringence $\Delta n = n_1 - n_2$ measured by light propagating along x_3 will generally not be zero, and the angle $\chi_n \le \pi/4$ between n_1 and x_1 will depend on the deformation. The angle χ_n may be visualized by the orientation of the extinction cross of isocline viewed between crossed polars under appropriate optical arrangements. Several effects may contribute to the strain-induced optical anisotropy, including (i) orientation of optically anisotropic chain elements, and (ii) an internal field effect called "form birefringence" arising from spatial variations of the refractive index, as with the anisotropy in a deformed single chain in a dilute solution, or phase separated regimes in a blend, or a semicrystalline polymer.[17i; 27a] Here, consideration is limited to homogeneous amorphous polymers or their concentrated solutions, for which the form birefringence may be neglected. In the simplest case, of interest here, the optical anisotropy of the chain elements is assumed to have ellipsoidal symmetry, with a major axis along the chain axis, so that the optical anisotropy is directly associated with anisotropy of the chain conformation.[16e; 27b; 120] Clearly, that is a major approximation that may not always be valid, and deviations from the behavior anticipated with the simplification may provide insight on the material,[93; 121; 122] see examples cited below.

$$
\Delta n = C\tau(\lambda) = (C/D_e)[D_e/D_e(\lambda)]\hat{\varepsilon}_R(\lambda)
$$

for a uniaxial elongation with stretch $\lambda = 1 + \varepsilon_{11}$ along x_1 ($\chi = 0$) under a tensile stress $\tau = S_{11} - S_{22}$, and

$$\begin{aligned}
\Delta n \sin[2\chi_n(\gamma)] &= 2C\sigma(\gamma) = 2(C/J_e)[J_e/J_e(\gamma)]\hat{\gamma}_R(\gamma) \\
\Delta n \cos[2\chi_n(\gamma)] &= CN_1(\gamma) \\
\cot[2\chi_n(\gamma)] &= N_1(\gamma)/2\sigma(\gamma) = m\hat{\gamma}_R(\gamma)
\end{aligned}$$

Steady-state response to a small amplitude oscillatory shear deformation:[99; 125]

ω.[99]

Transient strain-induced birefringence

Approximation $G_n(t)/G(t) = C$:

for a sample relaxed for $t < 0$. Thus, for an elongational deformation ($\chi_n = 0$) of an incompressible viscoelastic solid under a strain-defined history resulting in a transient stress $\tau(t) = S_{11}(t) - S_{22}(t)$ and transient strain $\varepsilon(t) = \varepsilon_{11}(t)$ for deformation along x_1,

$$\Delta n(t) = C\tau(t) = 3C\int_0^t du\, G(t-u)\frac{\partial\varepsilon(u)}{\partial u}$$

Similarly, for a recently small shear deformation to obtain a linear viscoelastic response, $\Delta n(t) = 2n_{12}(t)\sin[\chi_n(t)]$, so that since in this case $\sin[2\chi_n(t)] \approx 1$, the preceding gives

Steady-state shear flow in the linear response:

$$\Delta n = 2C\dot{\gamma}\int_0^\infty du\, G(u) = 2C\eta\dot{\gamma} = 2(C/J_s)\hat{\gamma}_R(\dot{\gamma})$$

with $\hat{\gamma}_R(\dot{\gamma})$ the total strain recoil on cessation of flow.

An important use of strain-induced birefringence measurements is in the estimation of the first-normal stress difference $N_1(t)$ in a transient response in a strongly nonlinear response. Neither $N_1(t;\gamma_o)$ in relaxation following a step-strain γ_o nor $N_1(t;\dot{\gamma})$ in shear deformation in nonlinear flows at a constant shear rate are trivial to measure mechanically. For example, although $N_1(t;\dot{\gamma})$ may be determined from the force required to prevent separation of a cone and plate during a shear deformation, the slight movement unavoidable in the feedback mechanism to produce a measure of the required force may complicate the interpretation of the transient response.[128] The error should be less serious in a steady flow.

Steady-state flow

Step-strain γ_o in the 1,2-plane gives

$$\begin{aligned}
\Delta n \sin[2\chi_n(t;\gamma_o)] &= 2C\sigma(t;\gamma_o) = 2C\gamma_o F(\gamma_o)G(t) \\
\Delta n \cos[2\chi_n(t;\gamma_o)] &= CN_1(t;\gamma_o) = C\gamma_o^2 F(\gamma_o)G(t) \\
\cot[2\chi_n(t;\gamma_o)] &= N_1(t;\gamma_o)/2\sigma(t;\gamma_o) = \gamma_o/2
\end{aligned}$$

.[129; 130]

Steady-state shear flow,

$$\begin{aligned}
\Delta n \sin[2\chi_n(t;\dot{\gamma})] &= 2C\sigma(t;\dot{\gamma}) \\
\Delta n \cos[2\chi_n(t;\dot{\gamma})] &= CN_1(t;\dot{\gamma}) \\
\cot[2\chi_n(t;\dot{\gamma})] &= N_1(t;\dot{\gamma})/2\sigma(t;\dot{\gamma}) = S^{(1)}(t;\dot{\gamma})\sigma(t;\dot{\gamma})
\end{aligned}$$

for the 1,2-plane, with $\sigma(t;\dot{\gamma})$ and $N_1(t;\dot{\gamma})$ computed as discussed in the section on nonlinear viscoelasticity, $\chi_n(t;\dot{\gamma}) \le \pi/4$ decreases with increasing $\dot{\gamma}$, and. Similarly, $\Delta n_{1,3}(t;\dot{\gamma}) = C(1 - \hat{\psi})N_1(t;\dot{\gamma})$ in the 1,3-flow plane in this approximation if it is assumed that $\hat{\psi}$ is independent of t and $\dot{\gamma}$. At steady-state flow, these relations become

$$\Delta n \sin[2\chi_n(\dot{\gamma})] = 2C\sigma(\dot{\gamma}) = 2(C/J_s)[J_s/J_s(\dot{\gamma})]\hat{\gamma}_R(\dot{\gamma})$$

$$\Delta n \cos[2\chi_n(\dot{\gamma})] \;=\; CN_1(\dot{\gamma}) \;=\; 2(C/J_s)[S^{(1)}(\dot{\gamma})/J_s(\dot{\gamma})][J_s/J_s(\dot{\gamma})]\hat{\gamma}_R(\dot{\gamma})^2$$
$$\cot[2\chi_n(\dot{\gamma})] \;=\; N_1(t;\dot{\gamma})/2\sigma(t;\dot{\gamma}) \;=\; S^{(1)}(\dot{\gamma})\sigma(\dot{\gamma}) \;=\; [S^{(1)}(\dot{\gamma})/J_s(\dot{\gamma})]\hat{\gamma}_R(\dot{\gamma})$$

where
$S^{(1)}(t;\dot{\gamma}) = N_1(t;\dot{\gamma})/2[\sigma(t;\dot{\gamma})]^2$
$\sigma(\dot{\gamma}) = \dot{\gamma}\eta(\dot{\gamma})$
$\hat{\gamma}_R(\dot{\gamma}) = J_s(\dot{\gamma})\dot{\gamma}\eta(\dot{\gamma})$ is the total recoverable strain following cessation of steady-state flow. Similarly, $\Delta n_{1,3}(\dot{\gamma}) = C(1 - \hat{\psi})N_1(\dot{\gamma})$ in the 1,3-flow plane if it is assumed that $\hat{\psi}$ is independent of $\dot{\gamma}$. The final forms emphasize the relation of the birefringence to the constrained recoil $\hat{\gamma}_R(\dot{\gamma})$ on cessation of flow, and are analogous to the relations given above for an elastic solid (i.e., replace $\dot{\gamma}$ by γ, J_s by J_e and $S^{(1)}(\dot{\gamma})/J_s(\dot{\gamma})$ by m). As discussed in the previous section, $S^{(1)}(\dot{\gamma})/J_S(\dot{\gamma})$ depends on the distribution of components (e.g., the molecular weight distribution), where $S^{(1)}(\dot{\gamma})/J_S(\dot{\gamma}) \le 1$, with the equality occurring for flows of monodisperse polymer with $\tau_c\dot{\gamma} < 1$. The analogy with the behavior for a linear elastic solid is strengthened by noting that $S^{(1)}(\dot{\gamma})/J_s(\dot{\gamma})$ tends toward 0.5 with increasing $\tau_c\dot{\gamma}$, similar to the value of m noted above for a linear elastic solid, as remarked above. Estimates of $N_1(t;\dot{\gamma})$ made in this way appear to be similar to those obtained by direct mechanical measurements.[106; 107; 109; 110] This correspondence could reflect the marked weighting of the response toward the longer time response in $G_n(t)$, and may not provide definitive evidence for constant $G_n(t)/G(t)$ for all t. In part, the use of the stress-optic approximation here is motivated by statistical mechanical theories which suggest that Δn and ΔS depend on similar averages over chain conformations for flexible chain polymers,[16h; 22h; 27b; 120] but the similarity with the expression for an elastic solid given above is evident, and is not accidental since the theories in both cases are based on additivity of incremental stresses attributed to molecular deformations, similar to the treatment of a collection of macroscopic beads and dashpots.[22h]

Relations comparable to the preceding do not appear to be available for a stress-defined history. Moreover, there are few data to evaluate the nature of $J_n(t)$, a situation that may change with the availability of commercial rheo-optical instrumentation to permit the implementation of stress-defined histories. The lack of experimental and theoretical attention may reflect both the lack of commercially available equipment to study the transient response with a stress-defined shear deformation and the perception that $J_n(t)$ is a constant, as required by the stress optic approximation with constant $G_n(t)/G(t)$, in which case birefringence measurements for a stress-defined history would be relatively uninteresting. However, as remarked in the preceding, the evidence that $G_n(t)/G(t)$ must be considered to be independent of t is not definitive. For example, $G_n(t)$ could relax more slowly than G(t) for large t, but still decay fast enough to give the response $G'_n(\omega) \propto \omega^2$ and $G''_n(\omega) \propto \omega$ reported experimentally for small ω.[100] In addition, as may be seen in the expression for $J_n(t)$, deviation of $G_n(t)/G(t)$ from a constant for small t will have an impact on $J_n(t)$ at large t. As mentioned above, birefringence measurements are sometimes made on amorphous materials near T_g, with the finding that a single constant C cannot be applied over the entire range of ω at a given T.[126; 127] This result is readily accommodated in terms of a distribution of retardation times to represent α(t), with the response corresponding to an Andrade creep region having a different value of C than that associated with the portion of the retardation times associated with the Rouse-like or entanglement responses.

Given the uncertain status of the stress-optic approximation, it is of interest to consider the consequences of a strain-optic approximation for use with stress-defined experiments. Since the birefringence is a constant in steady-state flow, it is apparent that $J_n(t)$ must not have the term proportional to t found in J(t), even if $J_n(t)$ is not a constant as required by the stress-optic approximation. Further, the preceding provides a clear relationship between the birefringence and the recoverable strain for an elastic solid under a small deformation and a fluid in a slow steady-state flow. For lack of a definitive treatment, it will be assumed that these features are preserved in a transient deformation, and that the birefringence at arbitrary time is related to the total constrained recoil that would be recovered if the stress were suddenly reduced to zero at that time; the calculation of this following an arbitrary stress history is discussed above in the section on creep and recovery in the section on linear viscoelastic phenomenology. Thus, for recently small deformations on an incompressible sample relaxed at the beginning of the deformation, such that the linear viscoelastic response functions may be used, it is presumed that $J_n(t) = (C/J_\infty)R(t)$, and that the deviatoric components of the refraction tensor are given by,

$$n_{ij}(t) = (C/J_\infty)\int_0^t ds\, R(t-s)\left[\frac{\partial S_{ij}(s)}{\partial s} - \frac{1}{3}\delta_{ij}\frac{\partial S_{\alpha\alpha}(s)}{\partial s}\right]$$

Consequently, for elongational or shear deformations, with total recoverable strains $\hat{\varepsilon}_R(t)$ and $\hat{\gamma}_R(t)$, respectively,

$$\Delta n(t) = (C/D_\infty)\hat{\varepsilon}_R(t) = (C/3D_\infty)\int_0^t du\, R(t-u)\frac{\partial \tau(u)}{\partial u} \qquad (124a)$$

$$\Delta n(t) = 2(C/J_\infty)\hat{\gamma}_R(t) = 2(C/J_\infty)\int_0^t du\, R(t-u)\frac{\partial \sigma(u)}{\partial u} \qquad (124b)$$

For example, for a step stress σ_0 initiated at zero time, and terminated at time T_e on a linear viscoelastic fluid

$$\Delta n(t) \;=\; 2(C/J_s)\sigma_o\int_0^t du\, R(t - u)\, \delta(u - 0) \;=\; 2(C/J_s)R(t)\sigma_o \qquad (125)$$

At a time ϑ following the onset of constrained recoil after creep terminated at time $t = T_e$,

$$\begin{aligned} \Delta n(\vartheta) &= 2(C/J_s)\{\hat{\gamma}_R(T_e) - \hat{\gamma}_R(\vartheta)\} && (126a) \\ &= 2(C/J_s)\{R(\vartheta + T_e) - R(\vartheta)\}\sigma_o && (126b) \end{aligned}$$

Strict application of the stress-optic approximation would make Δn independent of time by contrast with these expressions, but data to evaluate these alternatives do not seem to be available. In an alternative deformation history, the total recoverable strain $\hat{\gamma}_R(T_e, \gamma_o)$ that would be measured if the stress were dropped to zero at time T_e during stress relaxation of a fluid following a jump γ_o in the strain is given above by $\hat{\gamma}_R(T_e, \gamma_o) = \gamma_o[1 - \eta^{-1}\int_0^{T_e} ds\, G(s)]$. With this expression, $\Delta n(t) \approx 2(C/J_s)\hat{\gamma}_R(t,\gamma_o)$ is not equal to the relation $\Delta n(t) \approx 2CG(t)$ given above using the stress-optic approximation, unless $G(t)$ is given by an exponential function, in which case $R(t)$ is a constant, as would be consistent with the stress-optic approximation.

A few studies are available for a step stress τ_o initiated at zero time, and terminated at time T_e on a linear viscoelastic solid, for which $D(t) \approx R(t)/3$,

$$\begin{aligned} \Delta n(t) &= (C/D_e)\tau_o D(t) && 0 < t < T_e && (127a) \\ \Delta n(\vartheta) &= (C/D_e)\tau_o[D(\vartheta + T_e) - D(\vartheta)] && t \geq T_e && (127b) \end{aligned}$$

where $\vartheta = t - T_e$. Thus, if T_e is large enough that $D(t)$ approaches its equilibrium value D_e during creep, then $\Delta n(\vartheta)/C\tau_o = D_e - D(\vartheta)$ during recovery ($t \geq T_e$). A recent study on a loosely crosslinked rubber may illustrate the delicacy of birefringence measurements.[131] Whereas the data on the strain in creep and recovery appear qualitatively normal, the birefringence was observed to be positive in creep, and negative in recovery. The numerous dangling chains (chains attached only once to the network) may provide an explanation for this unexpected behavior if these chains relaxed during creep, and were subsequently oriented orthogonal to the stretch direction during the relatively large initial recovery, so that Δn was subsequently negative during recovery for $t > T_e$. This would provide an example of the failure of the initial assumption concerning the origin of the birefringence introduced above.

Application to nonlinear deformations is less readily evaluated. Steady-state shear flow reached by a stress or strain defined histories must be equivalent. As seen in the preceding, in such a case $\cot[2\chi_n(\dot{\gamma})] = [S^{(1)}(\dot{\gamma})/J_s(\dot{\gamma})]\hat{\gamma}_R(\dot{\gamma})$, with $S^{(1)}(\dot{\gamma})/J_s(\dot{\gamma}) \approx 1$ if the flow deformation may be characterized by use of $\mathbf{Q_o}$. The function $\cot[2\chi_n(t;\, \sigma_o)]$ in linear or nonlinear creep under a step-stress σ_o must approach this behavior in steady-state flow. Thus, using the constrained recoil $\hat{\gamma}_R(t;\, \sigma_o)$ on removal of the stress at time t, one might expect that

$$\cot[2\chi_n(t;\, \sigma_o)] \quad = \quad \Phi(t;\, \sigma_o)\hat{\gamma}_R(t;\, \sigma_o) \tag{129}$$

where $\eta(t;\, \dot{\gamma}) = \sigma(t;\, \dot{\gamma})/\dot{\gamma}$, $R(t;\, \sigma_o) = \hat{\gamma}_R(t;\, \sigma_o)/\sigma_o$, and $\Phi(t;\, \sigma_o) = S^{(1)}(t;\, \sigma_o)/R(t;\, \sigma_o)$. Presumably, $\Phi(t;\, \sigma_o)$ will vary from about unity for small t, since then the strain must be recently small, to its limiting value of about 0.5 in steady-state nonlinear flow. In principle, $\Phi(t;\, \sigma_o)$ could be estimated by an interative calculation involving the relations given in the section on nonlinear rheological behavior, as has been done for $J_s(\dot{\gamma})$.[43]

In summary, it appears that the stress-optic approximation, embodied in the expression $G_n(t)/G(t) \approx C$ for all t, may sometimes be used for strain-defined deformations to estimate the first-normal stress and the shear stress in a shear deformation, and the tensile stress in an elongational deformation, although it is clear that the approximation is not always valid, especially for deformation involving the short-time features of the response, e.g., the transition from the Andrade creep to the Rouse-like response in the retardation spectrum. The experimental situation is not clear for stress-defined deformations, with strict compliance with the relation $G_n(t)/G(t) \approx C$ requiring that $J_n(t)$ be independent of time. An alternative approximation may be to put $J_n(t)/R(t) \approx C/J_\infty$ in a strain-optic approximation, with neither the stress-optic or strain-optic relations expected to be exact.

1 Society of Rheology Website, http://www.umecheme.maine.edu/sor/default.htm., 1999.

2 Staverman, A. J.; Schwarzl, F. "Linear deformation behavior of high polymers" In *Die Physik der Hochpolymeren*; H. A. Stuart, ed.; Vol. IV; Springer-Verlag; Berlin, 1956; Chapt. 1.

3 Treloar, L. R. G. *The Physics of Rubber Elasticity*; 2rd ed.; Oxford University Press; London, 1958, (a) 156, (b) 64, (c) 177.

4 Coleman, B. D., Markovitz, H., and Noll, W. *Viscometric Flows of Non-Newtonian Fluids*; Springer-Verlag; New York, 1966, (a) 34, (b) 55, (c) 54, (d) 46.

5 McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley; New York, 1967.

6 Aklonis, J. J.; MacKnight, W. J.; Shen, M. C. *Introduction to Polymer Viscoelasticity*; Wiley-Interscience; New York, 1972.

7 Bartenev, G. M.; Zelenev, Y. V., eds. *Relaxation Phenomena in Polymers*; John Wiley & Sons (Halsted Press); New York, 1974.

8 Walters, K. *Rheometry*; John Wiley & Sons; New York, 1975, (a) 44, (b) 48, (c) 52, (d) 93, (e) 102, (f) 100.

9 Markovitz, H. "Rheology" In *Physics Vade Mecum*; H. L. Anderson, ed.; Am. Inst. Phys.; New York, 1981; p. 274-86.

10 Plazek, D. J. "Viscoelastic and steady-state rheological response" In *Methods of Experimental Physics*; R. A. Fava, ed.; Vol. 16C; Academic Press; New York, 1980; Chapt. 11.

11 Ferry, J. D. *Viscoelastic Properties of Polymers*; 3rd ed.; John Wiley & Sons Inc.; New York, 1980, (a) 37, (b) 40, (c) 48, (d) 96, (e) 132, (f) 154, (g) 603, (h) 168, (i) 1, (j) 177, (k) 224, (m) 17, (n) 3, (p) 5, (q) 68, (r) 33, (s) 103, (t) 70, (u) 69, (v) 60, (w) 83, (x) 63, (y) 91, (z) 287, (a') 227, (b') 266, (c') 366, (d') 229, (e') 232, (f') 390, (g') 388, (h') 411, (i') 545.

12 Bailey, R. T.; North, A. M.; Pethrick, R. A. *Molecular Motion in High Polymers* The International Series of Monographs on Chemistry, J. E. Baldwin, *et al.*, eds.; Clarendon Press; Oxford, 1981.

13 Christensen, R. M. *Theory of Viscoelasticity*; 2nd. ed.; Academic; New York, 1982, (a) 353, (b) 1, (c) 5, (d) 7.

14 Dealy, J. M. *Rheometers for Molten Plastics*; Van Nostrand Reinhold Co.; New York, 1982, (a) 1, (b) 116, (c) 126, (d) 148, (e) 75, (f) 61.

15 Bohdanecký, M.; Kovář, J. *Viscosity of Polymer Solutions* Polymer Science Library, A. D. Jenkins, ed.; Vol. 2; Elsevier Scientific Publ. Co.; Amsterdam, 1982, (a) 167, (b) 175, (c) 177.

16 Janeschitz-Kriegl, H. *Polymer Melt Rheology and Flow Birefringence*; Springer-Verlag; Berlin ; New York, 1983, (a) 455, (b) 4, (c) 467, (d) 464, (e) 355, (f) 60, (g) 177, (h) 217.

17 Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press; Oxford, UK, 1986, (a) 222, (b) 366, (c) 218, (d) 91, (e) 226, (f) 281, (g) 255, (h) 121, (i) 166.

18 Berry, G. C.; Plazek, D. J. "Rheology of polymeric fluids" In *Glass: Science and Technology*; D. R. Uhlmann; N. J. Kreidl, ed.; Vol. 3; Academic Press; New York, 1986; 319-62.

19 Bird, R. B.; Armstrong, R. C.; Hassager, O. *Dynamics of Polymeric Liquids. Vol. 1. Fluid Mechanics*; 2nd ed.; John Wiley & Sons, Inc.; New York, 1987, (a) 158, (b) 269, (c) 290.

20 Bird, R. B.; Curtiss, C. C.; Armstrong, R. C.; Hassager, O. *Dynamics of Polymeric Liquids. Vol. 2. Kinetic Theory*; 2nd ed.; John Wiley & Sons, Inc.; New York, 1987.

21 Collyer, A. A.; Clegg, D. W., eds. *Rheological Measurement*; Elsevier Science Co.; New York, 1988.

22 Larson, R. G. *Constitutive Equations for Polymer Melts and Solutions*; Butterworths; Boston, 1988, (a) 49, (b) 93, (c) 318, (d) 118, (e) 120, (f) 233, (g)120, (h) 95.

23 Tschoegl, N. W. *The Phenomenological Theory of Linear Viscoelastic Behavior*; Springer-Verlag; Berlin, 1989, (a) 513, (b) 551, (c) 69, (d) 47, (e) 560, (f) 21, (g) 508, (h) 55, (i) 413, (j) 401, (k) 406, (m) 157, (n) 409, (p) 157, (q) 425.

24 White, J. L. *Principles of Polymer Engineering Rheology*; John Wiley & Sons, Inc.; New York, 1990, (a) 83, (b) 163, (c) 174.

25 Matsuoka, S. *Relaxation Phenomena in Polymers*; Hanser; Munich, 1992.

26 Yanovsky, Y. G. *Polymer Rheology: Theory and Practice*; Chapman & Hall; New York, 1993, (a) 200, (b) 235.

27 Fuller, G. G. *Optical Rheometry of Complex Fluids* Topics in Chemical Engineering, K. E. Gubbins, ed.; Oxford University Press; New York, Oxford, 1995, (a) 117, (b) 109, (c) 149, (d) 167, (e) 193.

28 Coleman, B. D.; Noll, W. "Foundations of linear viscoelasticity" *Rev. Modern Phys.* **1961**, *33*, 239-49.

29 Petrie, C. J. S. *Elongational Flows: Aspects of the Behaviour of Model Elasticoviscous Fluids*; Pitman; London ; San Francisco, 1979.

30 Meissner, J.; Hostettler, J. "A new elongational rheometer for polymer melts and other highly viscoelastic liquids" *Rheol. Acta* **1994**, *33*, 1-21.

31 Macosko, C.; Starita, J. M. "New rheometer is put to the test" *SPE-J.* **1971**, *27 (11)*, 38-42.

32 Plazek, D. J. "Magnetic bearing torsional creep apparatus" *J. Polym. Sci. A-2* **1968**, *6*, 621.

33 Berry, G. C.; Birnboim, M. H.; Park, J. O.; Meitz, D. W.; Plazek, D. J. "A rotational rheometer for rheological rtudies with prescribed strain or stress history" *J. Polym. Sci.: Part B: Polym. Phys.* **1989**, *27*, 273.

34 Rabinowitsch, B. "Über die Viskosität und Elastizität von Solen" *Z. Phys. Chem., Abt. A* **1929**, *145*, 1-26.

35 Barr, G. *A Monograph of Viscometry*; Oxford University Press (Authorized facsimile by University Microfilms, Ann Arbor, MI, 1967); London, 1931.

36 Carslaw, H. S.; Jaeger, J. C. *Operational Methods in Applied Mathematics*; Dover Publications, Inc.; New York, 1948.

37 Shermergor, T. D. "Description of relaxation phenomena in structurally nonhomogeneous polymers by correlation functions" In *Relaxation Phenomena in Polymers*; G. M. Bartenev; Yu. V. Zelenev, eds.; John Wiley & Sons (Halsted Press); New York, 1974.

38 Berry, G. C. "Rheological and rheo-optical studies on nematic solutions of a rodlike polymer: Bingham Award Lecture" *J. Rheology* **1991**, *35*, 943.

39 Meissner, J. "Experimental problems and recent results in polymer melt rheometry" *J. Macromol. Chem., Macromol. Symp.* **1992**, *56*, 25-42.

40 Ostrowsky, N.; Sornette, D.; Parker, R.; Pike, E. R. "Exponential sampling method for light scattering polydispersity analysis" *Opt. Acta* **1981**, *28*, 1059-70.

41 Baumgaertel, M.; Winter, H. H. "Determination of discrete relaxation and retardation time spectra from dynamic mechanical data" *Rheol. Acta* **1989**, *28*, 511-19.

42 Sips, R. "General theory of deformation of viscoelastic substances" *J. Polym. Sci.* **1951**, *7*, 191-205.

43 Nakamura, K.; Wong, C. P.; Berry, G. C. "Strain criterion in nonlinear creep and recovery in concentrated polymer solutions" *J. Polym. Sci.: Polym. Phys. Ed.* **1984**, *22*, 1119-48.

44 Berry, G. C.; Plazek, D. J. "On the use of stretched-exponential functions for both linear viscoelastic creep and stress relaxation" *Rheol. Acta* **1997**, *36*, 320-9.

45 Riande, E.; Markovitz, H. "Approximate relations among compliance functions of linear viscoelasticity for amorphous polymers" *J. Polym. Sci.: Polm. Phys. Ed.* **1975**, *13*, 947-51.

46 Plazek, D. J.; Raghupathi, N.; Orbon, S. J. "Determination of dynamic storage and loss compliances from creep data" *J. Rheol.* **1979**, *23*, 477-88.

47 Markovitz, H. "The reduction principle in linear viscoelasticity" *J. Phys. Chem* **1965**, *69*, 671.

48 Markovitz, H. "Superposition in rheology" *J. Polym. Sci.: Symp.* **1975**, *50*, 431-56.

49 Berry, G. C.; "The viscosity of polymers and their concentrated solutions" *Adv. in Polym. Sci.* **1968**, *5*, 261-357.

50 Berry, G. C. "Crossover behavior in the viscosity of semiflexible polymers: Intermolecular interactions as a function of concentration and molecular weight" *J. Rheol.* **1996**, *40*, 1129-54.

51 Boyer, R. F. "The relation of transition temperatures to chemical structure in high polymers" *Rubber Rev.* **1963**, *36*, 1303-421.

52 Berry, G. C. "Thermodynamic and conformational studies of polystyrene. II. Intrinsic viscosity studies on dilute solutions of linear polystyrenes" *J. Chem. Phys.* **1967**, *46*, 1338.

53 Berry, G. C. "Molecular weight distribution" In *Encyclopedia of Materials Science and Engineering*; M. B. Bever, ed.; Pergamon Press; Oxford, 1986; 3759.

54 Russel, W. B.; Saville, D. A.; Schowalter., W. R. *Colloidal Dispersions*; Cambridge University Press; Cambridge, 1989, (a) 498, (b) 88, (c) 129, (d) 162, (e) 466, (f) 469, (g) 474.

55 Berry, G. C. "Remarks on a relation among the intrinsic viscosity, the radius of gyration, and the translational friction coefficient" *Journal of Polymer Science, Part B: Polymer Physics* **1988**, *26*, 1137-42.

56 Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row; New York, 1971, (a) 266, (b) 314.

57 Flory, P. J.; "Molecular configuration and thermodynamic properties from intrinsic viscosities" *J. Polym. Sci.* **1950**, *5*, 745-7.

58 Casassa, E. F.; Berry, G. C. "Reflections and comments on "Molecular configuration and thermodynamic properties from intrinsic viscosities" by Paul J. Flory and Thomas G Fox" *J. Polym. Sci., Pt. B: Polym. Phys.* **1996**, *34*, 203-6.

59 Casassa, E. F.; Berry, G. C. "Polymer solutions" In *Comprehensive Polymer Science*; G. Allen, ed.; Vol. 2; Pergamon Press; New York, 1988; Chapt. 3.

60 Brandrup, J.; Immergut, E. H., eds. *Polymer Handbook*; 3rd ed.; Wiley; New York, 1989.

61 Casassa, E. F.; Berry, G. C. "Angular distribution of intensity of Rayleigh scattering from comblike branched molecules" *J. Polym. Sci.: Part A-2* **1966**, *4*, 881.

62 Lodge, T. P. "Solvent dynamics, local friction, and the viscoelastic properties of polymer solutions" *J. Phys. Chem.* **1993**, *97*, 1480-7.

63 Harrison, G.; Lamb, J.; Matheson, A. J. "The viscoelastic properties of dilute solutions of polystyrene in toluene" *J. Phys. Chem.* **1966**, *68*, 1072-8.

64 Osaki, K. "Viscoelastic properties of dilute polymer solutions" *Adv. Polym. Sci.* **1973**, *12*, 1-64.

65 Birnboim, M. H. "The viscoelastic properties of low molecular weight polystyrene solutions in high frequency regime: Polymer-solvent interaction" *Proc. IUPAC Macro 82* **1982**, *July 12-16*, 872.

66 Schrag, J. L., *et al.* "Local modification of solvent dynamics by polymeric solutes" *J. Non-Cryst. Solids* **1991**, *131*, 537-43.

67 Yoshizaki, T.; Takaeda, Y.; Yamakawa, H. "On the correlation between the negative intrinsic viscosity and the rotatory relaxation time of solvent molecules in dilute polymer solutions" *Macromolecules* **1993**, *26*, 6891-6.

68 Yamakawa, H. "Concentration dependence of polymer chain configurations in solution" *J. Chem. Phys.* **1961**, *34*, 1360-72.

69 Batchelor, G. K. "The effect of Brownian motion on the bulk stress in a suspension of spherical particles" *J. Fluid Mech.* **1977**, *83*, 97-117.

70 Pal, R. "Rheology of emulsions containing polymeric liquids" In *Encyclopedia of Emulsion Technology*; Paul Becher, ed.; Vol. 4; Marcel Dekker, Inc.; New York, 1996; 93-263.

71 Park, J. O.; Berry, G. C. "Moderately concentrated solutions of polystyrene. 3. Viscoelastic measurements at the Flory Theta temperature" *Macromolecules* **1989**, *22*, 3022-9.

72 de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press; Ithaca, NY, 1979.

73 Narayanaswamy, O. S. "Annealing of glass" In *Glass: Science and Technology*; D. R. Uhlmann; N. J. Kreidl, ed.; Vol. 3; Academic Press; New York, 1986; 275-318.

74 Plazek, D. J.; Berry, G. C. "Physical aging of polymer glasses" In *Glass: Science and Technology*; D. R. Uhlmann; N. J. Kreidl, ed.; Vol. 3; Academic Press; New York, 1986; 363-99.

75 Graessley, W. W. "The entanglement concept in polymer rheology" *Adv. Polym. Sci.* **1974**, *16*, 1-179.

76 Berry, G. C.; Nakayasu, H.; "Viscosity of poly(vinyl acetate) and its concentrated solutions" *Journal of Polymer Science, Polymer Physics Edition* **1979**, *17*, 1825-44.

77 da Andrade, E. N. *Viscosity and Plasticity*; Chemical Publishing Co.; New York, 1951.

78 Berry, G. C. "The stress-strain behavior of materials exhibiting Andrade creep" *Polym Eng Sci* **1976**, *16*, 777-81.

79 Orbon, S. J.; Plazek, D. J. "The recoverable compliance of a series of bimodal molecular weight blends of polystyrene" *J. Polym. Sci.: Polym. Phys. Ed.* **1979**, *17*, 1871.

80 Berry, G. C. "Terminal retardation times and weights for the Rouse model for a crosslinked network" *J. Polym. Sci.: Part B: Polym. Phys.* **1987**, *25*, 2203-5.

81 Masuda, T.; Takahashi, M.; Onogi, S. "Steady-state compliance of polymer blends" *Appl. Polym. Symp.* **1973**, *20*, 49-60.

82 Kurata, M. "Effect of molecular weight distribution on viscoelastic properties of polymers. 2. Terminal relaxation time and steady-state compliance" *Macromolecules* **1984**, *17*, 895-8.

83 Fujita, H.; Einaga, Y. "Self diffusion and viscoelasticity in entangled systems. II. Steady-state viscosity and compliance of binary blends" *Polymer J.* **1985**, *17*, 1189-95.

84 Montfort, J. P.; Marin, G.; Monge, P. "Molecular weight distribution dependence of the viscoelastic properties of linear polymers: The coupling of reptation and tube-renewal effects" *Macromolecules* **1986**, *19*, 1979-88.

85 des Cloizeaux, J. "Relaxation of entangled polymeric melts" *Macromolecules* **1990**, *23*, 3992-4006.

86 Tsenoglou, C. "Molecular weight polydispersity effects on the viscoelasticity of entangled linear polymers" *Macromoleucules* **1991**, *24*, 1762-7.

87 Berry, G. C. "Rheological properties of blends of rodlike chains with flexible or semiflexible chains" *Trends in Polymer Science* **1993**, *1*, 309.

88 Berry, G. C. "Rheology of blends of liquid crystalline and flexible chain polymers" *Trends Poly. Sci.* **1996**, *4*, 289-92.

89 Plazek, D. J.; Chay, I. C. "The evolution of the viscoelastic retardation spectrum during the development of an epoxy resin network" *J. Polym. Sci.: Part B: Polym. Phys.* **1991**, *29*, 17-29.

90 Winter, H. H.; Mours, M. "Rheology of polymers near liquid-solid transitions" *Adv. Polym. Sci.* **1997**, *134*, 167-234.

91 Plazek, D. J. "Oh, thermorheological simplicity, wherefore art thou?" *J. Rheol.* **1996**, *40*, 987-1014.

92 Plazek, D. J.; Chelko, A. J., Jr. "Temperature dependence of the steady state recoverable compliance of amorphous polymers" *Polymer* **1977**, *18*, 15-8.

93 Inoue, T.; Mizukami, Y.; Okamoto, H.; Matsui, H.; Watanabe, H.; Kanaya, T.; Osaki, K. "Dynamic birefringence of vinyl polymers" *Macromolecules* **1996**, *29*, 6240-5.

94 Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier; Amsterdam, 1978.

95 Bero, C. A.; Plazek, D. J. "Volume-dependent rate processes in an epoxy resin" *J. Polym. Sci.: Part B: Polym. Phys.* **1991**, *29*, 39-47.

96 Lodge, A. S.; Meissner, J. "On the use of instantaneous strains, superposed on shear and elongational flows of polymeric liquids to test the Gaussian network hypothesis and to estimate the segment concentration and its variation during flow" *Rheol. Acta* **1971**, *11*, 351-2.

97 Coleman, B. D.; Markovitz, H. "Asymptotic relations between shear stresses and normal stresses in general incompressible fluids" *J. Polym. Sci.: Polym. Phys. Ed.* **1974**, *12*, 2195-207.

98 Coleman, B. D.; Markovitz, H. "Normal stress effects in second-order fluids" *J. Appl. Phys.* **1964**, *35*, 1-9.

99 Coleman, B. D.; Dill, E. H.; Toupin, R. A. "A phenomenological theory of streaming birefringence" *Arch. Rational Mech. Anal.* **1970**, *39*, 358-99.

100 Kannan, R. M.; Kornfield, J. A. "The third-normal stress difference in entangled melts: Quantitative stress-optical measurements in oscillatory shear" *Rheol. Acta* **1992**, *31*, 535-44.

101 Bernstein, B.; Kearsley, E. A.; Zapas, L. J. "A study of stress relaxation with finite strain" *Trans. Soc. Rheol.* **1963**, *7*, 391-410.

102 Wagner, M. H.; Laun, H. M. "Nonlinear shear creep and constrained recovery of a LDPE melt" *Rheol. Acta* **1978**, *17*, 138-48.

103 Wagner, M. H.; Stephenson, S. E. "The irreversibility assumption of network disentanglement in flowing polymer melts and its effects on elastic recoil predictions" *J. Rheol.* **1979**, *23*, 489-504.

104 Graessley, W. W.; Park, W. S.; Crawley, R. L. "Experimental tests of constitutive relations for polymers undergoing uniaxial shear flows" *Rheol. Acta* **1977**, *16*, 291-301.

105 Cox, W. P.; Merz, B. H. "Correlation of dynamic and steady flow viscosities" *J. Polym. Sci.* **1958**, *28*, 619-22.

106 Osaki, K.; Bessho, N.; Kojimoto, T.; Kurata, M. "Flow birefringence of polymer solutions in time-dependence field" *J. Rheol.* **1979**, *23*, 457-75.

107 Takahashi, M.; Masuda, T.; Bessho, N.; Osaki, K. "Stress measurements at the start of shear flow: Comparison of data from a modified Weissenberg Rheogoniometer and from flow birefringence" *J. Rheol.* **1980**, *24*, 516-20.

108 Menezes, E. V.; Graessley, W. W. "Nonlinear rheological behavior of polymer systems for several shear-flow histories" *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1817-33.

109 Pearson, D. S.; Kiss, A. D.; Fetters, L. J.; Doi, M. "Flow-induced birefringence of concentrated polyisoprene solutions" *J. Rheol.* **1989**, *33*, 517-35.

110 Rochefort, W. E.; Heffner, G. W.; Pearson, D. S.; Miller, R. D.; Cotts, P. M. "Rheological and rheooptical studies of poly(alkylsilanes)" *Macromolecules* **1991**, *24*, 4861-4.

111 Wong, C. P.; Berry, G. C. "Rheological studies on concentrated solutions of heterocyclic polymers" *Polymer* **1979**, *20*, 229-40.

112 Casson, N. "A flow equation for pigment-oil suspensions of the printing ink type" In *Rheology of Disperse Systems*; C. C. Mill, ed.; Pergamon Press; London, 1959; 84-104.

113 Markovitz, H. "Relative rates of creep and relaxation in shear, elongation and isotropic compression" *J. Polym. Sci.: Polym. Phys. Ed.* **1973**, *11*, 1769-77.

114 Kovacs, A. J.; Aklonis, J. J.; Hutchinson, J. M.; Ramos, A. R. "Isobaric volume and enthalpy recovery of glasses. II. A transparent multiparameter theory" *J. Polym. Sci.: Polym. Phys. Ed.* **1979**, *17*, 1097-162.

115 Philippoff, W. "Flow birefringence and stress" *J. Appl. Phys.* **1956**, *27*, 984-9.

116 Philippoff "Elastic stresses and birefringence in flow" *Trans. Soc. Rheol.* **1961**, *5*, 163-91.

117 Janeschitz-Kriegl, H. "Flow birefringence of elastico-viscous polymer systems" *Adv. Polym. Sci.* **1969**, *6*, 170-318.

118 Coleman, B. D.; Dill, E. H. "Photoviscoelasticity: Theory and practice" In *The photoelastic effect and its applications*; J. Kestens, ed.; Springer-Verlag; Berlin, New York, 1975; 455-505.

119 Wales, J. L. S. *The Application of Flow Birefringence to Rheological Studies of Polymer Melts.*; Delft University Press; Delft, 1976.

120 Riande, E.; Saiz, E. *Dipole Moments and Birefringence of Polymers*; Prentice Hall; Englewood Cliffs, N.J., 1992.

121 Read, B. E. "Viscoelastic behavior of amorphous polymers in the glass-rubber transition region: Birefringence studies" *Polym. Eng. Sci.* **1983**, *23*, 835-43.

122 Kornfield, J. A.; Fuller, G. G.; Pearson, D. S. "Third normal stress difference and component relaxation spectra for bidisperse melts under oscillatory shear" *Macromolecules* **1991**, *24*, 5429-41.

123 Takahashi, T. "Measurement of first and second normal stress difference of a polystyrene solution using a simultaneous mechanical and optical measurement technique" In *Fluid Measurement and Instrumentation: 1995*; G. L. Morrison, *et al.*, eds.; Vol. FWD-Vol. 211; Am. Soc. Mech. Eng.; New York, 1995; 31-4.

124 Olson, D. I.; Brown, E. F.; Burghardt, W. R. "Second normal stress difference relaxation in a linear polymer melt following step-strain" *J. Polym. Sci. Part B: Polym. Phys.* **1998**, *36*, 2671-5.

125 Coleman, B. D.; Dill, E. H. "Theory of induced birefringence in materials with memory" *J. Mech. Phys. Solids* **1971**, *19*, 215-43.

126 Osaki, K.; Okamoto, H.; Inoue, T.; Hwang, E.-J. "Molecular interpretation of dynamic birefringence and viscoelasticity of amorphous polymers" *Macromolecules* **1995**, *28*, 3625-30.

127 Mott, P. H.; Roland, C. M. "Birefringence of polymers in the softening zone" *Macromolecules* **1998**, *31*, 7095-8.

128 Lodge, A. S. "Stress relaxation after a sudden shear strain" *Rheol. Acta* **1975**, *14*, 664-5.

129 Osaki, K.; Bessho, N.; Kojimoto, T.; Kurata, M. "Flow birefringence of polymer solutions in time-dependent field. Relation between normal and shear stresses on application of step-shear strain" *J. Rheol.* **1979**, *23*, 617-24.

130 Osaki, K.; Kimura, S.; Kurata, M. "Relaxation of shear and normal stresses in step-shear deformation of a polystyrene solution. Comparison with the predictions of the Doi-Edwards theory" *J. Polym. Sci.: Polym. Phys. Ed.* **1981**, *19*, 517-27.

131 Mott, P. H.; Roland, C. M. "Birefringence of rubber during creep and recovery" *Macromolecules* **1996**, *29*, 8492-6.

132 Osaki, K.; Inoue, T. "Some phenomenological relations for strain-induced birefringence of amorphous polymers" *Nihon Reoroji Gakkaishi* **1991**, *19*, 130-2 (In English).

133 Krieger, I. M. "Rheology of monodisperse latices" *Adv. Colloid Interface Sci.* **1972**, *3*, 111-36.

134 Russel, W. B.; Gast, A. P. "Nonequilibrium statistical mechanics of concentrated colloidal dispersions: Hard spheres in weak flows" *J. Chem. Phys.* **1986**, *84*, 1815-26.

135 van der Werff, J. C.; de Kruif, C. G.; Blom, C.; Mellema, J. "Linear viscoelastic behavior of dense hard-sphere dispersions" *Phys. Rev. A* **1989**, *39*, 795-807.

136 Brady, J. F. "The rheological behavior of concentrated colloidal dispersions" *J. Chem. Phys.* **1993**, *99*, 567-81.

137 Shikata, T.; Pearson, D. S. "Viscoelastic behavior of concentrated spherical suspensions" *J. Rheol.* **1994**, *38*, 601-16.

138 Lionberger, R. A.; Russel, W. B. "High frequency modulus of hard sphere colloids" *J. Rheol.* **1994**, *38*, 1885-908.

139 Lionberger, R. A.; Russel, W. B. "Effectiveness of nonequilibrium closures for the many body forces in concentrated colloidal dispersions" *J. Chem. Phys.* **1997**, *106*, 402-16.

140 Chong, J. S.; Christiansen, E. B.; Baer, A. D. "Rheology of concentrated suspensions" *J. Appl. Polym. Sci.* **1971**, *15*, 2007-21.

141 Beenakker, C. W. J. "The effective viscosity of a concentrated suspension of spheres (And its relation to diffusion)" *Physica A* **1984**, *128A*, 48-81.

142 Beenakker, C. W. J.; Mazur, P. "Diffusion of spheres in a concentrated suspension. II" *Physica A* **1984**, *126A*, 349-70.

143 de Gennes, P. G.; Prost, J. *The Physics of Liquid Crystals*; Oxford U. P.; New York, 1993.

144 Mellema, J.; de Kurif, C. G.; Blom, C.; Vrij, A. "Hard sphere colloidal dispersions: Mechanical relaxation pertaining to thermodynamic forces" *Rheol. Acta* **1987**, *26*, 40-4.

145 Arora, A. K.; Tata, B. V. R., eds. *Ordering and Phase Transitions in Charged Colloids*; VCH Publisher; New York, 1996.

146 Yoshida, J.; Yamanaka, J.; Koka, T.; Ise, N.; Hashimoto, T. "Novel crystallization process in dilute ionic colloids" *Langmuir* **1998**, *14*, 569-74.

147 Weiss, J. A.; Larsen, A. E.; Grier, D. G. "Interactions, dynamics, and elasticity in charge-stabilized colloidal crystals" *J. Chem. Phys.* **1998**, *109*, 8659-66.

148 Meitz, D. W.; Yen, L.; Berry, G. C.; Markovitz, H. "Rheological studies of dispersions of spherical particles in a polymer solution" *J. Rheology* **1988**, *32*, 309-51.

1 Website, S. o. R.; in *http://www.umecheme.maine.edu/sor/default.htm*. 1999,.

2 Staverman, A. J.; Schwarzl, F. "Linear deformation behavior of high polymers" In *Die Physik der Hochpolymeren*; H. A. Stuart, ed.; Vol. IV; Springer-Verlag; Berlin, 1956; Chapt. 1.

3 Treloar, L. R. G. *The Physics of Rubber Elasticity*; 2rd ed.; Oxford University Press; London, 1958, (a) 156, (b) 64, (c) 177.

4 Coleman, B. D., Markovitz, H., and Noll, W. *Viscometric Flows of Non-Newtonian Fluids*; Springer-Verlag; New York, 1966, (a) 34, (b) 55, (c) 54, (d) 46.

5 McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley; New York, 1967.

6 Aklonis, J. J.; MacKnight, W. J.; Shen, M. C. *Introduction to Polymer Viscoelasticity*; Wiley-Interscience; New York, 1972.

7 Bartenev, G. M.; Zelenev, Y. V., eds. *Relaxation Phenomena in Polymers*; John Wiley & Sons (Halsted Press); New York, 1974.

8 Walters, K. *Rheometry*; John Wiley & Sons; New York, 1975, (a) 44, (b) 48, (c) 52, (d) 93, (e) 102, (f) 100.

9 Markovitz, H. "Rheology" In *Physics Vade Mecum*; H. L. Anderson, ed.; Am. Inst. Phys.; New York, 1981; p. 274-86.

10 Plazek, D. J. "Viscoelastic and steady-state rheological response" In *Methods of Experimental Physics*; R. A. Fava, ed.; Vol. 16C; Academic Press; New York, 1980; Chapt. 11.

11 Ferry, J. D. *Viscoelastic Properties of Polymers*; 3rd ed.; John Wiley & Sons Inc.; New York, 1980, (a) 37, (b) 40, (c) 48, (d) 96, (e) 132, (f) 154, (g) 603, (h) 168, (i) 1, (j) 177, (k) 224, (m) 17, (n) 3, (p) 5, (q) 68, (r) 33, (s) 103, (t) 70, (u) 69, (v) 60, (w) 83, (x) 63, (y) 91, (z) 287, (a') 227, (b') 266, (c') 366, (d') 229, (e') 232, (f') 390, (g') 388, (h') 411, (i') 545.

12 Bailey, R. T.; North, A. M.; Pethrick, R. A. *Molecular Motion in High Polymers* The International Series of Monographs on Chemistry, J. E. Baldwin, *et al.*, eds.; Clarendon Press; Oxford, 1981.

13 Christensen, R. M. *Theory of Viscoelasticity*; 2nd. ed.; Academic; New York, 1982, (a) 353, (b) 1, (c) 5, (d) 7.

14 Dealy, J. M. *Rheometers for Molten Plastics*; Van Nostrand Reinhold Co.; New York, 1982, (a) 1, (b) 116, (c) 126, (d) 148, (e) 75, (f) 61.

15 BohdaneckO(´y), M.; KováO(˘r), J. *Viscosity of Polymer Solutions* Polymer Science Library, A. D. Jenkins, ed.; Vol. 2; Elsevier Scientific Publ. Co.; Amsterdam, 1982, (a) 167, (b) 175, (c) 177.

16 Janeschitz-Kriegl, H. *Polymer Melt Rheology and Flow Birefringence*; Springer-Verlag; Berlin ; New York, 1983, (a) 455, (b) 4, (c) 467, (d) 464, (e) 355, (f) 60, (g) 177, (h) 217.

17 Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press; Oxford, UK, 1986, (a) 222, (b) 366, (c) 218, (d) 91, (e) 226, (f) 281, (g) 255, (h) 121, (i) 166.

18 Berry, G. C.; Plazek, D. J. "Rheology of polymeric fluids" In *Glass: Science and Technology*; D. R. Uhlmann; N. J. Kreidl, ed.; Vol. 3; Academic Press; New York, 1986; 319-62.

19 Bird, R. B.; Armstrong, R. C.; Hassager, O. *Dynamics of Polymeric Liquids. Vol. 1. Fluid Mechanics*; 2nd ed.; John Wiley & Sons, Inc.; New York, 1987, (a) 158, (b) 269, (c) 290.

20 Bird, R. B.; Curtiss, C. C.; Armstrong, R. C.; Hassager, O. *Dynamics of Polymeric Liquids. Vol. 2. Kinetic Theory*; 2nd ed.; John Wiley & Sons, Inc.; New York, 1987.

21 Collyer, A. A.; Clegg, D. W., eds. *Rheological Measurement*; Elsevier Science Co.; New York, 1988.

22 Larson, R. G. *Constitutive Equations for Polymer Melts and Solutions*; Butterworths; Boston, 1988, (a) 49, (b) 93, (c) 318, (d) 118, (e) 120, (f) 233, (g)120, (h) 95.

23 Tschoegl, N. W. *The Phenomenological Theory of Linear Viscoelastic Behavior*; Springer-Verlag; Berlin, 1989, (a) 513, (b) 551, (c) 69, (d) 47, (e) 560, (f) 21, (g) 508, (h) 55, (i) 413, (j) 401, (k) 406, (m) 157, (n) 409, (p) 157, (q) 425.

24 White, J. L. *Principles of Polymer Engineering Rheology*; John Wiley & Sons, Inc.; New York, 1990, (a) 83, (b) 163, (c) 174.

25 Matsuoka, S. *Relaxation Phenomena in Polymers*; Hanser; Munich, 1992.

26 Yanovsky, Y. G. *Polymer Rheology: Theory and Practice*; Chapman & Hall; New York, 1993, (a) 200, (b) 235.

27 Fuller, G. G. *Optical Rheometry of Complex Fluids* Topics in Chemical Engineering, K. E. Gubbins, ed.; Oxford University Press; New York, Oxford, 1995, (a) 117, (b) 109, (c) 149, (d) 167, (e) 193.

28 Coleman, B. D.; Noll, W. "Foundations of linear viscoelasticity" *Rev. Modern Phys.* **1961**, *33*, 239-49.

29 Petrie, C. J. S. *Elongational Flows: Aspects of the Behaviour of Model Elasticoviscous Fluids*; Pitman; London ; San Francisco, 1979.

30 Meissner, J.; Hostettler, J. "A new elongational rheometer for polymer melts and other highly viscoelastic liquids" *Rheol. Acta* **1994**, *33*, 1-21.

31 Macosko, C.; Starita, J. M. "New rheometer is put to the test" *SPE-J.* **1971**, *27 (11)*, 38-42.

32 Plazek, D. J. "Magnetic bearing torsional creep apparatus" *J. Polym. Sci. A-2* **1968**, *6*, 621.

33 Berry, G. C.; Birnboim, M. H.; Park, J. O.; Meitz, D. W.; Plazek, D. J. "A rotational rheometer for rheological rtudies with prescribed strain or stress history" *J. Polym. Sci.: Part B: Polym. Phys.* **1989**, *27*, 273.

34 Rabinowitsch, B. "Über die Viskosität und Elastizität von Solen" *Z. Phys. Chem., Abt. A* **1929**, *145*, 1-26.

35 Barr, G. *A Monograph of Viscometry*; Oxford University Press (Authorized facsimile by University Microfilms, Ann Arbor, MI, 1967); London, 1931.

36 Carslaw, H. S.; Jaeger, J. C. *Operational Methods in Applied Mathematics*; Dover Publications, Inc.; New York, 1948.

37 Shermergor, T. D. "Description of relaxation phenomena in structurally nonhomogeneous polymers by correlation functions" In *Relaxation Phenomena in Polymers*; G. M. Bartenev; Yu. V. Zelenev, eds.; John Wiley & Sons (Halsted Press); New York, 1974.

38 Berry, G. C. "Rheological and rheo-optical studies on nematic solutions of a rodlike polymer: Bingham Award Lecture" *J. Rheology* **1991**, *35*, 943.

39 Meissner, J. "Experimental problems and recent results in polymer melt rheometry" *J. Macromol. Chem., Macromol. Symp.* **1992**, *56*, 25-42.

40 Ostrowsky, N.; Sornette, D.; Parker, R.; Pike, E. R. "Exponential sampling method for light scattering polydispersity analysis" *Opt. Acta* **1981**, *28*, 1059-70.

41 Baumgaertel, M.; Winter, H. H. "Determination of discrete relaxation and retardation time spectra from dynamic mechanical data" *Rheol. Acta* **1989**, *28*, 511-19.

42 Sips, R. "General theory of deformation of viscoelastic substances" *J. Polym. Sci.* **1951**, *7*, 191-205.

43 Nakamura, K.; Wong, C. P.; Berry, G. C. "Strain criterion in nonlinear creep and recovery in concentrated polymer solutions" *J. Polym. Sci.: Polym. Phys. Ed.* **1984**, *22*, 1119-48.

44 Berry, G. C.; Plazek, D. J. "On the use of stretched-exponential functions for both linear viscoelastic creep and stress relaxation" *Rheol. Acta* **1997**, *36*, 320-9.

45 Riande, E.; Markovitz, H. "Approximate relations among compliance functions of linear viscoelasticity for amorphous polymers" *J. Polym. Sci.: Polm. Phys. Ed.* **1975**, *13*, 947-51.

46 Plazek, D. J.; Raghupathi, N.; Orbon, S. J. "Determination of dynamic storage and loss compliances from creep data" *J. Rheol.* **1979**, *23*, 477-88.

47 Markovitz, H. "The reduction principle in linear viscoelasticity" *J. Phys. Chem* **1965**, *69*, 671.

48 Markovitz, H. "Superposition in rheology" *J. Polym. Sci.: Symp.* **1975**, *50*, 431-56.

49 Berry, G. C.; "The viscosity of polymers and their concentrated solutions" *Adv. in Polym. Sci.* **1968**, *5*, 261-357.

50 Berry, G. C. "Crossover behavior in the viscosity of semiflexible polymers: Intermolecular interactions as a function of concentration and molecular weight" *J. Rheol.* **1996**, *40*, 1129-54.

51 Boyer, R. F. "The relation of transition temperatures to chemical structure in high polymers" *Rubber Rev.* **1963**, *36*, 1303-421.

52 Berry, G. C. "Thermodynamic and conformational studies of polystyrene. II. Intrinsic viscosity studies on dilute solutions of linear polystyrenes" *J. Chem. Phys.* **1967**, *46*, 1338.

53 Berry, G. C. "Molecular weight distribution" In *Encyclopedia of Materials Science and Engineering*; M. B. Bever, ed.; Pergamon Press; Oxford, 1986; 3759.

54 Russel, W. B.; Saville, D. A.; Schowalter., W. R. *Colloidal Dispersions*; Cambridge University Press; Cambridge, 1989, (a) 498, (b) 88, (c) 129, (d) 162, (e) 466, (f) 469, (g) 474.

55 Berry, G. C. "Remarks on a relation among the intrinsic viscosity, the radius of gyration, and the translational friction coefficient" *Journal of Polymer Science, Part B: Polymer Physics* **1988**, *26*, 1137-42.

56 Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row; New York, 1971, (a) 266, (b) 314.

57 Flory, P. J.; "Molecular configuration and thermodynamic properties from intrinsic viscosities" *J. Polym. Sci.* **1950**, *5*, 745-7.

58 Casassa, E. F.; Berry, G. C. "Reflections and comments on "Molecular configuration and thermodynamic properties from intrinsic viscosities" by Paul J. Flory and Thomas G Fox" *J. Polym. Sci., Pt. B: Polym. Phys.* **1996**, *34*, 203-6.

59 Casassa, E. F.; Berry, G. C. "Polymer solutions" In *Comprehensive Polymer Science*; G. Allen, ed.; Vol. 2; Pergamon Press; New York, 1988; Chapt. 3.

60 Brandrup, J.; Immergut, E. H., eds. *Polymer Handbook*; 3rd ed.; Wiley; New York, 1989.

61 Casassa, E. F.; Berry, G. C. "Angular distribution of intensity of Rayleigh scattering from comblike branched molecules" *J. Polym. Sci.: Part A-2* **1966**, *4*, 881.

62 Lodge, T. P. "Solvent dynamics, local friction, and the viscoelastic properties of polymer solutions" *J. Phys. Chem.* **1993**, *97*, 1480-7.

63 Harrison, G.; Lamb, J.; Matheson, A. J. "The viscoelastic properties of dilute solutions of polystyrene in toluene" *J. Phys. Chem.* **1966**, *68*, 1072-8.

64 Osaki, K. "Viscoelastic properties of dilute polymer solutions" *Adv. Polym. Sci.* **1973**, *12*, 1-64.

65 Birnboim, M. H. "The viscoelastic properties of low molecular weight polystyrene solutions in high frequency regime: Polymer-solvent interaction" *Proc. IUPAC Macro 82* **1982**, *July 12-16*, 872.

66 Schrag, J. L., *et al.* "Local modification of solvent dynamics by polymeric solutes" *J. Non-Cryst. Solids* **1991**, *131*, 537-43.

67 Yoshizaki, T.; Takaeda, Y.; Yamakawa, H. "On the correlation between the negative intrinsic viscosity and the rotatory relaxation time of solvent molecules in dilute polymer solutions" *Macromolecules* **1993**, *26*, 6891-6.

68 Yamakawa, H. "Concentration dependence of polymer chain configurations in solution" *J. Chem. Phys.* **1961**, *34*, 1360-72.

69 Batchelor, G. K. "The effect of Brownian motion on the bulk stress in a suspension of spherical particles" *J. Fluid Mech.* **1977**, *83*, 97-117.

70 Pal, R. "Rheology of emulsions containing polymeric liquids" In *Encyclopedia of Emulsion Technology*; Paul Becher, ed.; Vol. 4; Marcel Dekker, Inc.; New York, 1996; 93-263.

71 Park, J. O.; Berry, G. C. "Moderately concentrated solutions of polystyrene. 3. Viscoelastic measurements at the Flory Theta temperature" *Macromolecules* **1989**, *22*, 3022-9.

72 de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press; Ithaca, NY, 1979.

73 Narayanaswamy, O. S. "Annealing of glass" In *Glass: Science and Technology*; D. R. Uhlmann; N. J. Kreidl, ed.; Vol. 3; Academic Press; New York, 1986; 275-318.

74 Plazek, D. J.; Berry, G. C. "Physical aging of polymer glasses" In *Glass: Science and Technology*; D. R. Uhlmann; N. J. Kreidl, ed.; Vol. 3; Academic Press; New York, 1986; 363-99.

75 Graessley, W. W. "The entanglement concept in polymer rheology" *Adv. Polym. Sci.* **1974**, *16*, 1-179.

76 Berry, G. C.; Nakayasu, H.; "Viscosity of poly(vinyl acetate) and its concentrated solutions" *Journal of Polymer Science, Polymer Physics Edition* **1979**, *17*, 1825-44.

77 da Andrade, E. N. *Viscosity and Plasticity*; Chemical Publishing Co.; New York, 1951.

78 Berry, G. C. "The stress-strain behavior of materials exhibiting Andrade creep" *Polym Eng Sci* **1976**, *16*, 777-81.

79 Orbon, S. J.; Plazek, D. J. "The recoverable compliance of a series of bimodal molecular weight blends of polystyrene" *J. Polym. Sci.: Polym. Phys. Ed.* **1979**, *17*, 1871.

80 Berry, G. C. "Terminal retardation times and weights for the Rouse model for a crosslinked network" *J. Polym. Sci.: Part B: Polym. Phys.* **1987**, *25*, 2203-5.

81 Masuda, T.; Takahashi, M.; Onogi, S. "Steady-state compliance of polymer blends" *Appl. Polym. Symp.* **1973**, *20*, 49-60.

82 Kurata, M. "Effect of molecular weight distribution on viscoelastic properties of polymers. 2. Terminal relaxation time and steady-state compliance" *Macromolecules* **1984**, *17*, 895-8.

83 Fujita, H.; Einaga, Y. "Self diffusion and viscoelasticity in entangled systems. II. Steady-state viscosity and compliance of binary blends" *Polymer J.* **1985**, *17*, 1189-95.

84 Montfort, J. P.; Marin, G.; Monge, P. "Molecular weight distribution dependence of the viscoelastic properties of linear polymers: The coupling of reptation and tube-renewal effects" *Macromolecules* **1986**, *19*, 1979-88.

85 des Cloizeaux, J. "Relaxation of entangled polymeric melts" *Macromolecules* **1990**, *23*, 3992-4006.

86 Tsenoglou, C. "Molecular weight polydispersity effects on the viscoelasticity of entangled linear polymers" *Macromoleucules* **1991**, *24*, 1762-7.

87 Berry, G. C. "Rheological properties of blends of rodlike chains with flexible or semiflexible chains" *Trends in Polymer Science* **1993**, *1*, 309.

88 Berry, G. C. "Rheology of blends of liquid crystalline and flexible chain polymers" *Trends Poly. Sci.* **1996**, *4*, 289-92.

89 Plazek, D. J.; Chay, I. C. "The evolution of the viscoelastic retardation spectrum during the development of an epoxy resin network" *J. Polym. Sci.: Part B: Polym. Phys.* **1991**, *29*, 17-29.

90 Winter, H. H.; Mours, M. "Rheology of polymers near liquid-solid transitions" *Adv. Polym. Sci.* **1997**, *134*, 167-234.

91 Plazek, D. J. "Oh, thermorheological simplicity, wherefore art thou?" *J. Rheol.* **1996**, *40*, 987-1014.

92 Plazek, D. J.; Chelko, A. J., Jr. "Temperature dependence of the steady state recoverable compliance of amorphous polymers" *Polymer* **1977**, *18*, 15-8.

93 Inoue, T.; Mizukami, Y.; Okamoto, H.; Matsui, H.; Watanabe, H.; Kanaya, T.; Osaki, K. "Dynamic birefringence of vinyl polymers" *Macromolecules* **1996**, *29*, 6240-5.

94 Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier; Amsterdam, 1978.

95 Bero, C. A.; Plazek, D. J. "Volume-dependent rate processes in an epoxy resin" *J. Polym. Sci.: Part B: Polym. Phys.* **1991**, *29*, 39-47.

96 Lodge, A. S.; Meissner, J. "On the use of instantaneous strains, superposed on shear and elongational flows of polymeric liquids to test the Gaussian network hypothesis and to estimate the segment concentration and its variation during flow" *Rheol. Acta* **1971**, *11*, 351-2.

97 Coleman, B. D.; Markovitz, H. "Asymptotic relations between shear stresses and normal stresses in general incompressible fluids" *J. Polym. Sci.: Polym. Phys. Ed.* **1974**, *12*, 2195-207.

98 Coleman, B. D.; Markovitz, H. "Normal stress effects in second-order fluids" *J. Appl. Phys.* **1964**, *35*, 1-9.

99 Coleman, B. D.; Dill, E. H.; Toupin, R. A. "A phenomenological theory of streaming birefringence" *Arch. Rational Mech. Anal.* **1970**, *39*, 358-99.

100 Kannan, R. M.; Kornfield, J. A. "The third-normal stress difference in entangled melts: Quantitative stress-optical measurements in oscillatory shear" *Rheol. Acta* **1992**, *31*, 535-44.

101 Bernstein, B.; Kearsley, E. A.; Zapas, L. J. "A study of stress relaxation with finite strain" *Trans. Soc. Rheol.* **1963**, *7*, 391-410.

102 Wagner, M. H.; Laun, H. M. "Nonlinear shear creep and constrained recovery of a LDPE melt" *Rheol. Acta* **1978**, *17*, 138-48.

103 Wagner, M. H.; Stephenson, S. E. "The irreversibility assumption of network disentanglement in flowing polymer melts and its effects on elastic recoil predictions" *J. Rheol.* **1979**, *23*, 489-504.

104 Graessley, W. W.; Park, W. S.; Crawley, R. L. "Experimental tests of constitutive relations for polymers undergoing uniaxial shear flows" *Rheol. Acta* **1977**, *16*, 291-301.

105 Cox, W. P.; Merz, B. H. "Correlation of dynamic and steady flow viscosities" *J. Polym. Sci.* **1958**, *28*, 619-22.

106 Osaki, K.; Bessho, N.; Kojimoto, T.; Kurata, M. "Flow birefringence of polymer solutions in time-dependence field" *J. Rheol.* **1979**, *23*, 457-75.

107 Takahashi, M.; Masuda, T.; Bessho, N.; Osaki, K. "Stress measurements at the start of shear flow: Comparison of data from a modified Weissenberg Rheogoniometer and from flow birefringence" *J. Rheol.* **1980**, *24*, 516-20.

108 Menezes, E. V.; Graessley, W. W. "Nonlinear rheological behavior of polymer systems for several shear-flow histories" *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1817-33.

109 Pearson, D. S.; Kiss, A. D.; Fetters, L. J.; Doi, M. "Flow-induced birefringence of concentrated polyisoprene solutions" *J. Rheol.* **1989**, *33*, 517-35.

110 Rochefort, W. E.; Heffner, G. W.; Pearson, D. S.; Miller, R. D.; Cotts, P. M. "Rheological and rheooptical studies of poly(alkylsilanes)" *Macromolecules* **1991**, *24*, 4861-4.

111 Wong, C. P.; Berry, G. C. "Rheological studies on concentrated solutions of heterocyclic polymers" *Polymer* **1979**, *20*, 229-40.

112 Casson, N. "A flow equation for pigment-oil suspensions of the printing ink type" In *Rheology of Disperse Systems*; C. C. Mill, ed.; Pergamon Press; London, 1959; 84-104.

113 Markovitz, H. "Relative rates of creep and relaxation in shear, elongation and isotropic compression" *J. Polym. Sci.: Polym. Phys. Ed.* **1973**, *11*, 1769-77.

114 Kovacs, A. J.; Aklonis, J. J.; Hutchinson, J. M.; Ramos, A. R. "Isobaric volume and enthalpy recovery of glasses. II. A transparent multiparameter theory" *J. Polym. Sci.: Polym. Phys. Ed.* **1979**, *17*, 1097-162.

115 Philippoff, W. "Flow birefringence and stress" *J. Appl. Phys.* **1956**, *27*, 984-9.

116 Philippoff "Elastic stresses and birefringence in flow" *Trans. Soc. Rheol.* **1961**, *5*, 163-91.

117 Janeschitz-Kriegl, H. "Flow birefringence of elastico-viscous polymer systems" *Adv. Polym. Sci.* **1969**, *6*, 170-318.

118 Coleman, B. D.; Dill, E. H. "Photoviscoelasticity: Theory and practice" In *The photoelastic effect and its applications*; J. Kestens, ed.; Springer-Verlag; Berlin, New York, 1975; 455-505.

119 Wales, J. L. S. *The Application of Flow Birefringence to Rheological Studies of Polymer Melts.*; Delft University Press; Delft, 1976.

120 Riande, E.; Saiz, E. *Dipole Moments and Birefringence of Polymers*; Prentice Hall; Englewood Cliffs, N.J., 1992.

121 Read, B. E. "Viscoelastic behavior of amorphous polymers in the glass-rubber transition region: Birefringence studies" *Polym. Eng. Sci.* **1983**, *23*, 835-43.

122 Kornfield, J. A.; Fuller, G. G.; Pearson, D. S. "Third normal stress difference and component relaxation spectra for bidisperse melts under oscillatory shear" *Macromolecules* **1991**, *24*, 5429-41.

123 Takahashi, T. "Measurement of first and second normal stress difference of a polystyrene solution using a simultaneous mechanical and optical measurement technique" In *Fluid Measurement and Instrumentation: 1995*; G. L. Morrison, *et al.*, eds.; Vol. FWD-Vol. 211; Am. Soc. Mech. Eng.; New York, 1995; 31-4.

124 Olson, D. I.; Brown, E. F.; Burghardt, W. R. "Second normal stress difference relaxation in a linear polymer melt following step-strain" *J. Polym. Sci. Part B: Polym. Phys.* **1998**, *36*, 2671-5.

125 Coleman, B. D.; Dill, E. H. "Theory of induced birefringence in materials with memory" *J. Mech. Phys. Solids* **1971**, *19*, 215-43.

126 Osaki, K.; Okamoto, H.; Inoue, T.; Hwang, E.-J. "Molecular interpretation of dynamic birefringence and viscoelasticity of amorphous polymers" *Macromolecules* **1995**, *28*, 3625-30.

127 Mott, P. H.; Roland, C. M. "Birefringence of polymers in the softening zone" *Macromolecules* **1998**, *31*, 7095-8.

128 Lodge, A. S. "Stress relaxation after a sudden shear strain" *Rheol. Acta* **1975**, *14*, 664-5.

129 Osaki, K.; Bessho, N.; Kojimoto, T.; Kurata, M. "Flow birefringence of polymer solutions in time-dependent field. Relation between normal and shear stresses on application of step-shear strain" *J. Rheol.* **1979**, *23*, 617-24.

130 Osaki, K.; Kimura, S.; Kurata, M. "Relaxation of shear and normal stresses in step-shear deformation of a polystyrene solution. Comparison with the predictions of the Doi-Edwards theory" *J. Polym. Sci.: Polym. Phys. Ed.* **1981**, *19*, 517-27.

131 Mott, P. H.; Roland, C. M. "Birefringence of rubber during creep and recovery" *Macromolecules* **1996**, *29*, 8492-6.

132 Osaki, K.; Inoue, T. "Some phenomenological relations for strain-induced birefringence of amorphous polymers" *Nihon Reoroji Gakkaishi* **1991**, *19*, 130-2 (In English).

133 Krieger, I. M. "Rheology of monodisperse latices" *Adv. Colloid Interface Sci.* **1972**, *3*, 111-36.

134 Russel, W. B.; Gast, A. P. "Nonequilibrium statistical mechanics of concentrated colloidal dispersions: Hard spheres in weak flows" *J. Chem. Phys.* **1986**, *84*, 1815-26.

135 van der Werff, J. C.; de Kruif, C. G.; Blom, C.; Mellema, J. "Linear viscoelastic behavior of dense hard-sphere dispersions" *Phys. Rev. A* **1989**, *39*, 795-807.

136 Brady, J. F. "The rheological behavior of concentrated colloidal dispersions" *J. Chem. Phys.* **1993**, *99*, 567-81.

137 Shikata, T.; Pearson, D. S. "Viscoelastic behavior of concentrated spherical suspensions" *J. Rheol.* **1994**, *38*, 601-16.

138 Lionberger, R. A.; Russel, W. B. "High frequency modulus of hard sphere colloids" *J. Rheol.* **1994**, *38*, 1885-908.

139 Lionberger, R. A.; Russel, W. B. "Effectiveness of nonequilibrium closures for the many body forces in concentrated colloidal dispersions" *J. Chem. Phys.* **1997**, *106*, 402-16.

140 Chong, J. S.; Christiansen, E. B.; Baer, A. D. "Rheology of concentrated suspensions" *J. Appl. Polym. Sci.* **1971**, *15*, 2007-21.

141 Beenakker, C. W. J. "The effective viscosity of a concentrated suspension of spheres (And its relation to diffusion)" *Physica A* **1984**, *128A*, 48-81.

142 Beenakker, C. W. J.; Mazur, P. "Diffusion of spheres in a concentrated suspension. II" *Physica A* **1984**, *126A*, 349-70.

143 de Gennes, P. G.; Prost, J. *The Physics of Liquid Crystals*; Oxford U. P.; New York, 1993.

144 Mellema, J.; de Kurif, C. G.; Blom, C.; Vrij, A. "Hard sphere colloidal dispersions: Mechanical relaxation pertaining to thermodynamic forces" *Rheol. Acta* **1987**, *26*, 40-4.

145 Arora, A. K.; Tata, B. V. R., eds. *Ordering and Phase Transitions in Charged Colloids*; VCH Publisher; New York, 1996.

146 Yoshida, J.; Yamanaka, J.; Koka, T.; Ise, N.; Hashimoto, T. "Novel crystallization process in dilute ionic colloids" *Langmuir* **1998**, *14*, 569-74.

147 Weiss, J. A.; Larsen, A. E.; Grier, D. G. "Interactions, dynamics, and elasticity in charge-stabilized colloidal crystals" *J. Chem. Phys.* **1998**, *109*, 8659-66.

148 Meitz, D. W.; Yen, L.; Berry, G. C.; Markovitz, H. "Rheological studies of dispersions of spherical particles in a polymer solution" *J. Rheology* **1988**, *32*, 309-51.