Chapter 10
Optical Anisotropy

Abstract Macromolecular coils are deformed in flow, while optically anisotropic parts (and segments) of the macromolecules are oriented by flow, so that polymers and their solutions become optically anisotropic. This is true for a macromolecule whether it is in a viscous liquid or is surrounded by other chains. The optical anisotropy of a system appears to be directly connected with the mean orientation of segments and, thus, it provides the most direct observation of the relaxation of the segments, both in dilute and in concentrated solutions of polymers. The results of the theory for dilute solutions provide an instrument for the investigation of the structure and properties of a macromolecule. In application to very concentrated solutions, the optical anisotropy provides the important means for the investigation of slow relaxation processes. The evidence can be decisive for understanding the mechanism of the relaxation.

10.1 The Relative Permittivity Tensor

In order to examine the optical anisotropy, we begin with the relative permittivity tensor for the system ε_{ik}, which is defined (see, for example, Born and Wolf 1970; Landau et al. 1987) by the relation

$$\varepsilon_{ik} E_k = E_i + 4\pi P_i \tag{10.1}$$

where E_k is the average electric field strength acting in the medium and P_i is the polarisation per unit volume of the system expressed in terms of the polarisabilities of the constituent elements of the system.

One can make use of the heuristic model mentioned previously, in Section 1.1: each macromolecule consists of z segments and is surrounded by solvent molecules. It is not essential now to know whether the segments in the chain are connected or independent; the results of this section are applicable in both cases.

When considering the system consisting of solvent molecules and segments, the simple old-fashion (Vleck 1932; Fröhlich 1958) speculations allow us to

V.N. Pokrovskii, *The Mesoscopic Theory of Polymer Dynamics*,
Springer Series in Chemical Physics 95,
DOI 10.1007/978-90-481-2231-8_10,

determine the relative permittivity tensor of polymeric system in terms of the mean orientation of anisotropic segments of the macromolecules. The solvent molecules have an isotropic polarisability α, while the segment has an anisotropic polarisability α_{ik}. In the co-ordinate system connected with the segment, the anisotropy tensor is assumed to be diagonal. In any other co-ordinate system, the polarisability tensor of the segment has the form

$$\alpha_{ik} = c_{is} c_{ks} \alpha_{ss}$$

where c_{is} is the cosine of the angle between the ith axis of the laboratory system and the sth axis of the molecule. One can assume that the segment has axial symmetry, so that $\alpha_{22} = \alpha_{33}$, and introduce the unit vector $\boldsymbol{e}$ in direction of the axis. It allows us to rewrite the expression for the polarisability tensor of the segment in the form

$$\alpha_{ik} = \bar{\alpha}\delta_{ik} + (\alpha_{11} - \alpha_{22})\left(e_i e_k - \frac{1}{3}\delta_{ik}\right) \tag{10.2}$$

where $\bar{\alpha} = (\alpha_{11} + \alpha_{22} + \alpha_{33})/3$. In case that is more general, we have to introduce two unit vectors $\boldsymbol{e}^{\parallel}$ and $\boldsymbol{e}^{\perp}$ – along the direction of the axis of the segment and in perpendicular direction, respectively. In this case

$$\alpha_{ik} = \bar{\alpha}\delta_{ik} + (\alpha_{11} - \alpha_{33})\left(e_i^{\parallel} e_k^{\parallel} - \frac{1}{3}\delta_{ik}\right) + (\alpha_{22} - \alpha_{33})\left(e_i^{\perp} e_k^{\perp} - \frac{1}{3}\delta_{ik}\right). \tag{10.3}$$

The time of relaxation of the mean orientation of the lateral vector $\boldsymbol{e}^{\perp}$ is considered to be much less than the time of relaxation of the mean orientation of the axial vector $\boldsymbol{e}^{\parallel}$, so that the last term in (10.3) can be neglected for rather low frequencies and one can continue with the simpler case (10.2).

The true molecular field $\boldsymbol{F}$ acting both on the segment and on molecules of solvent differs from the average field $\boldsymbol{E}$ because the scale of the dimensions of the segments is molecular. Each solvent molecule makes an isotropic contribution to the polarisability vector; the contribution of each segment of the macromolecule is anisotropic and is expressed by the formula

$$\beta_s = c_{si} c_{ki} \alpha_{ii} F_k = \left[\bar{\alpha}\delta_{sk} + \Delta\alpha\left(e_s e_k - \frac{1}{3}\delta_{sk}\right)\right] F_k, \quad \Delta\alpha = \alpha_{11} - \alpha_{22}.$$

By taking into account all the molecules and segments and by designating with nz and n_{s} the densities of the number of segments and of the number of solvent molecules (n being the density of the number of macromolecules), we obtain, after averaging with respect to the orientations of the segments,

$$P_j = (nz\bar{\alpha}\delta_{jk} + nz\mathit{\Delta}\alpha s_{jk} + n_{\mathrm{s}}\alpha\delta_{jk})F_k \tag{10.4}$$

where a symbol has been introduced for the mean values of the directing cosines of the segment relative to the laboratory co-ordinate system – the orientation tensor

$$s_{jk} = \langle e_j e_k \rangle - \frac{1}{3}\delta_{jk}.$$

The internal field F_k is assumed to be the same for the segments and the solvent molecules.

Next, use is made of the simple hypothesis that all the positions of the molecules and segments are equally probable, and, following tradition, we shall formulate an expression for the internal field as a field within a spherical cavity (Vleck 1932; Fröhlich 1958)

$$F_i = E_i + \frac{4\pi}{3} P_i. \tag{10.5}$$

The internal field can be eliminated from relations (10.4) and (10.5), so that we have a set of equations for the components of the vector of polarisation

$$(A\delta_{sj} + a s_{sj})P_j = -(B\delta_{sj} + b s_{sj})E_j$$

where the following notations are introduced

$$A = \frac{4\pi}{3}(nz\bar{\alpha} + n_{\mathrm{s}}\alpha) - 1, \quad a = \frac{4\pi}{3} nz\Delta\alpha,$$
$$B = nz\bar{\alpha} + n_{\mathrm{s}}\alpha, \quad b = nz\Delta\alpha.$$

The written set of equations has a simple solution for the components of the polarisation vector. We use them to write, in accordance to equation (10.1), the relative permittivity tensor

$$\varepsilon_{ik} = \delta_{ik} + \frac{4\pi}{D}\left[-A^2 B\delta_{ik} + (AaB - A^2 b)s_{ik} + \frac{1}{2}a^2 B s_{jl}s_{jl}\delta_{ik}\right.$$
$$\left. + (Aab - a^2 B)s_{il}s_{ik} + \frac{1}{2}a^2 b s_{jl}s_{jl}s_{ik} - a^2 b s_{ij}s_{jl}s_{lk}\right],$$
$$D = A^3 - \frac{1}{2}Aa^2 s_{ik}s_{ik} + a^3|s_{ik}|.$$

In the case when there is no preferred orientation, that is $s_{ik} = 0$, the considered system is isotropic and is characterised by the relative permittivity constant

$$\varepsilon_0 = 1 + 4\pi \frac{nz\bar{\alpha} + n_{\mathrm{s}}\alpha}{1 - \frac{4\pi}{3}(nz\bar{\alpha} + n_{\mathrm{s}}\alpha)}$$

from which one can find the relations

$$\frac{4\pi}{3}(nz\bar{\alpha} + n_{\mathrm{s}}\alpha) = \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}, \qquad A = -\frac{3}{\varepsilon_0 + 2}.$$

The written relations define the relative permittivity tensor for the system, which is formulated below to within second-order terms in the orientation tensor

$$\begin{aligned}\varepsilon_{ik} &= \varepsilon_0\delta_{ik} + 4\pi nz\Delta\alpha\left(\frac{\varepsilon_0+2}{3}\right)^2 s_{ik}\\ &\quad + \frac{1}{2}\left[1-\varepsilon_0+4\pi\left(\frac{\varepsilon_0+2}{3}\right)^3\right](4\pi nz\Delta\alpha)^2\left(\frac{\varepsilon_0+2}{3}\right)^2 s_{jl}s_{lj}\delta_{ik}\\ &\quad + \frac{1}{3}(4\pi nz\Delta\alpha)^2\left(\frac{\varepsilon_0+2}{3}\right)^3 s_{il}s_{lk}. \end{aligned} \tag{10.6}$$

One can see that, to a first approximation, as it is well known (Vleck 1932; Fröhlich 1958), allowance for the internal field by the Lorentz procedure is equivalent to multiplication by the factor

$$\left(\frac{\varepsilon_0+2}{3}\right)^2.$$

In conformity with the significance of the terms employed by investigators of anisotropy (Tsvetkov et al. 1964), the effects associated with the first-order terms in equation (10.6) may be called the effects of intrinsic anisotropy, while the second-order effects may be referred to as the effects of mutual interaction. In the second approximation, the principal axes of the relative permittivity tensor do not coincide, generally speaking, with the principal axes of the orientation tensor. It is readily seen that interesting situations may arise when $\Delta\alpha < 0$; in this case, the coefficients of the first- and second-order terms have different signs.

Let us note that the contribution from anisotropy due to the difference in the isotropic part of the polarisability between segments and solvents molecules, $\bar{\alpha} - \alpha_0$, ought to be added to expression (10.6). This is a first-order term in the orientational tensor (Tsvetkov et al. 1964). We shall not consider this contribution to the anisotropy, as it is not so important for the very concentrated solutions under consideration.

10.2 The Permittivity Tensor for Polymer Systems

Now, we have to return to the subchain model of macromolecule, which was used to calculate the stresses in the polymeric system, and express the tensor of the mean orientation of the segments of the macromolecule in terms of the subchain model.

Equation (10.6), formulated in the previous section, defines the relative permittivity tensor in terms of the mean orientation of certain uniformly distributed anisotropic elements, which we shall interpret here as the Kuhn segments of the model of the macromolecule described in Section 1.1. We shall now discuss the characteristic features of a polymer systems, in which the segments of the macromolecule are not independently distributed but are concentrated in macromolecular coils.

10.2.1 Dilute Solutions

In the equilibrium situation, at a given end-to-end distance R of a macromolecule, the tensor of mean orientation of segments of a chain is determined (Flory 1969) as

$$\langle e_i e_k \rangle - \frac{1}{3}\delta_{ik} = \frac{3}{5(zl)^2}\left(R_i R_k - \frac{1}{3}R^2\delta_{ik}\right). \tag{10.7}$$

As before, we shall consider each macromolecule to be divided into N subchains and assume that every subchain of the macromolecule is in the equilibrium. So, using the above formula relating the tensor of the mean orientation of the segments of the macromolecules $\langle e_j e_k \rangle$ to the distance between the ends of the subchains, we arrive from relation (10.6), taken in the first approximation, at Zimm's (1956) expression for the relative permittivity tensor

$$\varepsilon_{ik} = \varepsilon_0\delta_{ik} + n\Gamma\left(\langle r_i^\alpha A_{\alpha\gamma} r_k^\gamma \rangle - \frac{1}{3}\langle r_j^\alpha A_{\alpha\gamma} r_j^\gamma \rangle \delta_{ik}\right) \tag{10.8}$$

where n is the density of the number of macromolecules in the solution, and the matrix A has the form specified by formula (1.8), while the coefficient of the anisotropy of the macromolecular coil Γ, for the macromolecule as a freely-jointed chain of Kuhn segments, is given by the following expression

$$\Gamma = 4\pi\Delta\alpha\left(\frac{\varepsilon_0 + 2}{3}\right)^2 \frac{3N}{5zl^2}$$

where z is the number of Kuhn segments in the macromolecule, and $\Delta\alpha$ is the anisotropy of the polarisability of a Kuhn segment.

The anisotropy of the coil has been calculated for other models of the macromolecule. Expressions for the anisotropy coefficient are known in the case where the macromolecule has been represented schematically by a continuous thread (the persistence length model) (Gotlib 1964; Zgaevskii and Pokrovskii 1970) and also in the case where the microstructure of the macromolecules has been specified. In the latter case, the anisotropy coefficient of the macromolecule is expressed in terms of the bond polarisabilities and other microcharacteristics of the macromolecule (Flory 1969).

When account is taken of the excluded volume effects, one has also to take into account the possible effect of the shielding of the inner segments of the macromolecular coil, the latter effect being the greater the longer the macromolecule, so that the expression for the anisotropy coefficient, which has to be covariant in relation to subdivisions into subchain, assumes the form

$$\Gamma = 4\pi\Delta\alpha\left(\frac{\varepsilon_0 + 2}{3}\right)^2 \frac{3N^{2\nu}}{5\langle R^2 \rangle}. \tag{10.9}$$

The dependence of the polarisability coefficient on the length of the macromolecule follows from equation (10.9) as

$$\Gamma \sim M^{-2\nu}.$$

Expression (10.8) for the relative permittivity tensor in terms of the normal co-ordinates introduced by means of equations (1.13), assumes the form

$$\varepsilon_{ik} = \varepsilon_0 \delta_{ik} + n\Gamma \sum_{\alpha=1}^{N} \lambda_\alpha \left(\langle \rho_i^\alpha \rho_k^\alpha \rangle - \frac{1}{3} \langle \rho_j^\alpha \rho_j^\alpha \rangle \delta_{ik} \right)$$

or in terms of the ratios $x_{ik}^\nu = \langle \rho_i^\nu \rho_k^\nu \rangle / \langle \rho^\nu \rho^\nu \rangle_0$

$$\varepsilon_{ik} = \varepsilon_0 \delta_{ik} + \frac{3n\Gamma}{2\mu} \sum_{\alpha=1}^{N} \left(x_{ik}^\alpha - \frac{1}{3} x_{jj}^\alpha \delta_{ik} \right). \tag{10.10}$$

The last equation can be compared with equations (9.1) and (9.3) for the stresses in dilute solutions. On can see that, when internal viscosity is neglected ($\varphi_\nu = 0$), there is a relation between the permittivity tensor and stress tensor in the form

$$\begin{gathered} \varepsilon_{ij} - \varepsilon_0 \delta_{ij} = 2\bar{n} C \left(\sigma_{ij} + p\delta_{ij} - 2\eta_{\mathrm{s}} \gamma_{ij} \right), \\ C = \frac{\Gamma}{4\bar{n}\mu T} = \frac{2\pi}{45\bar{n}T} (\varepsilon_0 + 2)^2 \Delta\alpha \end{gathered} \tag{10.11}$$

where $\bar{n}$ is an isotropic value of the refractive index ($\bar{n}^2 = \varepsilon_0$) and C is the stress-optical coefficient, which is universally expressed through the segment anisotropy $\Delta\alpha$. The stress-optical law (10.11) reflects the fact that both the stresses and the optical anisotropy of a polymer solution under motion are determined by the mean orientation of segments of the chains.

Expression (10.10) for the relative permittivity tensor is valid only to a first approximation as regards the orientation of the segments and describes the anisotropy of the system associated with the intrinsic anisotropy of the segments. Apart from it, it was assumed that distribution of orientation of the segments inside every subchain are considered to be in equilibrium though under deformation. However, this expression has appeared to be very well applicable to dilute polymer solutions at low frequencies and small velocity gradient (Tsvetkov et al. 1964; Janeschitz-Kriegl 1983). In more general situations, one has to take into account that the mean orientation of segments under deformation of the macromolecular coil deviates from equilibrium value (10.7). One can believe that the stress-optical law (10.11) is valid in this case, so that an expression for the permittivity tensor can be found as combination of equations (9.1) and (10.11), whereby the internal viscosity is taking into account. However, an independent calculation of the tensor of orientation and the permittivity tensor in non-equilibrium situations is much desirable.

10.2.2 Entangled Systems

The situation is different for very concentrated polymer solutions. Though equation (10.6) is applicable for this case, formula (10.7) is not valid neither for the entire macromolecule nor for a separate subchain. The subchain of a macromolecule in the deformed entangled system is not in equilibrium even in the first approximation, and the problem about distribution of orientation of the interacting, connected in chains, segments apparently is not solved yet.

In this situation, which is also discussed in Section 7.5, we refer to experimental evidence according to which components of the relative permittivity tensor are strongly related to components of the stress tensor. It is usually stated (Doi and Edwards 1986) that the stress-optical law, that is proportionality between the tensor of relative permittivity and the stress tensor, is valid for an entangled polymer system, though one can see (for example, in some plots of the paper by Kannon and Kornfield (1994)) deviations from the stress-optical law in the region of very low frequencies for some samples. In linear approximation for the region of low frequencies, one can write the following relation

$$\varepsilon_{ij} - \varepsilon_0 \delta_{ij} = 2\bar{n} C \left(\sigma_{ij} + p\delta_{ij}\right) \tag{10.12}$$

where $\bar{n}$ is a value of the refractive index ($\bar{n}^2 = \varepsilon_0$) and C is the stress-optical coefficient, which is assumed to be universally expressed through the segment anisotropy $\varDelta\alpha$ by formula (10.11). Relation (10.12) reflects the fact that both the stresses and the optical anisotropy of a polymeric liquid under motion are determined by the mean orientation of the interacting segments. One can use expression (9.19) for the stress tensor to write

$$\varepsilon_{ij} = \varepsilon_0 \delta_{ij} + 6nT\,\bar{n}C \sum_{\alpha=1}^{N} \left\{ x_{ij}^{\alpha} - \frac{1}{3}\delta_{ij} + u_{ij}^{\alpha} \right\}. \tag{10.13}$$

One admits that the relative permittivity tensor of the system is determined by the mean orientation of the segments, so that we consider expression (10.13) to be equivalent to the first-order terms of relation (10.6) and, at comparison, obtain the expression for the mean orientation of segments of macromolecules in an entangled system

$$\langle e_i e_k \rangle - \frac{1}{3}\delta_{ik} = \frac{3}{5z} \sum_{\alpha=1}^{N} \left\{ x_{ij}^{\alpha} - \frac{1}{3}\delta_{ij} + u_{ij}^{\alpha} \right\} \tag{10.14}$$

where z is number of segments in a macromolecules. The set of the variables $x_{ij}^{\alpha} = \frac{\langle \rho_i^{\alpha} \rho_k^{\alpha} \rangle}{\langle \rho_i^{\alpha} \rho_k^{\alpha} \rangle_0}$ represents the conformation of the macromolecular coil, while the variables u_{ij}^{α} are mainly connected with the mean orientation of the segments s_{ij}. The variables x_{ij}^{α} and u_{ij}^{α} appear to be independent from each other and can be found as a solutions of the relaxation equations (7.25) and (7.38) for weakly entangled systems and equations (7.29) and (7.40) for strongly entangled systems.

Relaxation equations for the mean orientation can be restored (see also Section 7.5). In the case of strongly entangled system, in linear approximation, assuming that $E/B \ll B$, we have

$$\frac{\mathrm{d}\langle e_i e_k \rangle}{\mathrm{d}t} = -\frac{1}{\tau}\left(\langle e_i e_k \rangle - \frac{1}{3}\delta_{ik}\right) + \frac{\pi^2}{15}\frac{1}{z}B\frac{\tau^*}{\tau}\gamma_{ik}. \tag{10.15}$$

One can see that, in this approximation, disturbed conformation of macromolecules does not affect the mean orientation of segments in the steady state, that can be found from equation (10.15) as

$$\langle e_i e_k \rangle = \frac{1}{3}\delta_{ik} + \frac{\pi^2}{15}\frac{1}{z}\tau^* B\gamma_{ik}. \tag{10.16}$$

In contrast to the case of dilute polymer solutions (relation (10.7)), mean orientation of segments does not depend (to the first approximation) on the large-scale conformation of the macromolecule. However, an independent calculation of the tensor of orientation in non-equilibrium situations is much desirable.

10.3 Optical Birefringence

The value of the refractive index n of light in the anisotropic medium depends on the direction of propagation $\boldsymbol{s}$ and on the direction of the polarisation of the light. For the given relative permittivity tensor ε_{jl}, the refractive index can be determined from the relation (Born and Wolf 1970; Landau et al. 1987)

$$\varepsilon_{jl}E_l = n^2[E_j - s_j(\boldsymbol{s}\cdot\boldsymbol{E})]. \tag{10.17}$$

It follows from (10.17) that the refractive index for an isotropic medium is determined by the permittivity constant only

$$n^2 = \varepsilon_0.$$

In the case of an anisotropic system, it is convenient to consider particular cases. Further on, expressions for characteristics of optical birefringence in two typical cases will be shown.

Methods for the experimental estimation of birefringence can be found in the monograph by Tsvetkov et al. (1964), Janeschitz-Kriegl (1983) and in papers by Lodge and Schrag (1984), Inoue et al. (1991), and Kannon and Kornfield (1994).

10.3.1 Simple Elongation

In the simplest cases, the optical anisotropy of polymer systems is studied under the conditions of simple elongation, when the elongation velocity gradient ν_{11} is given. The system investigated then becomes, generally speaking, a “triaxial dielectric crystal” with components of the relative permittivity tensor

$$\begin{Vmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & \varepsilon_{22} & 0 \\ 0 & 0 & \varepsilon_{33} \end{Vmatrix}.$$

For a system under elongational deformation along direction 1, for a beam of light propagating in direction 3, according to (10.17) one obtains different refractive indices for different polarisation of the beam, so that, for polarisation in directions 1 and 2, one has a difference of refractive indices

$$\Delta n = \frac{1}{2\bar{n}}(\varepsilon_{11} - \varepsilon_{22}) \tag{10.18}$$

where $\bar{n}$ is the average refractive index. This relation is written on the assumption that the difference between refractive indices is small, so that non-linear terms are omitted.

10.3.2 Simple Shear

For a system undergoing simple shear, when the velocity gradient $\nu_{12} \neq 0$, the relative permittivity tensor is non-diagonal

$$\begin{Vmatrix} \varepsilon_{11} & \varepsilon_{12} & 0 \\ \varepsilon_{12} & \varepsilon_{22} & 0 \\ 0 & 0 & \varepsilon_{33} \end{Vmatrix}.$$

However, the tensor can be turned to diagonal form by rotating the coordinate frame round axis 3 by an angle χ (the extinction angle), defined by the formula

$$\tan 2\chi = \frac{2\varepsilon_{12}}{\varepsilon_{11} - \varepsilon_{22}}. \tag{10.19}$$

The differences between the refractive indices (the extent of double refraction) in the different principal directions can be determined from equation (10.17). For a beam propagated in direction 3, we find that

$$\Delta n = \frac{1}{2\bar{n}}\sqrt{(\varepsilon_{11} - \varepsilon_{22})^2 + 4\varepsilon_{12}^2}. \tag{10.20}$$

This relation as well as relation (10.18) is valid in linear approximation and can be therefore rewritten as

$$\Delta n = \frac{1}{\bar{n}}\varepsilon_{12}, \tag{10.21}$$

while the extinction angle $\chi = \pi/4$.

A little bit more complicated situation appears, if one considers a beam propagating across the flow in direction characterised by the unit vector

$$s_1 = \sin\theta, \quad s_2 = \cos\theta, \quad s_3 = 0.$$

This experimental situation is described, for example, in the work of Brown et al. (1995). It is convenient to choose the electric vector of the beam in plane (1–2) or in direction 3, whereas the differences between the refractive indices can be easily found from equation (10.17)

$$\Delta n = \frac{1}{2\bar{n}}\left(\frac{\varepsilon_{11}\varepsilon_{22} - \varepsilon_{12}^2 - \varepsilon_{22}\varepsilon_{33}(1-\sin^2\theta) - \varepsilon_{11}\varepsilon_{33}(1-\cos^2\theta)}{\varepsilon_{22}(1-\sin^2\theta) - \varepsilon_{11}(1-\cos^2\theta) - 2\varepsilon_{12}\sin\theta\cos\theta}\right.$$
$$\left. - \frac{2\varepsilon_{12}\varepsilon_{33}\sin\theta\cos\theta}{\varepsilon_{22}(1-\sin^2\theta) - \varepsilon_{11}(1-\cos^2\theta) - 2\varepsilon_{12}\sin\theta\cos\theta}\right).$$

For $\theta = 0$, this formula reduces to

$$\Delta n = \frac{1}{2\bar{n}}\left(\varepsilon_{11} - \varepsilon_{33} - \frac{\varepsilon_{12}^2}{\varepsilon_{22}}\right).$$

10.3.3 Oscillatory Deformation

One frequently deals with the linear effects of anisotropy which are induced by oscillatory velocity gradients or by oscillatory strains

$$u_{ik}(t) = -i\omega\gamma_{ik}(t) \sim e^{-i\omega t}.$$

In this case, it is convenient to characterise the behaviour of the system by the dynamo-optical coefficient

$$S(\omega) = S'(\omega) + iS''(\omega)$$

due to Lodge and Schrag (1984), or by the strain-optical coefficient

$$O(\omega) = O'(\omega) - iO''(\omega)$$

due to Inoue et al. (1991). These quantities are introduced by relations

$$\begin{aligned} \varepsilon_{ik} &= \varepsilon_0\delta_{ik} + 4\bar{n}S(\omega)\gamma_{ik}, \\ \varepsilon_{ik} &= \varepsilon_0\delta_{ik} + 4\bar{n}O(\omega)u_{ik}. \end{aligned} \tag{10.22}$$

It is easy to find, from the above-written formulae, that the components of dynamic characteristics are connected by relations

$$O'(\omega) = \omega S''(\omega), \qquad O''(\omega) = \omega S'(\omega). \tag{10.23}$$

Relations (10.22) are quite similar to the definitions of dynamic viscosity $\eta(\omega)$ and dynamic modulus $G(\omega)$, so that relations (10.23) are similar to the relations between the components of dynamic modulus and dynamic viscosity (equations (6.10)).

Dynamo-optical and strain-optical coefficients can be estimated from measurements of birefringence Δn under elongational flow or shear flow, correspondingly

$$\Delta n = 3S(\omega)\nu_{11} = 3O(\omega)u_{11}, \tag{10.24}$$
$$\Delta n = 2S(\omega)\nu_{12} = 2O(\omega)u_{12}. \tag{10.25}$$

Note that a frequency-dependent stress-optical coefficient $C(\omega)$ can be introduced by comparing the stress tensor and the relative permittivity tensor

$$\varepsilon_{ij} - \varepsilon_0\delta_{ij} = 2\bar{n}C(\omega)(\sigma_{ij} + p\delta_{ij})$$

where

$$C(\omega) = \frac{S(\omega)}{\eta(\omega)} = \frac{O(\omega)}{G(\omega)}.$$

10.4 Anisotropy in a Simple Steady-State Shear Flow

Let us consider the anisotropy of polymer system undergoing simple steady-state shear. This situation can be realised experimentally in a simple way (Tsvetkov et al. 1964). The quantity measured in experiment are the birefringence Δn and the extinction angle χ which are defined by formulae (10.19) and (10.20), correspondingly, through components of the relative permittivity tensor.

10.4.1 Dilute Solutions

One can turn to equation (10.10) to find the components of the relative permittivity tensor. Using expressions for the moments (2.42), one determines the gradient dependence of the quantities for dilute polymer solutions to within second-order terms

$$\begin{aligned} \Delta n &= 2CnT\sum_{\nu=1}^{N}\tau_\nu^{\perp}\nu_{12}, \\ \tan 2\chi &= \frac{1}{2A\nu_{12}}, \qquad \chi = \frac{\pi}{4} - A\nu_{12} \end{aligned} \tag{10.26}$$

where two non-dimensional quantities, the stress-optical coefficient C and the characteristic angle A, have been introduced as

$$C = \frac{\Gamma}{4\bar{n}\mu T} = \frac{2\pi}{45\bar{n}T}(\varepsilon_0 + 2)^2\Delta\alpha, \tag{10.27}$$
$$A = \frac{1}{2}\sum_{\nu=1}^{N}(1 + \varphi_\nu)(\tau_\nu^{\perp})^2 \cdot \left(\sum_{\nu=1}^{N}\tau_\nu^{\perp}\right)^{-1}. \tag{10.28}$$

We can see from equation (10.27) that the stress-optical coefficient depends neither on the molecular weight of the polymer nor on the number of subchains and is proportional to the polarisability of the Kuhn segment $\varDelta\alpha$. The stress-optical coefficient can be estimated by investigation of the shear motion of a very dilute polymer solution, as the ratio of the characteristic extent of double refraction $[\varDelta n]$ to the initial characteristic (intrinsic) viscosity defined by equation (6.23)

$$2C = \frac{[\varDelta n]}{[\eta]_0}, \quad [\varDelta n] = \lim_{\substack{c\to 0\\ \nu_{12}\to 0}} \frac{n_1 - n_2}{c\eta_{\mathrm{s}}\nu_{12}}. \tag{10.29}$$

As far as the characteristic angle (10.28) is concerned, taking into account the dependence of the relaxation time and of the internal viscosity on the number of the mode (formulae (2.27) and (2.31)), one can write, with the aid of the zeta-function $\zeta(x)$,

$$A = \frac{1}{2}\frac{\tau_1}{\zeta(z\nu)}\left[\zeta(2z\nu) + \varphi_1\zeta(2z\nu - \theta)\right].$$

The first term of the expression is proportional to the solvent viscosity η_{s} and the second to the internal viscosity (kinetic rigidity) of the macromolecule, so that measurement of the anisotropy of solutions in different solvents makes it possible to estimate the quantity

$$\tau_1\varphi_1 \sim M^{z\nu-\theta}.$$

The experimental results (Tsvetkov et al. 1964) for macromolecules of different lengths shows that

$$\tau_1\varphi_1 \sim M^{1\to 1.2}$$

and one can write an approximate empirical relation

$$\theta - z\nu + 1 = 0. \tag{10.30}$$

An independent empirical confirmation of this relation was discussed in Section 6.2.4. The relation was mention in Section 2.5 and used at the choice of specific values of the parameters for calculation of dynamic properties of dilute solutions in Section 6.2.2.

Of course, all the derived relations are valid for velocity gradients which are not too large. Otherwise, second-order terms of equation (10.6) should be taken into account, when equation (10.10) is being written, which complicates the situation. We may note that very interesting phenomena may occur, for example, at high velocity gradients. If $\varGamma < 0$, the so-called anomalous dependencies (discovered in Tsvetkov's laboratory and discussed, in particular, by Gotlib and Svetlov 1964a, 1964b) of the extent of double refraction and of the extinction angle on the velocity gradient are observed in experiments, indicating that the principal axes of the tensor of the average orientation of optical anisotropy do not coincide. In order to interpret these phenomena, one has to turn firstly to equations of type (10.6) for the relative permittivity tensor that are non-linear as regards orientation.

10.4.2 Entangled Systems

Now we refer to formula (10.13) for the relative permittivity tensor to determine the characteristic quantities in this case of strongly entangled linear polymers. We use expansions (7.32) and (7.43) for the internal variables to obtain the expression for the components of the tensor through velocity gradients

$$\varepsilon_{12} = \frac{\pi^2}{3} nT\,\bar{n}C\,\tau^*B\,\nu_{12},$$
$$\varepsilon_{22} - \varepsilon_{11} = \frac{2\pi^2}{3} nT\,\bar{n}C\,\tau\tau^*B\,\nu_{12}^2.$$

Then we can write the characteristic quantities

$$\Delta n = \frac{\pi^2}{3} nT\,C\,\tau^*B\,\nu_{12}, \qquad \tan\chi = \frac{1}{\tau\nu_{12}}. \tag{10.31}$$

Of course, these relations are trivial consequences of the stress-optical law (equation (10.12)). However, it is important that these relations would be tested to confirm whether or not there is any deviations in the low-frequency region for a polymer system with different lengths of macromolecules and to estimate the dependence of the largest relaxation time on the length of the macromolecule. In fact, this is the most important thing to understand the details of the slow relaxation behaviour of macromolecules in concentrated solutions and melts.

10.5 Oscillatory Birefringence

10.5.1 Dilute Solutions

One can turn to discussion of the dynamo-optical coefficient, defined by equation (10.22). The expression for the relative permittivity tensor (10.10) and equation (2.41) for the moments allow one to write

$$S(\omega) = nTC\sum_{\alpha=1}^{N} \frac{\tau_\alpha^\perp}{1 - i\omega\tau_\alpha^\parallel}.$$

The stress-optical coefficient C is defined by equation (10.27) and the relaxation times $\tau_\alpha^\perp$ and $\tau_\alpha^\parallel$ are defined by relations (2.30). One can see that the dynamo-optical coefficient of dilute polymer solutions depends on the non-dimensional frequency $\tau_1\omega$, the measure of internal viscosity φ_1 and indices $z\nu$ and θ

$$S(\omega) = nTC\tau_1 f(\tau_1\omega, \varphi_1, z\nu, \theta).$$

For the components of dynamo-optical coefficient, one can find the equations, established by Thurston and Peterlin (1967),

$$
\begin{aligned}
S'(\omega) &= nTC \sum_{\alpha=1}^{N} \frac{\tau_\alpha^{\perp}}{1+(\tau_\alpha^{\parallel}\omega)^2}, \\
S''(\omega) &= nTC \sum_{\alpha=1}^{N} (1+\varphi_\alpha) \frac{(\tau_\alpha^{\perp})^2\omega}{1+(\tau_\alpha^{\parallel}\omega)^2}.
\end{aligned}
\tag{10.32}
$$

One can see that, in the case when the intramolecular viscosity is neglected ($\varphi_1 = 0$), the frequency dependence of the components of the dynamo-optical coefficient (10.32) agrees with the analogous dependence of the shear viscosity (see equation (6.20) and Fig. 14). The stress-optical law can be written in the form

$$
\frac{S'(\omega)}{\eta'(\omega) - \eta_{\mathrm{s}}} = C, \qquad \frac{S''(\omega)}{\eta''(\omega)} = C. \tag{10.33}
$$

Pokrovskii and Kokorin (1987) extended the results to the more general case where the internal viscosity parameter assume arbitrary values and the excluded-volume effects are taken into account.

Of course, equations (10.32) and (10.33) are valid in linear approximation for velocity gradients which are not too large and for low frequencies. Is the stress-optical law valid, at the higher frequencies, when the intramolecular relaxation processes have to be taken into account? Deviations from the stress-optical law can emerge, if one assumes the equilibrium distribution of segment orientation, when the expression for the relative permittivity tensor was written, whereas the internal viscosity in dynamic viscosity is included in proper way. At correct consideration, the deviations from the stress-optical law do not appear in the theory. At very high frequencies, the real part of the dynamo-optical coefficient is zero, while the real part of dynamic viscosity remains finite. By investigating optical anisotropy and stresses at high frequencies, one can estimate from the experimental data the importance of intramolecular relaxation processes in the dynamics of the macromolecule.

The work by Lodge et al. (1982) contains the experimental data on the frequency dependencies of the dynamo-optical coefficient for infinitely dilute solutions of polymer, which are represented as frequency dependence of the magnitude and the phase angle, respectively

$$
S_{\mathrm{m}} = \left((S')^2 + (S'')^2\right)^{1/2}, \qquad \tan\theta_{\mathrm{s}} = \frac{S''}{S'}.
$$

10.5.2 Entangled Systems

The strain-optical coefficient $O(\omega)$, defined by equation (10.22), can be corresponded to dynamic modulus calculated in Section 6.4.2. Taking all the previous speculations into account, an expression for the strain-optical coefficient can be written in general way as

$$
O(\omega) = nT \sum_{a=1}^{6} \sum_{\alpha=1}^{N} (-\mathrm{i}\omega) \frac{C_a\, p_\alpha^{(a)} \tau_\alpha^{(a)}}{1 - \mathrm{i}\omega\tau_\alpha^{(a)}} \tag{10.34}
$$

where the times of relaxation $\tau_\alpha^{(1)}$, $\tau_\alpha^{(2)}$, $\tau_\alpha^{(3)}$, $\tau_\alpha^{(4)}$, $\tau_\alpha^{(5)}$, $\tau_\alpha^{(6)}$ and the corresponding weights $p_\alpha^{(1)}$, $p_\alpha^{(2)}$, $p_\alpha^{(3)}$, $p_\alpha^{(4)}$, $p_\alpha^{(5)}$, $p_\alpha^{(6)}$ are the same as calculated for dynamic modulus in Sections 6.4.2, while the stress-optical coefficients C_1, C_2, C_3, C_4, C_5, C_6 are assume can be different for different relaxation branches. It is possible that the different relaxation branches are connected with different types of motion and are characterised with different values of the stress-optical coefficient. The stress-optical coefficients are proportional to the polarisability of the structural units of the macromolecule, which can be different for different types of motion of the chain (Gao and Weiner 1994). The strain-optical coefficient of entangled system depends on the non-dimensional frequency $\tau^*\omega$ and on the non-dimensional parameters

$$O(\omega) = nT\, f(C_1, C_2, C_3, C_4, C_5, B, \chi, \tau^*\omega).$$

The contributions into dynamic modulus and, consequently, into strain-optical coefficient from the high-frequency branches are discussed in Section 6.4.2. In the case, when the all stress-optical coefficients are equal, a graphs for the components the strain-optical coefficient have the same form as the graph for the components of the dynamic modulus, which, for example, are shown in Fig. 17. In general case, expression (10.34) allows us to describe different types of the frequency dependence of the strain-optical coefficient and this can gives an explanation to the “curious behaviour” of the strain-optical coefficient of polymer solutions and melts. In fact, considering strain-optical coefficient in a great range of frequencies, scholars have to admit that the stress-optical coefficient C depends either on frequency or is different for different relaxation branches, to explain experimental data (Inoue et al. 1991; Okamoto et al. 1995). We cannot discuss comparison between the experimental and theoretical curves any more, because it is an illustration of a phenomenon which ought to be investigated carefully.

In application to very concentrated solutions, the optical anisotropy provides the important means for the investigation of slow relaxation processes. It is important to confirm whether or not there is any deviations from the stress-optical law in the low-frequency region for a polymer melt with different lengths of macromolecules. In fact, this is the most important thing to understand the details of the slow relaxation behaviour of macromolecules in concentrated solutions and melts. The evidence can be decisive for understanding the mechanism of the relaxation.