Relation between the Emission Anisotropy and the Dichroic Ratio for Solute Alignment in Stretched Polymer Films*

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For the determination of the angle β between the absorption and emission transition moments it seems appropriate to investigate the emission anisotropy as a function of the absorption dichroic ratio, R_d, rather than of the stretch ratio, R_s, of a polymer film. The angles β thus determined for linear molecules of 1,8-diphenyloctatetraene (DPO), 1,6-diphenylhexatriene (DPH), 1,4-diphenylbutadiene (DPB), 4-dimethylamino-4′-nitrostilbene (DNS), and p-terphenyl (TP) are considerably smaller and closer to the zero value. Slight deviations of the angles obtained from $\beta = 0°$ result from the effect of limited rotational motions of the luminescent molecules in the polymer.

1. Introduction

The knowledge of the mutual orientation of the transition moments (the angle β) responsible for the absorption and emission, as well as the orientation of the above moments relative to the molecular framework is indispensable for the determination of the relation between the structure and the optical properties of a luminescent molecule (LM). Such information can be obtained by investigating the absorption and emission anisotropies of oriented systems in which the distribution of the LM in the ground state is anisotropic [1–3]. Liquid crystals [4, 5], compressed biological membranes [6], and, more and more frequently, stretched polymer films are employed as orienting systems [1, 3, 7]. The degree of the orientation of the environment (e.g. the multiplicity of the film stretching) has been assumed to be the measure of the arrangement of the LM. As is known, however, the arrangement of the investigated LM is essentially affected, apart from the stretch ratio, R_s, by the shape of the molecule [8]. As a result, for linear LM of different lengths, different degrees of arrangement are obtained with the same stretch ratio, R_s, of the polymer.

Thus, in the case of existing prolate molecules, the changes in the emission anisotropy due to the stretching of the polymer film should be investigated as a function of the measured dichroic ratio

$$R_d = A_{\parallel}/A_{\perp}. \tag{1}$$

($A_{\parallel}$ and $A_{\perp}$ are the components of the absorbance $A = \varepsilon C l$ parallel and perpendicular to the stretching direction (the Z-axis) of the polymer film, where ε is the molar absorption coefficient in litres per mol · cm, C is the concentration in mol/litres and l is the length in cm), which is the measure of the orientation degree of the LM.

The investigations of the emission anisotropy carried out together with the measurements of the absorption dichroic ratio enable the angle β between the absorption and emission transition moments to be determined more accurately.

2. Theoretical Basis

The following expression was obtained, based on simple geometrical considerations, for the absorption anisotropy of uniaxial polymer films with axially symmetric long LM [2]:

$$K(R_s, \varphi) = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \tag{2}$$

$$= \{\tfrac{3}{2}a^2[1 - (a^2 - 1)^{1/2} \arcsin 1/a] - \tfrac{1}{2}\}(\tfrac{3}{2}\cos^2\varphi - \tfrac{1}{2}),$$

where

$$a^2 = R_s^2/(R_s^2 - 1) \quad \text{for} \quad R_s > 1. \tag{3}$$

φ denotes the angle between the long molecular axis and the direction of the absorption transition moment.

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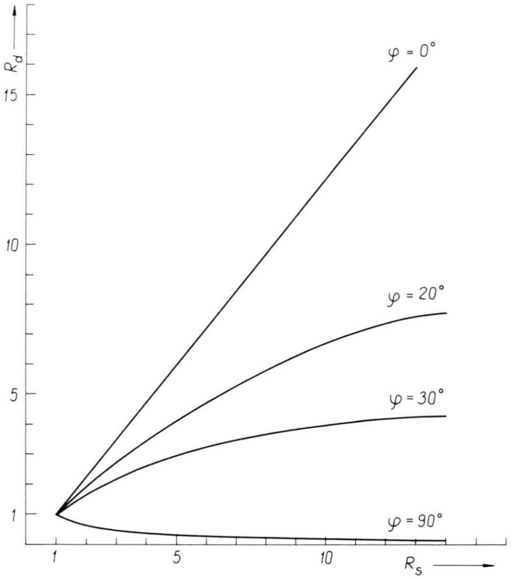

Fig. 1. Theoretical dependence of the dichroic ratio R_d on stretch ratio R_s for different values of φ.

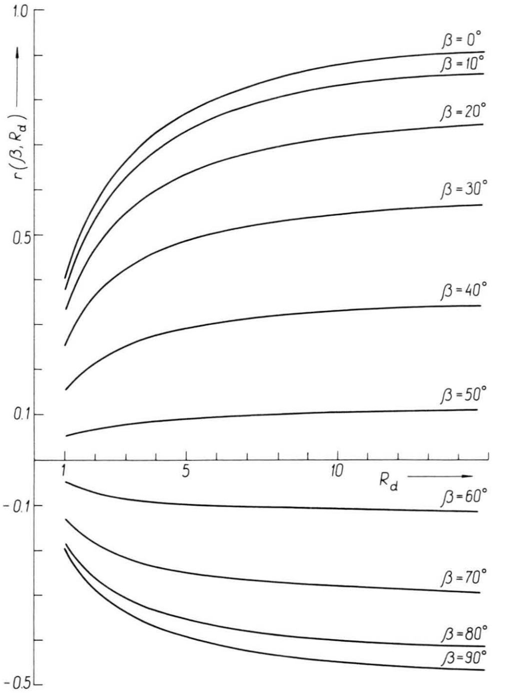

Fig. 2. Theoretical dependence of $r(\beta, R_d)$ on the dichroic ratio R_d for different values of β.

The dichroic ratio (1) can be written, based on expression (2), in the following way:

$$R_d = \frac{1 + 2K(R_s, \varphi)}{1 - K(R_s, \varphi)} \tag{4}$$

$$= 2\frac{1 + a^2[1 - (a^2 - 1)^{1/2} \arcsin 1/a](3\cos^2\varphi - 1) - \cos^2\varphi}{1 - a^2[1 - (a^2 - 1)^{1/2} \arcsin 1/a](3\cos^2\varphi - 1) + \cos^2\varphi}.$$

Figure 1 shows the dichroic ratio, R_d, vs. the stretch ratio, R_s, of the polymer for several values of the angle φ. Although (4) differs to a great extent from the expression obtained by Tanizaki [9], the values of R_d calculated for different angles φ and the same stretch ratios R_s by using these formulae are identical. Hence the same plots have been obtained. Formula (4) is, however, much simpler than Tanizaki's expression [9].

The theoretical considerations and the investigations of the linear dichroism carried out for linear symmetrical molecules indicate that the absorption transition moment lies along the long axis of the molecule, which implies that $\varphi = 0°$. The dependence of the dichroic ratio, R_d, on the stretch ratio, R_s, shown in Fig. 1 based on (4) for $\varphi = 0°$, is linear and can be described by

$$R_d = \tfrac{5}{4} R_s - \tfrac{1}{4}. \tag{5}$$

Hence, when $\varphi = 0°$ one obtains

$$R_s = \tfrac{4}{5} R_d + \tfrac{1}{5}. \tag{6}$$

This function, representing the true degree of the orientation of long molecular axes, taking also into account such factors as the degree of the orientation of the polymer, the shape factor, etc., can be determined from measurements of the absorption dichroic ratio, $R_d = A_{\parallel}/A_{\perp}$.

The formula for the emission anisotropy obtained in the preceding paper [1],

$$r(\beta, R_d) = \left\{\frac{3}{2}\,\frac{(a^2 - 1)^{1/2} + 2a^2(a^2 - 1)^{-1/2} - 3a^2 \arcsin 1/a}{2(a^2 - 1)^{-1/2} - 2\arcsin 1/a} - \frac{1}{2}\right\} \cdot \left(\tfrac{3}{2}\cos^2\beta - \tfrac{1}{2}\right), \tag{7}$$

remains valid, with a being given by

$$a^2 = \frac{(0.8\,R_d + 0.2)^2}{(0.8\,R_d + 0.2)^2 - 1} \quad \text{for} \quad R_d > 1\,. \tag{8}$$

Figure 2 shows $r(\beta, R_d)$ as a function of R_d for different angles β.

3. Comparison with Experiment and Discussion

The emission anisotropies, $r(\beta, R_d)$, measured in stretched polyvinyl alcohol (PVA) films for linear DPO, DPH and DPB molecules examined previously, and for DNS and TP as a function of the dichroic ratio, $R_d = A_{\parallel}/A_{\perp}$ are shown in Figure 3. For higher stretch ratios, the measured values of the emission anisotropy are included between the theoretical curves $r(\beta, R_d)$ plotted for $\beta = 0°$ and $\beta = 10°$. For the highest stretch ratio of the film, the measured emission anisotropies closely approach the theoretical curve with $\beta = 0°$. The angles β found for DPO, DPH, DPB, DNS and TP amount to 4°, 5°, 7°, 5° and 8°, respectively. The angles β thus determined are distinctly smaller than those found with the previous method [1]. The corrected function given by (6) leads in fact to much better agreement between the experimental results and theoretical predictions concerning the emission anisotropy.

It is worth noting that for an isotropic PVA film (for $R_d = 1$), the measured limiting fluorescence anisotropies differ markedly from the theoretical value $r_f = 0.4$, amounting to 0.354, 0.360, 0.330, 0.363, and 0.318 for DPO, DPH, DPB, DNS, and TP, respectively. The angle β calculated with the Perrin equation [10] for the LM examined in an isotropic rigid film exceeds a value of 15°. Such a high value of β results from limited rotational motions [11–14], which means that in isotropic PVA films and in many other media considered rigid or highly viscous, the LM have little freedom of limited rotational motions. Such motions occurring in the PVA polymer are effectively eliminated by the stretching of the film. As a result of the deformation of the polymer caused by stretching, the LM are compressed mechanically inside the polymer cavities, which causes a restriction of their thermal rotations but does not affect the character of the intramolecular processes, this being evidenced by the fact that the location and the shape of the absorption and fluorescence spectra are independent of the degree of the polymer film stretching. Upon the elimination of such restricted rotational motions, the values of the limiting anisotropy, r_0, of the LM investigated ranged from 0.388 to 0.397, thus being very close to the value of the fundamental emission anisotropy, $r_f = 0.4$.

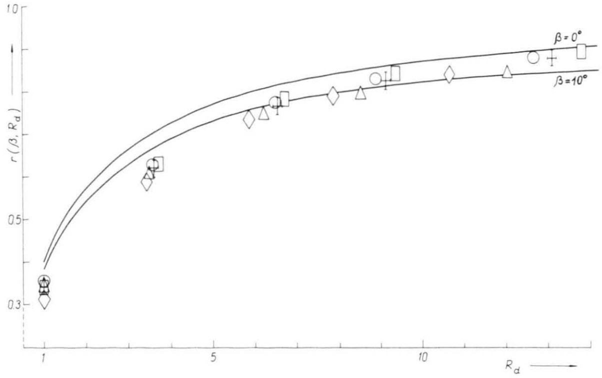

Fig. 3. Dependence of $r(\beta, R_d)$ on the dichroic ratio R_d for DPO (□), DPH (+), DPB (△), DNS (○) and TP (◇). Full lines represent the theoretical curves obtained according to formula (7) for $\beta = 0°$ and $\beta = 10°$.

It can be concluded that the results obtained by employing the method outlined above indicate that for the linear LM investigated, the directions of the transition moments in the longwave absorption band and in the emission from the S_1 state are parallel to the long axis of the molecule.*

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* *Note added in proof*: In the previous paper [3] in expression (14) before the fraction on the right hand instead of 3/2 is 1.

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