

THE ENERGY TRANSFER FOR AN ORIENTED DYE MOLECULES
IN STRETCHED POLY(VINYL ALCOHOL) FILMS

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For various stretch ratios, the degrees of polarization(P) of Acridine Orange(AO) cations in stretched poly(vinyl alcohol) (PVA) films has been measured as a function of the concentration of AO cations. The plots of $1/P$ versus concentration are linear with the slope dependent on the stretching ratio, for concentrations ranging from 4×10^{-5} to 10^{-4} M. This has been interpreted as the results of energy transfer between partially oriented like molecules.

AO polarized fluorescence spectra in stretched films have been studied by Hanle et al.¹⁾ and Jakobi and Kuhn²⁾ with the attempt to determine the orientations of the transition moments. In general the long axis of molecule is parallel to the stretching direction,²⁾ in contrast with the interpretation by Hanle et al.¹⁾ There have been many reports about measurements of dichroism of stretched polymer sheets.^{3,6)} But only a few studies of polarized fluorescence have been done, with using stretched polymer films as partially oriented assembly of molecules.^{1,2,4)} In a previous paper⁵⁾ we have reported the concentration depolarization of AO cations incorporated in PVA films. This study has chosen as its subject the energy transfer between oriented molecules in stretched polymer films, and presents the effect of partial orientations due to stretching on the concentration depolarization of fluorescence.

PVA films containing purified AO cations were prepared as has been described in the previous paper. The dry PVA sheet ($6 \times 6 \text{ cm}^2$) was uniaxially stretched in an oven at $65-70^\circ\text{C}$ with the velocity of about 4 cm/min . Two points, 1 cm apart in the stretching directions, were marked and the stretch ratio(Rs) was defined as the ratio of the distances between the marks after and before stretching. The extension up to 4 fold could then be achieved. The vertically polarized exciting light is focused on the specimen at an angle of 60° to the surface of it and fluorescence is observed at right angle with the exciting beam. The correction of the polarization degrees was performed by the ordinary method, in the same way as for the case of random orientation. As a function of stretch ratio, the measurements of polarized fluorescence intensity were made with two ways of excitation; I) the stretching direction parallel to the polarized incident light; F_{\parallel} , and II) the former perpendicular to the latter; F_{\perp} . The polarization ratio is given by I_{\parallel}/I_{\perp} , where I_{\parallel} or I_{\perp} means the fluorescence intensity observed for the parallel or crossed combination

of the polarizer and analyser.

Results reproducibly obtained are presented in Fig. 1. The intensity of polarized fluorescence were measured at the fluorescence maximum with the excitation at 485 nm. The open symbols denote the parallel excitation (F_{\parallel}) (Fig. 1a) and the solid symbols perpendicular one (F_{\perp}) (Fig. 1b).

In case of the parallel excitation, I_{\parallel}/I_{\perp} increases with the stretch ratio at low concentrations and the highest P value reaches to 0.79. It indicates the existence of the preferential orientation and of the partially uniaxial symmetry.

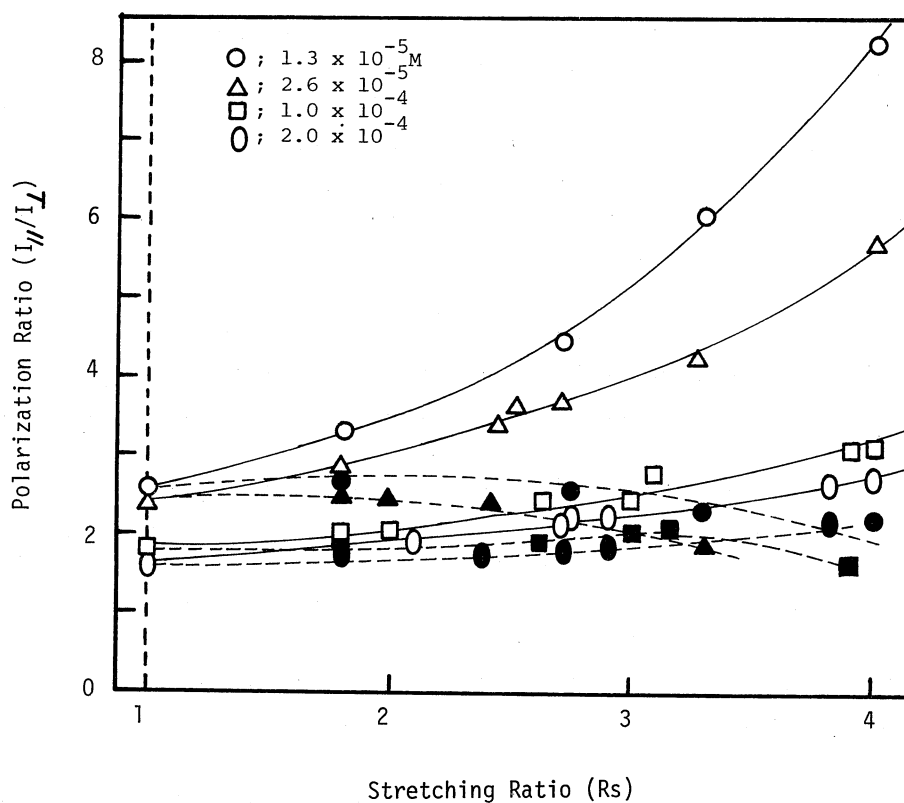


Fig. 1. The dependence of the polarization ratio (I_{\parallel}/I_{\perp}) on the stretching ratio.

a) open symbols, F_{\parallel} :

stretching direction parallel to vertically polarized exciting light.

b) solid symbols, F_{\perp} :

the former perpendicular to the latter.

The absorption spectra also indicate a partial uniaxial orientation of the transition moment along the stretching direction. The averaged orientation angle of the absorption transition moment is calculated to be 21° at $R_s = 4$ and 45° at $R_s = 3$, according to the model developed by Tanizaki.⁶⁾ This could be attributed to the change in the distribution function of the orientation with the stretch ratio. The distribution function is a superposition of two different kinds of distributions, one is isotropic and another is uniaxial. The ratio of the two different types of distribution varies with the stretch ratio. As the stretch ratio increases the number of molecules of the isotropic distribution decreases and the uniaxial one becomes significant. At a stretch ratio of about 4, the distribution of orientation seems to be almost uniaxial. This may be reflected in the fluorescence polarization.

There are two different mechanisms, dependent upon the concentration range, which can be used to describe the relation of polarization degrees with stretch ratios. In the first place, a low concentration range is treated. The polarization ratio (I_{\parallel}/I_{\perp}) indicates the distribution of the excitation, since the energy transfer between dye molecules is ineffective. In the parallel excitation only the molecules aligned along the stretching direction are excited, therefore polarization ratio increases rather swiftly with further stretching. In the perpendicular excitation, however, the molecules of which transition moment are perpendicular to the stretching direction are very few and cannot strongly contribute to the fluorescence intensity. Therefore, the profile of fluorescence property is governed by the degree of alignment.

In order to establish the type of orientation, it is necessary to correct the effects of birefringence.^{7,8)} Here it seems negligible because of above optical arrangements. It is assumed as follows: 1) The transition moment for fluorescence is the same as that for absorption. 2) Dye molecules align along a unique orientation axis at a certain angle, λ , to the stretching direction, with the molecular plane parallel to the film plane. 3) The energy transfer does not occur at low concentrations. On the basis of these assumptions, the value of λ for $R_s = 4$ is calculated to be 15.8° according to Nishijima's equation.⁹⁾ This could be compared with the value, 21° , obtained from the absorption spectra.

The angular distribution of polarized fluorescence intensity of various molecules has been investigated by Fujiwara and Kokubun.⁷⁾ They have demonstrated that AO cations become almost uniaxially aligned on stretching.

In the second place, a high concentration range is treated. Here the energy transfer between oriented molecules is very efficient, the polarization of the fluorescence is caused by the distribution of the oriented transition moment and not by the excitation. In the parallel excitation, the absorption of light is exclusively caused by the transition moment aligned to the direction, but the energy transfer re-distributes the excitation over various orienting molecules. Thus, even in the parallel excitation, the depolarization of fluorescence occurs. Figure 2 serves to illustrate for this. The linear relation in the plot of $1/P$ vs. concentration can be taken as an indication for the energy transfer process in a partially oriented system. The relation differs much from the case of random orientation. Figure 2a and 2b respectively corresponds to parallel and crossed excitation as well

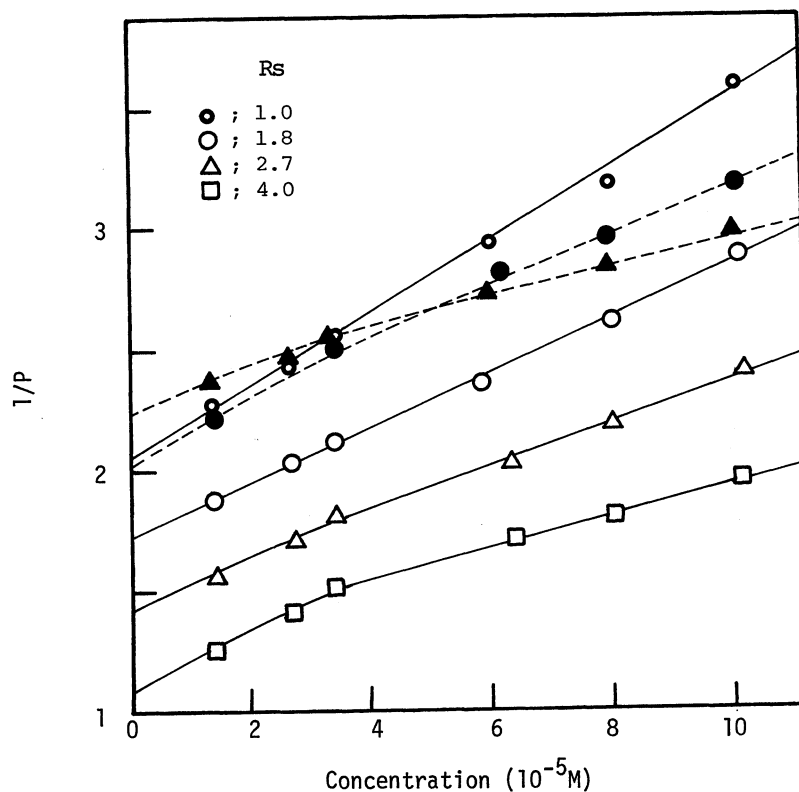


Fig. 2. Relation between $1/P$ and concentrations.

a) open symbols; F_{\parallel} .

b) solid symbols; F_{\perp} .

as in Fig. 1. In the perpendicular excitation, there exist still enough molecules to absorb the incident light polarized perpendicular to the stretching direction, though the number of the effective molecules are greatly reduced. Therefore, the depolarization is also detected in the perpendicular excitation.

The number of molecules which have the transition moments perpendicular to the stretching direction decreases with further stretching. This decreases the probability of energy transfer between dye molecules and then results in the increase in the polarization ratio on stretching at high concentrations. At stretch ratio larger than some critical value, the decrease in the effective number of excited molecules leads to the reduction of the polarization ratio and also polarization degrees as shown in Fig. 1.

For dipole-dipole interactions, the rate of excitation transfer between a donor(D) and an acceptor(A) is¹⁰⁾

$$K = B\kappa^2/R^6 = 1/\tau_D \cdot (R_0/R)^6 \quad B = 9\ln 10 \phi_D J(\tilde{\nu}) / 128\pi^5 N' n^4 \tau_D \quad (1)$$

where N' is Avogadro's number per cubic centimeter, n the refractive index, τ_D and ϕ_D the emission lifetime and quantum yield of the donor, $J(\tilde{\nu})$ the spectral

overlap integral between donor emission and acceptor absorption, R the D-A separation, κ the orientation factor for dipole-dipole coupling. In the case of parallel excitation, the unique angle of orientation (λ) is equal to 15.8° , then κ^2 is determined to be 3.71. This is near to 4.0 for the complete uniaxial orientation and much larger than 0.470 for rigid random orientation,¹¹⁾ and it is expected that the transfer rate may considerably increase.

The relation between $1/P$ and concentrations shows three different profiles corresponding to the concentration range. At concentrations below $4 \times 10^{-5}M$, the energy transfer rate is very low, and the orientation effect appears remarkably. At the medium concentration of $4 \times 10^{-5} - 10^{-4}M$, the plots of $1/P$ vs. concentration give a linear relation shown in Fig. 2. Above $10^{-4}M$, the plots deviate from above linear lines to new linear ones with different slopes depending on the stretch ratios. Similar phenomena have been observed also for the random orientation above this concentration. It may be attributed to the dye dimer formation. This case will be discussed elsewhere.

Here, the result obtained for the medium concentration range is discussed. The slope of $1/P$ vs. concentration plot shows a difference between the parallel and perpendicular excitation. There are included two reverse contributions in the behavior of fluorescence property, one from the partial orientation to the polarization degrees and another from the higher degree of alignment to the transfer rate. Because the quenching of fluorescence polarization does not serve as the principal tool for the detection of energy transfer in the oriented system.

The critical distances R_0 and the transfer rates K are calculated from the slopes of $1/P$ vs. concentration plots, and listed in Table 1, relative to the random orientation. In the present case most of the energy transfer does not induce the fluorescence depolarization, and these values of R_0 and K are only apparent. There is the significant difference in variation of the transfer rate with stretch ratio between the case of the parallel excitation and perpendicular one. It may reveal the anisotropy of energy transfer in a partially oriented system.

Further study is now in progress to deduce the energy transfer mechanism from the simultaneous investigation of dichroic absorption and fluorescence polarization, on the basis of the real orientation function.

Table 1. Summary of the results for a partially oriented system

Rs	R_0		K	
	F_{\parallel}	F_{\perp}	F_{\parallel}	F_{\perp}
1.0	1.00		1.00	
1.8	0.99	0.91	0.94	0.57
2.7	0.97	0.85	0.81	0.36
4.0	0.96	0.76

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