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Polarized fluorescence and orientational order parameters of a liquid-crystalline conjugated polymer

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We report a study of the orientational order of aligned thin films of the liquid crystalline conjugated polymer poly(9,9-dioctylfluorene). Steady state polarized fluorescence measurements were used to determine the orientational order parameter $\langle P_2 \rangle$ and $\langle P_4 \rangle$. The influence of intermolecular and intramolecular excitation energy transfer on the degree of polarization is discussed. The role of film morphology is also examined by comparison of the results for glassy and crystalline films. [S0163-1829(99)05525-3]

I. INTRODUCTION

Recently there has been strong interest in polarized emission from functional polymers both for electroluminescence (EL) applications[1–5] and for use as a polarizing emissive filter in a liquid crystal display (LCD).[6,7] In the former case, polarized EL backlights for LCD's, light sources for integrated optics, and laser diodes are the topics of interest. Promising results in this area have been presented previously for poly(9,9-dioctylfluorene) (PFO) (Refs. 8–10) and further development of materials and device structures is under way. The focus of the present paper is a detailed study of polarized fluorescence from PFO thin films—in particular by transferring the experience of the determination of orientational order parameters for stretched polymeric films to such orientated liquid crystalline materials. We show that such measurements provide helpful insight into the effects of intermolecular and intramolecular excitation energy transfer (EET) on the degree of polarization and the role of film morphology in controlling emissive properties.

Absorption experiments are widely used to characterize optical dichroism for thin polymer films and have been previously reported for PFO.[8,10] Here, we report more detailed studies of the orientational distribution of the fluorene chromophore segments using steady state polarized fluorescence. In the absence of depolarizing phenomena, including EET or molecular rotation, the macroscopic fluorescence tensor is determined by the single molecule fluorescence tensor and the orientational transformation matrix that relates the molecular and macroscopic axes. Their elements are linked with orientational order parameters characterizing the orientational distribution function (ODF).[11] Hence, polarized fluorescence spectroscopy has been extensively used to study orientational characteristics of anisotropic samples such as liquid crystalline materials[12–19] and stretched polymers.[20–26] We note also that polarized EL is governed by the same matrices and hence the development of polarized backlights and other devices can benefit directly from the information obtained via polarized fluorescence studies.

The fluorescence tensor is of fourth order, because it results from the product of two second rank tensors, namely the absorption and emission tensor. In the case of rotational symmetric system, fluorescence polarization depends on both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ while optical dichroism (or birefringence) depends on $\langle P_2 \rangle$ only. In order to determine order parameters for anisotropic samples, sufficient information must be available about the fluorescence tensor of the single molecule. Usually, this is achieved by an independent photoselection measurement using an isotropic sample at very high dilution, for which EET can be ruled out. In fluorescent conjugated polymers such as PFO, dilution cannot, clearly, separate the individual fluorene chromophores connected within a single polymer chain. Nevertheless, significant information can still be extracted from polarized fluorescence measurements as will be discussed in detail below.

II. MATERIALS AND EXPERIMENTAL TECHNIQUES

The chemical structure of PFO is shown in Fig. 1. The polymer was synthesized via a Suzuki coupling reaction[27] and was carefully purified to remove ionic impurities and catalyst residues. Typical number and weight average molecular weights, as determined by coupled GPC and classical light scattering measurements,[10] are $M_w = 56\,000$ and $M_n = 34\,000$ (polydispersity=1.65). A typical polymer chain

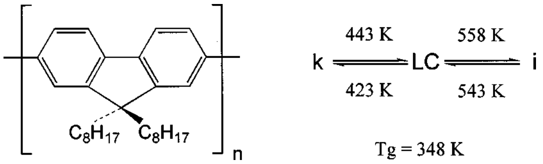

FIG. 1. Structure of PFO and phase behavior of PFO.

thus has $\geqslant 100$ repeat units. The polymer is readily soluble in a range of organic solvents[10] and has a structured emission in the blue with a solid state quantum yield, dependent on film morphology,[28] of $\approx 50 \pm 10\,\%$. The liquid crystalline phase behavior of PFO has been previously described.[8] PFO is a well-behaved thermotropic liquid crystal for which the mesophase extends over 120 K. It can be aligned, using standard techniques, and subsequently quenched into a glassy state. The material is also characterized by chemical regularity and excellent purity, which leads to a large room temperature hole mobility of $4 \times 10^{-4}\,\mathrm{cm}^2/\mathrm{V\,s}$ in the isotropic phase.[29]

The film samples of PFO (samples I, II, III, and IV) were prepared by spin-coating from toluene solution onto commercially available Spectrosil substrates (UQG Ltd., Cambridge, UK) that had been precoated with rubbed polyimide (PI) alignment layers. The refractive index of the Spectrosil is reported to fall in the range of 1.479 up to 1.457 for wavelengths between 340 and 650 nm. The PI layer was prepared from a Liquicoat® precursor solution (Merck, Darmstadt, Germany) in the standard way (according to the manufacturer's instructions) and was rubbed unidirectionally with a nylon cloth. Its refractive index characteristics are not well documented. Refractive indices were directly measured for the Spectrosil and PI coated Spectrosil substrates using a spectroscopic ellipsometer.

Samples I and IV underwent no further treatment subsequent to spin coating the solution onto the polyimide layer. They were found to be optical isotropic. Samples II and III were aligned on the rubbed polyamide substrate according to the protocol described in Ref. 8 and were quenched rapidly to room temperature. Their morphology can thus be described as a glassy liquid crystalline monodomain. A crystalline sample (sample $\mathrm{III}_{\mathrm{Cr}}$) was subsequently prepared by heating sample III up to 200 °C followed by slow cooling (-0.2 K/min) to room temperature.

Fluorescence experiments were performed on two commercial, 90° angle, steady state spectrofluorimeters (Perkin Elmer MPF-44A and Spex-Fluorolog 1680) with two rotating polarizers. The method used for the evaluation of the polarized fluorescence data is described in detail elsewhere.[26] The Absorption spectra were measured with a UV/VIS spectrophotometer (Zeiss DMR10). The ellipsometric experiments were performed using a Sopra ES4G spectroscopic ellipsometer.

III. BACKGROUND TO POLARIZED FLUORESCENCE MEASUREMENTS

In order to obtain a definitive description of the emission properties of an anisotropic sample with even the simplest uniaxial symmetry it is necessary to measure three independent components of the fluorescence intensity and to determine the parameter p that describes the molecular anisotropy of the chromophore system. In practice, the excitation and emission polarizer are set parallel to one of the macroscopic axes X, Y, or Z which needs the knowledge of where these axes lie in the specimen. Two ratios of three fluorescence intensities are used to get rid of the determination of instrumental constants, quantum yields, and the average extinction. Measurements of isotropic samples provide us with the molecular anisotropy p. For such samples there are only two independent components F_{UU} and F_{UV} ($U \neq V$) of the fluorescence tensor. The degree of polarization (or anisotropy) r is defined by

$$r = \frac{F_{ZZ} - F_{ZY}}{F_{ZZ} + 2F_{ZY}}. \tag{1}$$

We assume that rotational mobility can be neglected within the lifetime of the excited state of the fluorescent molecule for polymer films below the glass transition temperature. Consequently, in the absence of EET and orientation, r equals the molecular property called fundamental anisotropy r_0, which is constrained to $-0.2 \leqslant r_0 \leqslant 0.4$. If the molecular tensors of absorption and emission are diagonal in the same molecular framework and have the same anisotropy and uniaxial symmetry, the molecular anisotropy p is given by r_0 via Eq. (2):

$$r_0 = \frac{(2 - 3p)^2}{10}. \tag{2}$$

Even for isotropic and optically clear films the correct determination of r is not trivial. The measurement of two components F_{ZZ} and F_{ZY} is usually not sufficient. In order to determine r for an isotropic film we rotate the polarizers in the excitation and emission beam to a vertical (index V) and horizontal (index H) position and the intensities I_{VV}, I_{VH}, I_{HV}, and I_{HH} are each measured. The nomenclature has a direct bearing on the direction of the electric vector of the transmitted light. The question of how to evaluate the components of the fluorescence tensor from the measured polarized intensities leads to a requirement for the determination of several correction factors mainly connected with the specific instrumental setup used. Additionally the deviation from the 90° angle beam geometry inside the sample equipment has to be considered which is due to the refractive index difference between sample and quartz covering. Concerning the later Regardless of an entire description, we mainly need two correction factors G_1 and G_2 for our objective.[26] The difficulty in interpreting the measured polarized fluorescence intensities arises mainly from the fact that the direction of propagation of light in the spectrometer is different from the direction within the sample. This complicates the usual method to determine G_1 and G_2. With a knowledge of G_1 one can then evaluate the degree of polarization

$$r = \frac{I_{VV} - G_1 I_{VH}}{I_{VV} + 2G_1 I_{VH}}. \tag{3}$$

Since we have studied orientated liquid crystalline samples of a calamitic material, we assume uniaxial symmetry around the macroscopic Z axis and the geometric and photophysical rotational symmetry of the molecules. Although the repeat unit of PFO does not precisely fulfil these assumptions, we assume that the slight deviations are somehow averaged out over one effectively conjugated segment. However, it should be noted that the assumption of uniaxial symmetry of the molecules is reliable and furthermore quite treatable in the

TABLE I. Ellipsometric results for the sample layer thicknesses and their refractive indices.

material	thickness	*n* (384 nm)	*n* (423 nm)
PFO	80 nm	1.58	1.56
PI	40 nm	1.69	1.66
Spectrosil	2 mm	1.485	1.48

following but strictly spoken it is not experimentally proven either for the chromophoric subunits or for the polymeric structures in the case of thin films.

As a first approach we determine the two orientation coefficients $\langle P_2\rangle$ and $\langle P_4\rangle$, using r_0 (more precisely p) and the ratios F_{ZY}/F_{ZZ} and F_{YY}/F_{ZY} of the three independent components of the fluorescence tensor:[26,30]

$$\langle P_2\rangle = 1/2(3\langle\cos^2\theta\rangle - 1), \tag{4}$$

$$\langle P_4\rangle = 1/8(35\langle\cos^4\theta\rangle - 30\langle\cos^2\theta\rangle + 3), \tag{5}$$

where θ is the angle between the symmetry axis of the chromophore (z) and the orientation direction (Z). The angle θ is related to the components of the fluorescence tensor by

$$\langle\cos^4\theta\rangle = \frac{16pF_{YY}/F + (12-10p)F_{ZZ}/F + p(6-7p+3p^2)}{(2-3p)^2(3-p)} \tag{6}$$

and

$$\langle\cos^2\theta\rangle = 0.5 + 0.5\langle\cos^4\theta\rangle - \frac{16(1-p)F_{YY}/F + 4pF_{ZZ}/F + 4p(1-p)}{(2-3p)^2(3-p)}, \tag{7}$$

wherein F is

$$\begin{aligned} F &= F_{ZZ} + 4F_{ZY} + 2F_{YY} + 2F_{YX} \\ &= (3-2p+p^2)^{-1}[(3-2p)F_{ZZ} + 8F_{YY} + 4(3-p)F_{ZY}]. \end{aligned} \tag{8}$$

We previously showed[26] how to determine $\langle P_2\rangle$ and $\langle P_4\rangle$ in detail for stretched polymeric films based on F_{ZY}/F_{ZZ} and F_{YY}/F_{ZY} using values for p, G_1, and G_2 determined from measurements on isotropic samples. The orientation coefficients are calculated from fluorescent components not affected by birefringence.[26] Other, more complex possible influences such as local field effects have been neglected.

IV. RESULTS AND DISCUSSION

A. Determination of the refractive indices and layer thickness by ellipsometry

The refractive indices and thickness of the layers were determined for sample I by ellipsometric investigations.
The results of these measurements are summarized in Table I. We used the refractive indices of PFO for 384 and 424 nm to calculate the effective angles between excitation and fluorescence light beam within the PFO film, as required for the instrumental correction of our 90° geometry spectrometer. Since the refraction index variations in the birefringent anisotropic samples are only an order of magnitude below the index difference between sample and quartz they cause a minor negligible effect.

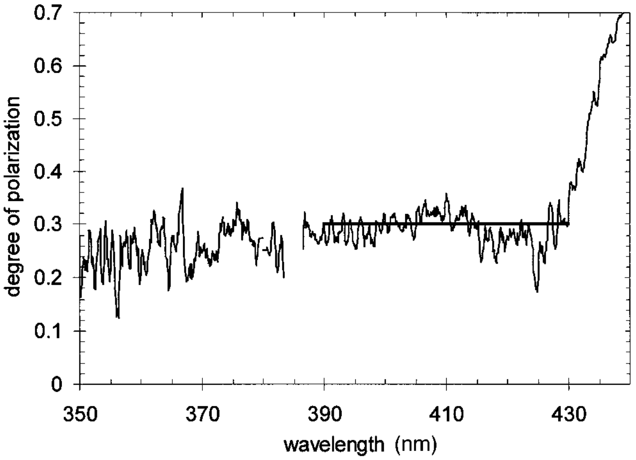

FIG. 2. Degree of polarization for the excitation spectrum of polystyrene/PFO=9999/1 ($\lambda_{EM}=450$ nm; stray light influences the results above 430 nm).

B. Investigations of the polyimide alignment layers

The absorption spectrum of PI was investigated with a UV/VIS spectrometer. It is characterized by peak maxima at 221 and 280 nm with an absorbance of 0.572 and 0.276, respectively. No optical dichroism was found. The PI layer has a fluorescence excitation maximum at wavelengths below 260 nm and an emission maximum at 326 nm. Consequently, most of the emission spectrum was cut off by the thin film polarizers used. These are transparent only for wavelengths above 275 nm. Further, the fluorescence intensity of PI is extremely weak compared to PFO and can be neglected in the measurements on PFO samples where the PI layer lies below the PFO film.

C. Determination of r_0

In contrast to investigations on stretched polymeric films[26] the determination of r_0 turned out to be more difficult here. The as spin coated, isotropic samples of pure PFO could not be used to determine r_0 on account of the almost complete depolarization that occurs due to efficient intermolecular EET. Blends of PFO dispersed in polystyrene were used to prevent intermolecular EET by increasing the average intermolecular spacing. The degree of polarization increased, as expected,[31] with the extent of dilution and saturated at a value of $r=0.3$ (which implies $p=0.0893$) for samples with a weight ratio Polystyrene/PFO=9999/1 (Fig. 2). This value may still be limited by intramolecular EET which, of course, cannot be excluded even for highly dilute blends. Figure 2 shows that the value for the degree of polarization increases only slightly with increasing wavelength in the excitation spectrum up to about 430 nm (above 430 nm, stray light reaches the detector dominating the results). This, so-called red-edge effect is much more pronounced for other conjugated polymers.[31–33] Our earlier papers modeled

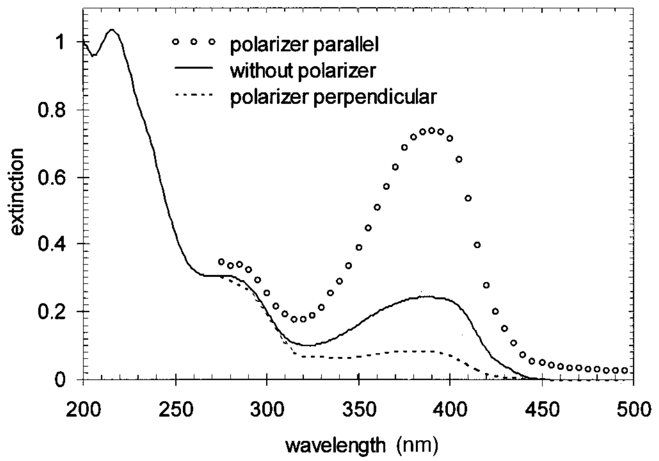

FIG. 3. Polarized UV/VIS absorption spectra for sample II. The low wavelength cutoff for the polarized spectra arises from the transmission cutoff of the polarizer.

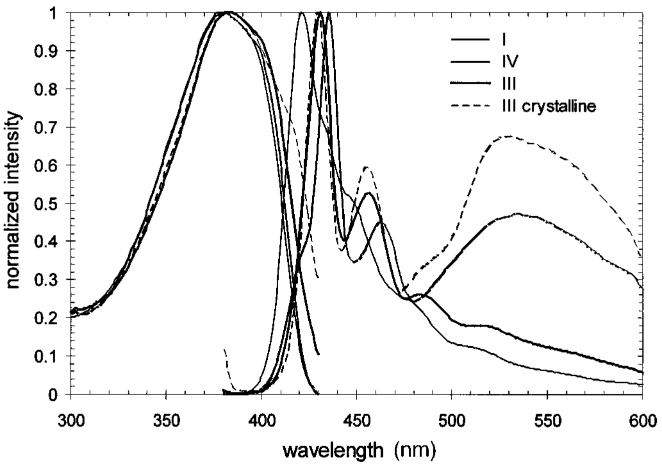

FIG. 4. Excitation and fluorescence spectra for different samples studied. Wavelength of fluorescence for the excitation spectra 450 nm, wavelength of excitation for the fluorescence spectra 360 nm.

the conjugated polymer chain as a distribution of independent oligomer segments. At the red edge of the excitation spectrum, the energetically lowest chromophores (i.e., those with the most extended conjugated system) are expected to be preferentially excited. Because they have only a limited capability to transfer their energy, the polarization ratio is maximised on the red edge. For PFO diluted in polystyrene there is no remarkable red-edge effect in the degree of polarization data, i.e., in PFO the intrachain EET does not significantly depolarize fluorescence. PFO polymer chains show a characteristic ratio in excess of 20 (Ref. 10) and hence many individual intrachain EET steps are expected to be necessary before the correlation of orientation between the absorbing and the emitting sites is lost. We find a relatively high value of $r=0.3$. For comparison the r_0 value of a dilute blend of *p*-terphenyl in polystyrene was also measured and a value of $r_0=0.33$ was obtained. The complete depolarization observed for as spin-coated, isotropic PFO films, however, shows that intermolecular EET can dominate under certain circumstances. We conclude that depolarization by intramolecular EET requires motion over significantly greater distances than for intermolecular EET. The determination of r based on the data for wavelength between 390 and 430 nm for PFO dispersed in polstyrene is sufficient that we can reliably take $r_0=r=0.3$.

D. Polarized absorption of PFO films

A comparison of the two UV/VIS spectra measured with a polarizer aligned, respectively, parallel and perpendicular to the orientation direction of the film showed that the absorption was indeed isotropic for sample I and IV. Samples II (see Fig. 3) and III were found, conversely, to have anisotropic absorption spectra. The UV/VIS absorption had a well-defined peak at 387 nm associated with delocalized π-π^* transitions of the fluorene backbone. We determined $\langle P_2\rangle$ for sample II from the polarization ratio at this peak as measured with the same polarizer that was used for the fluorescence experiments. The molecular anisotropy p was determined via Eq. (2) where $r_0=0.3$ was taken as discussed above. Then $\langle P_2\rangle$ was calculated from

$$\langle P_2\rangle^{\mathrm{UV}}=\left(1-\frac{3}{2}p\right)^{-1}\frac{E_{\parallel}-E_{\perp}}{E_{\parallel}+2E_{\perp}}. \tag{9}$$

This gave

$$\langle P_2\rangle^{\mathrm{UV}}=0.82\pm0.01.$$

E. Unpolarized fluorescence measurements

The excitation spectra (Fig. 4) for all samples are very similar and closely resemble the absorption spectra reported in Ref. 8. Maxima were found between 380 and 385 nm. Additionally, a shoulder of was detected between 395 and 400 nm. The emission spectra, however, show a more complex structure with different spectra for each of the samples (Fig. 4). Furthermore, spectral changes were found over the time period of the study. The influence of degradation induced by light exposure shares the main features in common with comparable investigations;[34] namely, the extinction and emission intensities were found to decrease with light exposure time, but no shift of the maxima was found.

By analysis of the spectra it becomes apparent that they can each be interpreted as differently weighted superpositions of the same spectral features (Fig. 4). The intensities and wavelengths of the different emission maxima are controlled by the different preparation and storage procedures through their influence on selforganisation at the molecular level. The effects of absorption or desorption of solvent, water, etc., are also important. It should be emphasized that complex systems result from the spin coating process and that the emission spectra are sensitive to the details of the physical state in which a polymer chain find itself. Large variations in emission spectra that depend on preparation conditions have been reported for several conjugated polymers before.[35–37] However, the features seen in the spectra for PFO films can be split in two categories. The higher energy (lower wavelength) maxima can be attributed to the vibronic levels of a single electronic excitation: The peak separation, 0.16±0.01 eV, is nearly equidistant and is essentially the same for all samples. The broad unstructured fluorescence in the longer wavelength region beyond 480 nm is

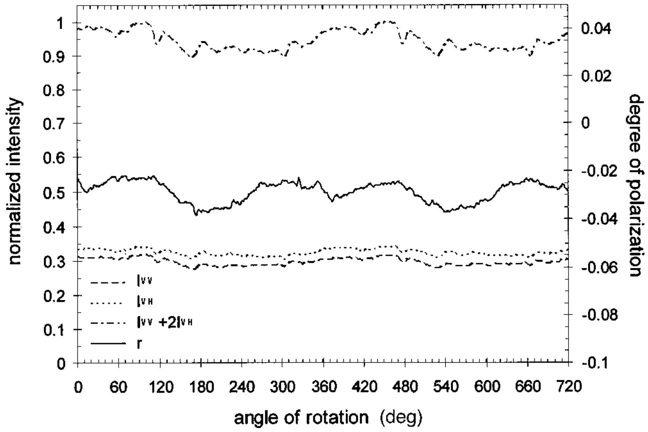

FIG. 5. Normalized fluorescence intensities I_{VV}, I_{VH}, and $(I_{VV}+2I_{VH})$ (left hand ordinate scale) and degree of polarization r (right hand ordinate scale), versus rotational angle for the isotropic sample IV ($\lambda_{EX}=380\,\mathrm{nm}$, and $\lambda_{EM}=435\,\mathrm{nm}$).

typical of dimer associates such as excimers. This latter feature was particularly prominent for the crystalline sample. The spectra of samples I, II, and III do not show this feature and therefore imply samples for which such associates are absent. We note that the excimerlike band also does not occur for diluted blends. This result arises from the fact that the stiff backbone PFO prevents effectively chain folding and consequently the formation of intramolecular dimers.

It is obvious that the emission caused by dimeric species is unsuitable to study the orientational order because their small molecular anisotropy. For all polarized photoluminescence investigations we have avoided the excimerlike band and ensured a good signal-to-noise ratio by using $\lambda_{EX}=380\,\mathrm{nm}$ and $\lambda_{EM}=435\,\mathrm{nm}$ as excitation and detection wavelength close to the found maxima, respectively.

F. Polarized fluorescence measurements

Polarized fluorescence measurements were carried out for isotropic as well as aligned PFO samples. We used a rotatable experimental setup, where the sample was rotated around the normal of the film plane. To avoid the effects of birefringence, only positions where the orientation axis Z of the sample is respectively normal to or within the plane determined by the excitation and emission beam were used for calculation of the orientational order parameters. Using a rotating sample is a suitable experimental setup to avoid misalignments of the sample.

For the isotropic samples I and IV the degree of polarization r was found to be similar for both samples and was close to zero (sample I: $r=-0.05$ and sample IV: $r=-0.03$). Furthermore, small deviations are found versus the rotational angle of the sample (sample I: $r=-0.05\pm0.03$ and sample IV: $r=-0.03\pm0.01$) (Fig. 5). The variation in the value r was observed to be periodic with π radians. There was no evidence of a variation with a periodicity $\pi/2$ radians as would be expected for a birefringent anisotropic sample. We can thus exclude any marked orientation of polymer chains in these samples, a conclusion in agreement with the polarized absorption measurements reported above. The systematic angular variation of the signal most likely arises from either imperfect adjustment of the rotation axis, an inhomogeneous chromophore density, the presence of locally ordered regions, or a combination of these factors. We note that the results for the two isotropic films are entirely consistent with an almost complete depolarization of the fluorescence due to EET. Hence, as already discussed it proved necessary to use samples of PFO dispersed at low concentration in a polystyrene matrix in order to determine the molecular property r_0.

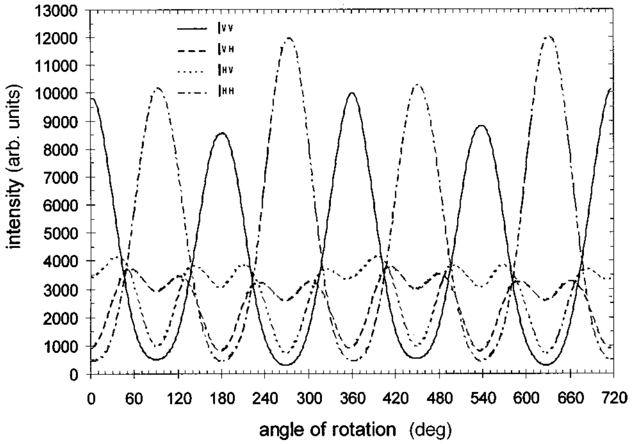

FIG. 6. Fluorescence intensities I_{VV}, I_{VH}, I_{HV}, and I_{HH} versus sample rotational angle for sample II ($\lambda_{EX}=380\,\mathrm{nm}$, and $\lambda_{EM}=435\,\mathrm{nm}$).

In spite of complete depolarization due to EET, the data proved convincingly that the samples are isotropic. This is based on the negligible deviations of r. Furthermore, complete depolarization cannot be expected for an anisotropic sample as estimated from the first approximation

$$\frac{r}{r_0}=k_D\tilde{G}^S(k_D)+(1-k_D\tilde{G}^S(k_D))\langle {}^2P_2\rangle, \tag{10}$$

where $k_D\tilde{G}^s(k_D)$ is the Laplace-transformed value of the probability $G^S(t)$ that the excitation resides at the chromophore where it has been formed, using the reciprocal lifetime k_D. $\langle {}^2P_2\rangle$ is the orientational order parameter of the mutual (pair) ODF of the chromophores. In the case of an ‘‘orientational gas,’’ i.e., no interaction between the orienta-

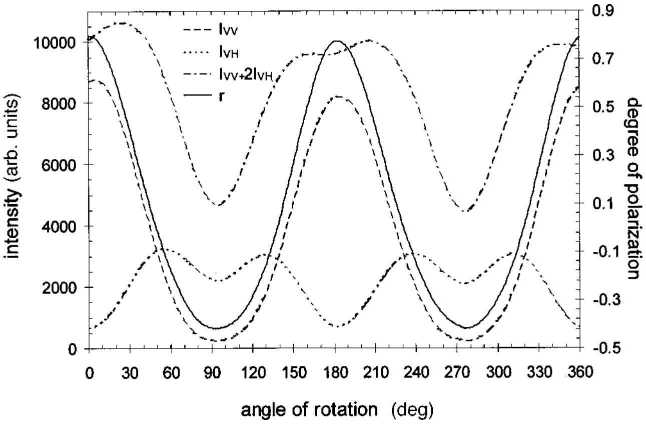

FIG. 7. Fluorescence intensities I_{VV}, I_{VH}, $(I_{VV}+2I_{VH})$, and the resulting value of degree of polarization r versus sample rotational angle for sample III ($\lambda_{EX}=380\,\mathrm{nm}$, and $\lambda_{EM}=435\,\mathrm{nm}$).

TABLE II. Values of $\langle P_2\rangle$ and $\langle P_4\rangle$ determined from the fluorescence measurements for the oriented films, namely, samples II and III (in both glassy and crystalline state).

Sample	$\langle P_2\rangle$ (average)	$\langle P_4\rangle$ (average)
II	0.86±0.02	0.65±0.02
III	0.89±0.02	0.73±0.02
III crystalline	0.95±0.02	0.88±0.02

tional units, $\langle {}^2P_2\rangle = \langle P_2\rangle^2$. In the limit case of perfect parallel orientation, $\langle P_2\rangle = \langle {}^2P_2\rangle = 1$, and EET will not affect the polarization of fluorescence.

For the oriented films, samples II and III, polarized fluorescence spectra were recorded at several distinct angles to check that there was no dimer associates emission contribution. The normalized spectra at different angles exactly coincided and hence it could be concluded that a single emission species, perhaps with a certain distribution of molecular length and shape, acts as the orientational unit.

Figure 6 shows the four fluorescence intensities I_{VV}, I_{VH}, I_{HV}, and I_{HH}, for sample II. Figure 7 shows I_{VV}, I_{VH}, $(I_{VV}+2I_{VH})$, and the resulting value of r for sample III. The rotational experiment was performed with $\lambda_{EX}=380$ nm and $\lambda_{EM}=435$ nm, close to the maxima of excitation and fluorescence spectra, respectively. The uniaxial nature of the oriented samples gives rise to the observed periodicity and we note the good reproducibility over several periods of rotation. The amplitude of r is two orders of magnitude larger than for the two isotropic samples. No obvious indications of fluorescence depolarisation were found indicating that during the lifetime of fluorescence the EET is restricted to molecular segments that have the same orientation. This is just as expected for a high molecular orientation. Moreover, in the case of liquid crystalline order, the local orientation correlation is large (i.e., the pair orientation coefficient $\langle {}^2P_2\rangle \geqslant \langle P_2\rangle^2$) and thus the major source of depolarization is absent.

The intensities referring to the vertical and horizontal positions of the sample, which were marked by the intensity extremities, are used to calculate the orientational parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ with the procedures described in Ref. 26 based on equations (3)–(8). The results are listed in Table II.

In Fig. 8 the determined $\langle P_2\rangle/\langle P_4\rangle$ data are plotted in the $\langle P_2\rangle/\langle P_4\rangle$ plane. From the plot of $\langle P_4\rangle$ versus $\langle P_2\rangle$ various types of ODF can be distinguished.[38] The mathematical limits, the limits for a monotonously increasing ODF and the relation for the most probable, in the statistical sense, ODF are displayed. We find that the $\langle P_2\rangle/\langle P_4\rangle$ results for the oriented films, namely, samples II, III, and $\mathrm{III}_{\mathrm{cr}}$ fit well to the most probable ODF.

The results of polarized fluorescence and polarized UV/VIS absorption measurements are in good agreement although the polarized fluorescence systematically gave slightly higher values. This difference is not, however, very significant since the deviations are less than the accuracy limits of the data. Since the mean orientation of the samples as indicated by $\langle P_2\rangle$ is very high (i.e., close to 1) for the oriented samples and since we do not found any orientation for the isotropic samples, any deviation from the assumed uniaxial symmetry of the materials is concluded to be of minor importance.

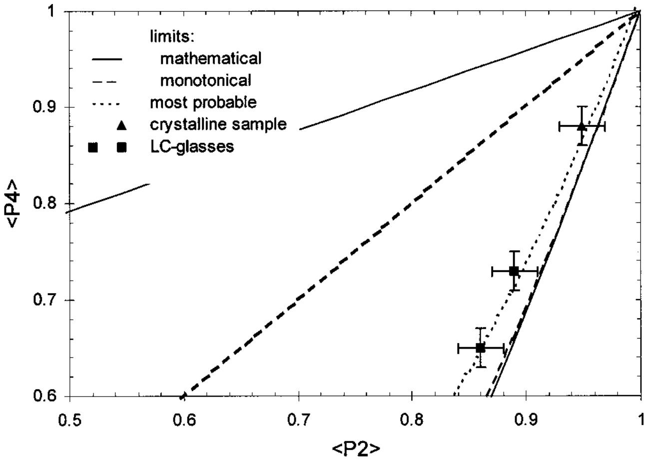

FIG. 8. Experimental data and the theoretical relationships expected for $\langle P_4\rangle$ and $\langle P_2\rangle$.

V. CONCLUSION

The orientational order of aligned samples of the liquid crystalline conjugated polymer PFO was studied using steady state polarized fluorescence spectroscopy. The orientational parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ were deduced and they indicated a very high degree of orientational order. The relation between $\langle P_2\rangle$ and $\langle P_4\rangle$ corresponds to the most probable ODF. The data were satisfactorily analyzed within the confines of a simple model for the molecular geometry indicating that the basic assumptions of the model are sufficiently fulfilled. The depolarization of fluorescence caused by intermolecular and intramolecular EET was seen to have significant effects that had to be taken into account in determining the anisotropy parameters needed to calculate $\langle P_2\rangle$ and $\langle P_4\rangle$.

The results obtained highlight the suitability of the investigated PFO for polarized luminescence applications. Aligned films of PFO show both a high macroscopic orientation and a high molecular anisotropy as simultaneously required to obtain a high degree of polarization of the emitted light.

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