Field-induced changes of dipole orientation in PVDF determined by infrared spectroscopy

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Based on theoretical considerations, an i.r.-technique is presented which allows the mean CF_2 dipole orientation to be determined in uniaxially drawn poly(vinylidene fluoride) (PVDF) in dependence on an external electric field applied to the sample during spectra registration. The method includes measurements at different angles of incidence. Information about dipole orientation in *trans*-sequences of different lengths or in crystallites and in non-crystalline regions may, in principle, be obtained.

(Keywords: poly(vinylidene fluoride); infrared spectroscopy; electric field; dipole orientation)

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) has been the subject of many investigations because of its pyro- and piezoelectric properties. These properties are due to the polar structure which is generated in the material by application of a strong electric field. PVDF can exist in at least three conformations leading to the crystalline modifications α, β, γ, δ or α_p (Reference 1). The field-induced structure formation process may be connected with changes of the CF_2 dipole orientation as well as with conformation transitions[2–12]. However, for the β-form of PVDF this process reduces to field-induced dipole orientation changes. Such material is, therefore, appropriate to investigate this effect.

Some authors have determined dipole orientation functions, $f(\theta)$, for crystalline regions (where θ is the angle between the dipole and the applied electric field, *Figure 1a*) by X-ray experiments and discussed them in relation to existing models of the poling process[13,14]. Mean values $\langle \cos^2 \theta \rangle$ were obtained from infrared (i.r.) spectroscopic investigations on PVDF films containing α as well as β form with an electric field applied to the sample[15]. Recently, the mean dipole orientation in highly oriented β PVDF films during the application of an electric field was calculated from the absorbances of the i.r. bands at 510 and 445 cm^{-1} (Reference 16). These bands are thought by some authors to be due to CF_2 bending vibrations of *trans*-sequences in crystalline and non-crystalline regions (510 cm^{-1}) and CF_2 rocking vibrations of the crystalline β-modification (445 cm^{-1})[2,17–21]. Separate evaluation of the dipole orientations for each of these bands is possible by experiments using various angles of incidence.

The aim of the present paper is, by means of such measurements with an applied electric field, first to check previous results[16] by another i.r. technique and, secondly, to get further information about the mean dipole orientation in the structural units associated with the respective band. Infrared spectroscopic investigations with rotated samples were carried out earlier on polymers[22–24], but to our knowledge experiments using a rotated sample with an electric field applied simultaneously have not so far been reported.

EXPERIMENTAL

PVDF films (Bemberg) were uniaxially stretched at 110°C (stretch ratio ≈ 4)[25]. The conformational composition of the resulting films was estimated using a method based on comparison of the intensities of i.r. bands characteristic of the various conformations[26]. From the spectrum of the equivalent unoriented sample which had been calculated from the polarized spectra (electric vector parallel and perpendicular to the stretch direction, respectively) of the drawn film, it was concluded that the percentage of *trans*-conformation was $\approx 95\%$. This is in accordance with previous values for films prepared that way[27]. The molecular chain axes in these films have a strong preferred orientation parallel to the stretch direction as shown by X-ray and i.r. measurements[11,27]. By use of the intensity distribution in the X-ray pole figure of the (001)-net plane, the mean value of $\cos^2 \theta_c$ was calculated to be $\langle \cos^2 \theta_c \rangle = 0.983$ (where θ_c is the angle between the draw direction and the chain axis). This parameter was also estimated on the basis of the dichroic ratio of the CF_2 wagging band at 470 cm^{-1}, resulting in $\langle \cos^2 \theta_c \rangle \approx 0.97$.

The refraction indices of the film were measured by means of an optical interference microscope. The mean values obtained for perpendicularly incident light polarized parallel (n_z) and perpendicular (n_x) to the draw direction (z), respectively, are $n_z = 1.45$ and $n_x = 1.41$, with an uncertainty of about ± 0.01. Measurements on ultramicrotome sections gave a refraction index difference $n_y - n_x \approx 0.013$ (n_y, el. vector perpendicular to draw direction and parallel to film normal) with an uncertainty for n_y of about ± 0.015. The sample thickness was 23.5 μm. Thin carbon layers, evaporated onto the polymer, were used as electrodes (length 2 cm, width 0.8 cm)[28]. The sample holder is shown in *Figure 1b*. The angular reproducibility was $\approx 0.5°$. The samples were

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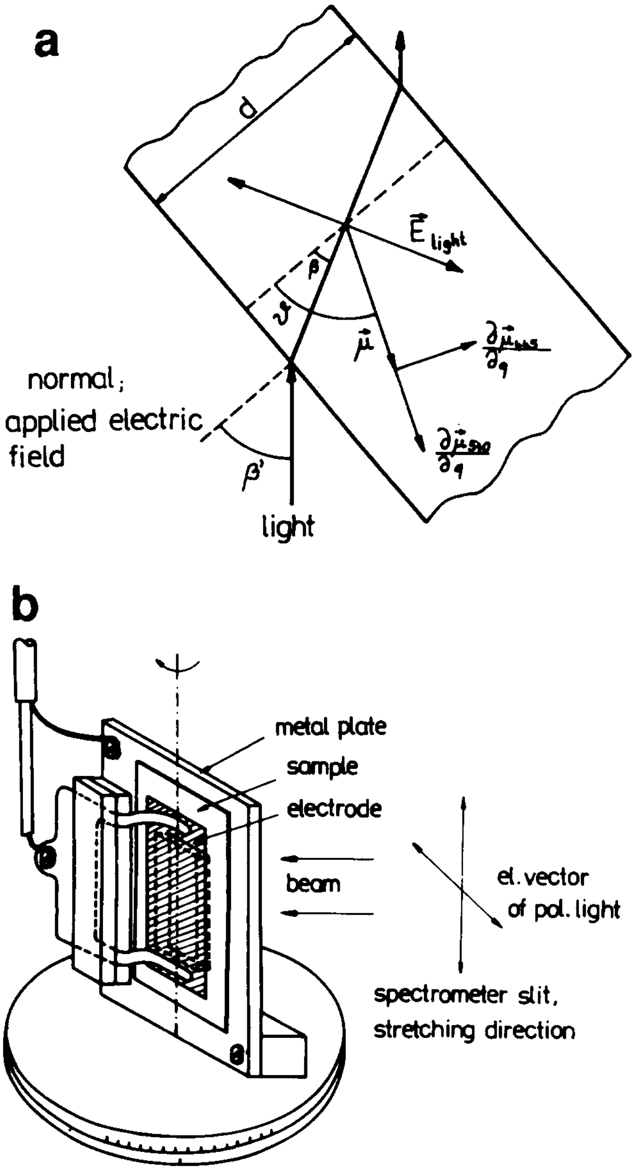

Figure 1 Experimental geometry: (a) cross section of the PVDF film, stretching direction perpendicular to paper plane; (b) schematic drawing of the sample holder

poled up to $E_p = -240\ \mathrm{MV\,m^{-1}}$. Measurements were made with the electric field E_p applied to the sample for rotation angles of 0, 20, 26 and 30°; the sample was rotated without switching off the field. The same experiment was repeated with the field switched off. In addition, infrared spectra with perpendicular incidence were registered for 15 field strengths applied during measurement. The maximum field strength in the poling direction was again equal to E_p, whereas in the opposite direction it was $E = +46\ \mathrm{MV\,m^{-1}}$, which corresponds to the point of least dipole orientation in this case[29].

The spectra were registered in the region 600–370 cm^{-1} by use of a computer-assisted dispersive i.r. spectrometer M80 (Carl Zeiss Jena), which measured discontinuously at wavenumbers in adjustable distances. The main parameters were: distance 1.6 cm^{-1}, measuring time for one point 20 s and polarized light (el. vector perpendicular to stretch direction and spectrometer slit). The intensity losses caused by the carbon electrodes and the sample holder (without sample) at various angles were dependent on the wavenumber in a non-linear way as shown by detailed measurements. Therefore, the baseline method used was slightly modified: the actual absorbance values due to these effects were taken into account when evaluating the bands. The angle-dependent influence of reflection, which may be important in certain cases[22,30,31], was theoretically estimated to be very small for the polarization direction and tilt angles used.

THEORY

The absorbances A_{510} and A_{445} are calculated on the basis of the two following main approximations derived from the experimental section. First, all chain axes are aligned parallel to the draw direction (i.e. $\langle\cos^2\theta_c\rangle = 1$). Then all CF_2 dipoles lie in a plane perpendicular to this direction.

Second, the refraction index for light polarized perpendicular to the draw direction and propagating in the plane thus described is independent of the angle of incidence (i.e. $n_x = n_y$). Then a theoretical treatment considerably easier than the exact calculation[24] becomes possible.

With these approximations the absorbance A is proportional to

$$A \propto \int_0^{2\pi} f(\boldsymbol{\mu})\left(\frac{\partial\boldsymbol{\mu}}{\partial q}\boldsymbol{E}_{\mathrm{light}}\right)^2 \mathrm{d}\theta \qquad (1)$$

where $f(\boldsymbol{\mu})$ is the orientation distribution function of the dipole moment $\boldsymbol{\mu}$, $\partial\boldsymbol{\mu}/\partial q$ the vector of dipole moment change and $\boldsymbol{E}_{\mathrm{light}}$ the el. vector of incident light, if the draw direction is set perpendicular to the incident light (*Figure 1a*). With $\partial\boldsymbol{\mu}/\partial q \parallel \boldsymbol{\mu}$ for the deformation vibration at 510 cm^{-1} and $\partial\boldsymbol{\mu}/\partial q \perp \boldsymbol{\mu}$ for the rocking vibration at 445 cm^{-1} the following equations result from (1) for perpendicularly incident polarized light

$$A_{510} = K_{510}d\frac{1}{2\pi}\int_0^{2\pi} f_{510}(\theta)\sin^2\theta\,\mathrm{d}\theta \qquad (2)$$

$$A_{445} = K_{445}d\frac{1}{2\pi}\int_0^{2\pi} f_{445}(\theta)\cos^2\theta\,\mathrm{d}\theta \qquad (3)$$

where d is thickness, $f_{510}(\theta)$ and $f_{445}(\theta)$ are orientation distribution functions of the dipoles contributing to the respective band. In equations (2) and (3) internal field effects are taken into account phenomenologically by means of the factors K_{510} and K_{445}, which are dependent on polarizabilities and other parameters[32]. If the sample is rotated about the draw direction by β' (*Figure 1a*) the absorbances, demonstrated for A_{510} only, can be described by

$$A_{510}(\beta) = \frac{K_{510}d}{\cos\beta}\frac{1}{2\pi}\int_0^{2\pi} f_{510}(\theta)\sin^2(\theta-\beta)\,\mathrm{d}\theta \qquad (4)$$

In the framework of the present approach the angle β is given by $\sin\beta = n_x^{-1}\sin\beta' = n_y^{-1}\sin\beta'$. By means of some trigonometric relations one gets from (4)

$$A_{510}(\beta) = \frac{K_{510}d}{2\cos\beta}\frac{1}{2\pi}\int_0^{2\pi} f_{510}(\theta)\,[1-(\cos 2\theta\cos 2\beta + \sin 2\theta\sin 2\beta]\,\mathrm{d}\theta \qquad (5)$$

The integral over the sine term is vanishing due to the symmetry of the distribution function, $f_\nu(\theta) = f_\nu(-\theta)$, where ν denotes the two wavenumbers. Using the normalization condition

$$\frac{1}{2\pi}\int_0^{2\pi} f_v(\theta)\,\mathrm{d}\theta = 1$$

the following equations are obtained

$$A_{510}(\beta) = \frac{K_{510}d}{2\cos\beta}\,(1 - \cos 2\beta\langle\cos 2\theta\rangle_{510}) \qquad (6)$$

$$A_{445}(\beta) = \frac{K_{445}d}{2\cos\beta}\,(1 + \cos 2\beta\langle\cos 2\theta\rangle_{445}) \qquad (7)$$

with

$$\langle\cos 2\theta\rangle_v = \frac{1}{2\pi}\int_0^{2\pi} f_v(\theta)\cos 2\theta\,\mathrm{d}\theta$$

Equations (6) and (7) clearly show the dependence of the measured absorbances on dipole orientation and rotation angle. Defining a mean dipole orientation angle $\hat{\theta}_v$ by $\cos 2\hat{\theta}_v = \langle\cos 2\theta\rangle_v$, it can be concluded that the term $A(\beta)\cos\beta$ for $\hat{\theta}_v = \frac{1}{4}\pi$ will be constant, if β is changed. This means that, in this case, changes of $A(\beta)$ are caused by varying path length within the sample.

For $\hat{\theta}_v < \frac{1}{4}\pi$ the term $A_{510}(\beta)\ \cos\beta$ increases with growing β, but $A_{445}(\beta)\cos\beta$ decreases in this case; for $\hat{\theta}_v > \frac{1}{4}\pi$ the bands behave in the opposite manner.

Equations (6) and (7) imply a linear relation between $A\cos\beta$ and $\cos 2\beta$. Taking into consideration measurements at different field strengths $\boldsymbol{E}_i$ these equations may be rewritten as follows ($x = \cos 2\beta$, $y_v = 2Av(\beta, \boldsymbol{E}_i)\cos\beta$)

$$y_{510}(\beta, \boldsymbol{E}_i) = m_{510}(\beta, \boldsymbol{E}_i)x + n_{510}(\boldsymbol{E}_i) \qquad (8)$$

$$y_{445}(\beta, \boldsymbol{E}_i) = m_{445}(\beta, \boldsymbol{E}_i)x + n_{445}(\boldsymbol{E}_i) \qquad (9)$$

The four parameters in (8) and (9) are defined by $n_{510} = K_{510}d$, $m_{510} = -n_{510}\cos 2\hat{\theta}_{510}$, $n_{445} = K_{445}d$ and $m_{445} = n_{445}\cos 2\hat{\theta}_{445}$. We stress that (8) and (9) are in general independent of each other. Therefore, the parameters of each band can be determined separately by fitting the absorbances to the respective linear equation. In this way, via $\hat{\theta}_{510}$ and $\hat{\theta}_{445}$, information about possibly different mean orientations of the dipoles contributing to the respective band becomes available. Field induced changes of the parameter values are obtained through measurements at different $\boldsymbol{E}_i$ and by solving (8) and (9) for each $\boldsymbol{E}_i$.

For comparison with earlier results[16] we now assume that, first, the parameters n_{510}, n_{445} are not influenced by the field and, second, the two bands have the same mean dipole orientation angle, i.e. $\hat{\theta}_{445}(\boldsymbol{E}_i) = \hat{\theta}_{510}(\boldsymbol{E}_i)$. Thereby equations (8) and (9) become a coupled system. If, as reported in the present paper, the measurements were made at two field strengths, there are now only four parameters (instead of eight), n_{510}, n_{445}, $\hat{\theta}(\vec{E}_1)$ and $\hat{\theta}(\vec{E}_2)$, which are determined by the linear fit procedure. The same information can be obtained independently by an algorithm using the fact that in this approximation a linear relationship exists between $A_{510}(\boldsymbol{E}_i)$ and $A_{445}(\boldsymbol{E}_i)$ for perpendicular incident light as could be derived from equations (6) and (7):

$$A_{510}(\boldsymbol{E}_i) = -\frac{K_{510}}{K_{445}}A_{445}(\boldsymbol{E}_i) + K_{510}d \qquad (10)$$

By means of this relation the mean dipole orientation for the respective field strengths $\boldsymbol{E}_i$ as well as the other parameters can be determined by using the slope and intercept of function (10) and the relations $A_{510} = K_{510}d\sin^2\hat{\theta}$ and $A_{445} = K_{445}d\cos^2\hat{\theta}$.

RESULTS AND DISCUSSION

Figure 2 shows the spectra of the poled sample taken at different angles of rotation without and with an applied electric field. In accordance with the high percentage of β-PVDF the bands due to the α-phase (530 cm^{-1}) and the γ-phase (430 cm^{-1}) are very weak. The very small absorption caused by the CF$_2$-wagging mode at 470 cm^{-1}, being strong in parallel polarization (not shown), reveals the chain axes to be highly aligned parallel to the stretch direction. *Figure 2* demonstrates the influence of the applied field on the behaviour of the bands at 510 and 445 cm^{-1} when the sample is rotated. From the considerable intensity changes of the 510 cm^{-1} band with a strong field applied one can immediately conclude that $\hat{\theta} \ll 45°$, whereas the small changes without an applied field suggest a $\hat{\theta}$-value near 45°.

Before the detailed quantitative evaluation, the errors introduced by the approximations should be estimated. As outlined in the Appendix, chains lying in the film plane at an angle $\pm\theta_c$ to the draw direction will cause a decrease of the mean orientation angle for the 445 cm^{-1} band, whereas chains in the plane formed by the film normal and the draw direction will give rise to increasing orientation angles, and vice versa, for the 510 cm^{-1} band. With $\langle\cos^2\theta_c\rangle \approx 0.97$ the changes of dipole orientation angles are smaller than $\pm 0.4°$ even in the worst case (all chains in the same direction) but, for an equidistribution of the chain axes on a cone around z, resulting errors considerably smaller should be expected because of at least partial cancellation.

The spectra were evaluated quantitatively by using the optical refraction index $n = 1.41$ $(= n_x = n_y)$. Variations of this value by 0.015 cause the dipole orientation angle to change by $< 0.5°$. Calculations using the formulae of Jarvis *et al.*[24] showed that this orientation angle varies by $< 0.05°$ if differences between n_x and n_y up to 0.1 are taken into account. Thus, neglecting the small refraction index difference found experimentally appears to be justified.

Figure 3 demonstrates the linearity of the relation between the product $A(\beta)\cos\beta$ and the angle-dependent abscissa $x = \cos 2\beta$, as required by theory. The straight lines were fitted with four or eight parameters by using equations (8) and (9). The resulting values as well as the parameters obtained by a linear fitting procedure in *Figure 4*, using equation (10), are summarized in *Table 1*. The differences between the results of the four-parameter fitting process and the respective $\hat{\theta}$-values obtained from *Figure 4* prove to be small, thus underlining the common theoretical basis of the two different experimental approaches. *Figure 4* indicates a slight deviation of the measured values from the straight line for strong applied fields. If the fitting process is performed only for the linear part, the differences mentioned above decrease, especially for a vanishing field. Comparing the field-dependent $\hat{\theta}$-values demonstrates again the considerable difference between the mean dipole orientation of a poled sample with an applied field and with the field switched off; the $\hat{\theta}$-value before poling had been determined earlier to be well above 45°[25].

Figure 3 reveals systematic deviations of the straight lines calculated theoretically by use of four independent

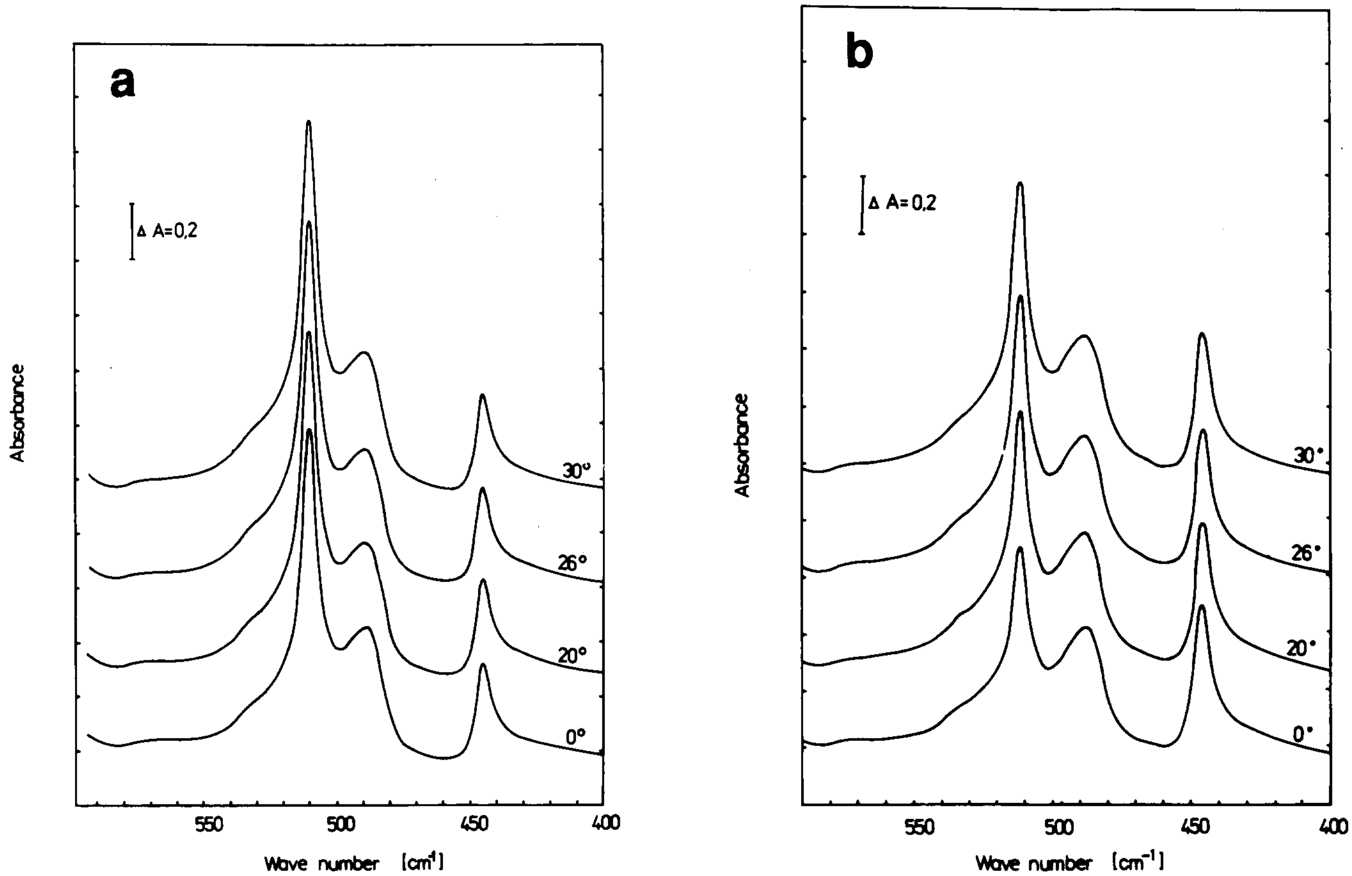

Figure 2 Infrared spectra of the poled PVDF film at different rotation angles: (a) without field; (b) in the presence of an electric field ($E = -240\,\mathrm{MV\,m^{-1}}$)

parameters from the experimental results, particularly for the 445 $\mathrm{cm^{-1}}$ band. This suggests field-dependent parameters and, possibly, different mean orientation angles $\hat{\theta}_{445}$ and $\hat{\theta}_{510}$ of the dipoles contributing to the respective bands. The fitting process using eight parameters yields almost identical remanent dipole orientations for the two bands, whereas with the field applied a difference appears between the mean orientation of the dipoles. To check the significance of the $\hat{\theta}$-difference found with the field applied, an error calculation was performed for the slopes and intercepts of the respective straight lines and from these for the mean dipole orientations. The results are given in *Table 1*. Unfortunately, the uncertainties of $\hat{\theta}_{445}$ are large, but nevertheless this value seems to be $<\hat{\theta}_{510}$. If so, this could cause a deviation from linearity in *Figure 4*, with the slope decreasing with increasing field, which is actually slightly indicated by the measurements. In conclusion, the experimental results seem to suggest differences between the two bands concerning their origin. These could include different lengths of the *trans*-sequences contributing to the bands, and different states of order, with the absorption at 445 $\mathrm{cm^{-1}}$ being caused by CF_2 vibrations in crystallites and the absorption at 510 $\mathrm{cm^{-1}}$ coming from crystallites as well as non-crystalline regions[2,17–21]. Adopting the latter viewpoint, the measurements suggest that, starting from nearly identical remanent orientation of the different dipoles

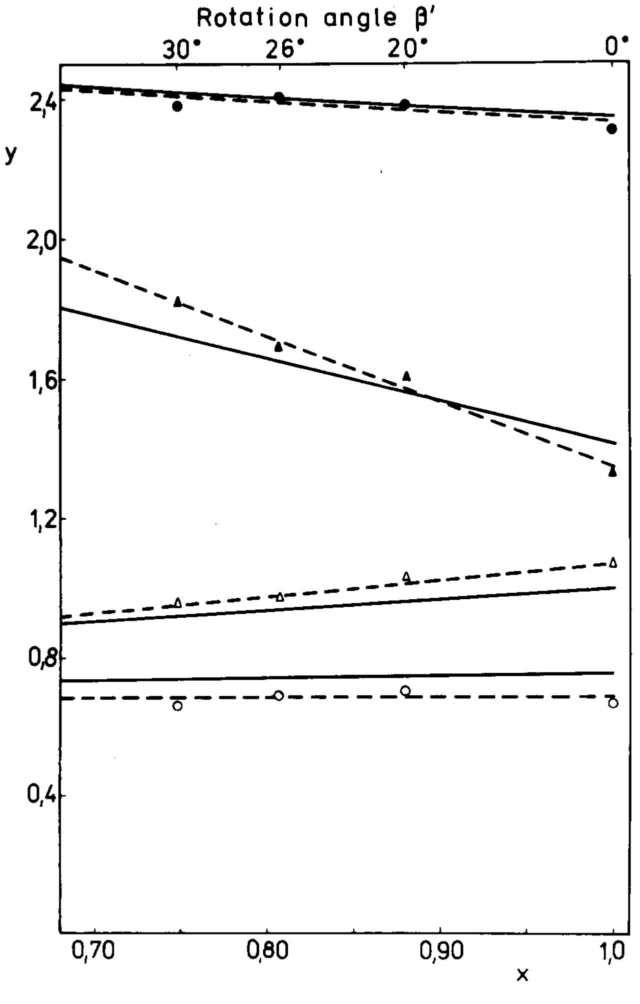

Figure 3 Measured values and fitted straight lines according to equations (8) and (9) against rotation angle ($y = 2A\cos\beta$, $x = \cos 2\beta$): ●, 510 $\mathrm{cm^{-1}}$, without field; ▲, 510 $\mathrm{cm^{-1}}$, with field; ○, 445 $\mathrm{cm^{-1}}$, without field; △, 445 $\mathrm{cm^{-1}}$, with field. Field strength: $E = -240\,\mathrm{MV\,m^{-1}}$. ——, four parameters; – – –, eight parameters (see text and *Table 1*)

Table 1 Intercepts and slopes of the fitted straight lines in *Figures 3* and *4* and respective dipole orientations

Fitting procedure[a]	E (MV m^{-1})	n_{510}	m_{510}	n_{445}	m_{445}	$\hat{\theta}_{510}$ (deg)	$\hat{\theta}_{445}$ (deg)
A	0	$A_{510} = -3.00\,A_{445} + 2.19$				46	
	-240					33	
B	0	2.64	-0.29	0.068	0.076	42	
	-240		-1.22		0.32	31	
C	0	2.66 ± 0.21	-0.33 ± 0.25	0.67 ± 0.11	0.020 ± 0.13	41.5 (+3; −3)	44 (+3; −3)
	-240	3.22 ± 0.16	-1.87 ± 0.19	0.59 ± 0.07	0.48 ± 0.09	27 (+2; −2)	18 (+7; −14)

[a] A, Equation (10) used. B, four independent parameters (equations (8), (9)): n_{510}, n_{445}, $\hat{\theta}(E_1)$, $\hat{\theta}(E_2)$. C, eight independent parameters (equations (8), (9)), see text

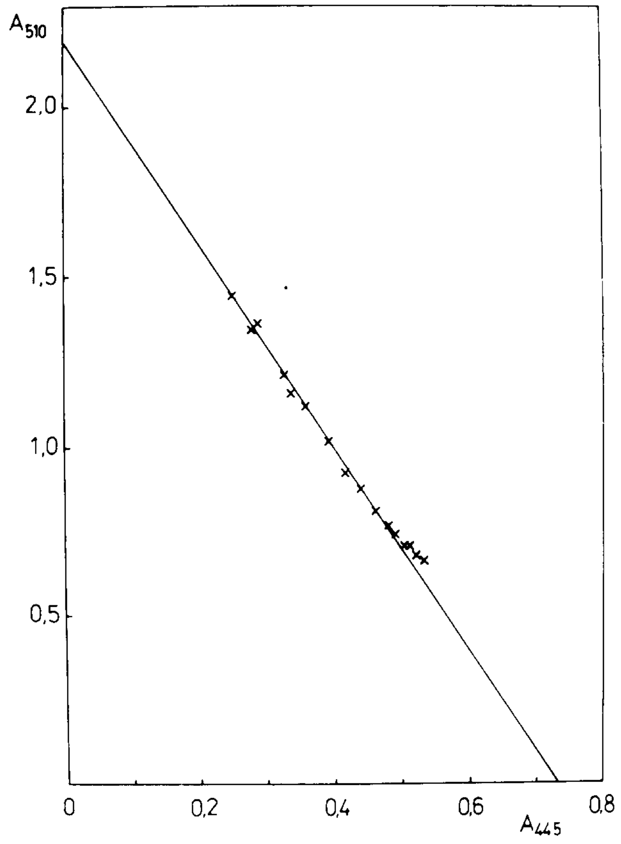

Figure 4 Plot of absorbance A_{510} *versus* A_{445}. Measurement with perpendicularly incident light at different electric field strengths ranging from +46 (left) to −240 MV m^{-1} (right). ———, fit according to equation (10)

corresponding to the bands, the field-induced reversible orientation change of the dipoles in crystallites is larger than that in non-crystalline regions. This might be explained by the dipoles in crystallites not moving continuously by small angles under the influence of an electric field but jumping by larger angles into their new positions.

The nearly identical remanent dipole orientation may be explained by the fact that, due to high chain axes orientation, the non-crystalline parts of the material are partially ordered and associated with the crystal lattice[20]. Further measurements using more rotation angles and different field strengths are needed to confirm these findings.

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APPENDIX

The influence of a small, but non-vanishing, angle between the chain axes and the draw direction (z-axis) can be roughly estimated for different dipole orientations by considering separately the effects caused, on the one hand, by chains which lie in the plane built up by the film normal and the z-axis with an angle $\pm\theta_c$ between the latter and the chain axes (case 1) and, on the other hand, by chains lying in the film plane but at an angle $\pm\theta_c$ to the draw direction (case 2).

The absorbances A_x and A_y (x, y-directions of the el. vector of the polarized light) can be approximated by

$$A_{x,y} \sim \int_0^{2\pi} f(\vec{\mu}) \left(\frac{\partial \boldsymbol{\mu}}{\partial q} \boldsymbol{E}_{\text{light}} \right)_{x,y}^2 \mathrm{d}\theta \qquad \text{(A1)}$$

Since field-induced dipole orientation changes take place within the plane perpendicular to the chain axis, the angle θ is always measured in this plane, i.e. in case 1 θ is the angle between a dipole and the plane containing the film normal and the z-axis.

By use of geometrical relations between dipole direction ($\boldsymbol{\mu}$), $\partial\boldsymbol{\mu}/\partial q$ and $\boldsymbol{E}_{\text{light}}$ and of the equation $A(\beta) = A_x \cos^2\beta + A_y \sin^2\beta$ for oblique incidence (light propagation $\perp$ z-axis) one obtains the following for the measured absorbance, e.g. of the CF_2 rocking vibration, when the varying path length within the sample is taken into account. Case 1:

$$A_{445}(\beta) = \frac{K_{445}d}{4\cos\beta}[(1-\cos^2\theta_c)(\langle\cos 2\theta\rangle + \cos 2\beta) + (1+\cos^2\theta_c)(1 + \langle\cos 2\theta\rangle \cos 2\beta)] \qquad \text{(A2)}$$

Case 2:

$$A_{445}(\beta) = \frac{K_{445}d}{4\cos\beta}[(\cos^2\theta_c - 1)(\langle\cos 2\theta\rangle + \cos 2\beta) + (1+\cos^2\theta_c)(1 + \langle\cos 2\theta\rangle \cos 2\beta)] \qquad \text{(A3)}$$

Similar relations result for the band at $510\,\text{cm}^{-1}$. After bringing these relations into the form of equations (8) and (9), the measurements can easily be evaluated to reveal the tendencies and order of magnitude of the $\hat{\theta}_v$ changes caused by small angles θ_c. This shows, that e.g. for the $445\,\text{cm}^{-1}$ band $\hat{\theta}_v$ increases (case 1) or decreases (case 2) by $<0.4°$ if $\cos^2\theta_c = 0.97$.