

# Measurement of Polar Orientation in Poled Side-Chain NLO Polymers Using Infrared Spectroscopy

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## SYNOPSIS

Infrared spectroscopy has been used to provide an independent estimate of dipole orientation in poled films of a side-chain polymer based on poly(methyl methacrylate) with an oxy-nitrostilbene side group attached via an aliphatic spacer. In particular, we used the dichroism of the absorption band assigned to the NO<sub>2</sub> symmetric stretching vibration as a measure of the orientation of the nitrostilbene group. This yields  $\langle P_2(\cos \theta) \rangle$ , where  $\theta$  is the angle between the transition dipole moment and the symmetry axis of the sample. We then used a Langevin-type model to calculate  $\langle \cos \theta \rangle$  from  $\langle P_2(\cos \theta) \rangle$  and concluded that values of  $\langle \cos \theta \rangle$  as high as 0.5 are being achieved. We find, however, that  $\langle P_2(\cos \theta) \rangle$  obtained by comparison of normal incidence measurements on unpoled and poled films does not agree with  $\langle P_2(\cos \theta) \rangle$  obtained from tilted-film measurements on poled films. We propose that this discrepancy arises because the local field in a poled sample affects the polarizability of the molecules. To confirm this, we applied high fields to unpoled films in the infrared spectrometer at room temperature. The results clearly show a large reduction in absorbance with the applied field when the infrared electric field vector has a component perpendicular to the plane of the film. A major error therefore occurs as a consequence of the internal field in poled samples if  $\langle P_2(\cos \theta) \rangle$  is derived from the tilted film measurements, whereas  $\langle P_2(\cos \theta) \rangle$  derived from normal incidence measurements is essentially correct. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The development of electroactive side-chain polymers with potentially useful nonlinear optical (NLO), piezoelectric, and pyroelectric properties has been widely reported.<sup>1-4</sup> This has, in part, been encouraged by the opportunities for chemical synthesis of materials for particular applications and also because of the stability and ease of fabrication that give polymer films an advantage over inorganic materials.

To display these effects, the films must be made noncentrosymmetric. This is normally done by applying an electric field at high enough temperatures for the polar molecules to acquire a preferential orientation in the applied field and then cooling the system prior to the removal of the field so that the

polar orientation is "frozen in."<sup>5</sup> This operation is known as poling. Depending upon the glass transition temperature and the magnitude of the  $\beta$  relaxation at room temperature, the dipole orientation may be quite stable with time.<sup>6-8</sup> Several authors have measured the linear electrooptic effect and second harmonic generation in such poled films<sup>9-11</sup> and UV-visible spectroscopy has been used to obtain an independent measure of the orientation parameters of poled side chain polymers.<sup>12</sup>

In this laboratory, we have used the pyroelectric coefficient to provide a rapid assessment of the efficiency of different poling processes. Using this technique, we have compared the activity and long-term stability of guest-host materials, side-chain polymers, and copolymers.<sup>13</sup> We have also been able to determine the effects of different mesogens and mesogen concentrations and have demonstrated the effects of different spacer lengths between the mesogen and the main chain.<sup>6</sup> The pyroelectric coefficient does not, however, give a direct quantitative

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measure of polar orientation, nor is it specific to the NLO group, but reflects the polar orientation of all the dipoles in the system.

We have, therefore, investigated the use of infrared spectroscopy to provide an independent measure of side-chain orientation. For a sample with cylindrical symmetry, the technique essentially measures  $\langle P_2(\cos \theta) \rangle$ , where  $\theta$  is the angle between the transition dipole moment  $\mu$  and the symmetry axis of the sample. What is required for an understanding of the piezoelectric, pyroelectric, and second-order NLO properties, however, is a knowledge of the odd order terms in the distribution. The pyroelectric coefficient depends upon  $\langle \cos \theta \rangle$ , for example, and the most important second-order NLO coefficient depends upon  $\langle \cos^3 \theta \rangle$ . We estimate these from  $\langle P_2(\cos \theta) \rangle$  by the use of a Langevin-type model. Given  $\langle P_2(\cos \theta) \rangle$ , we calculate  $\mu_p E_L / kT$ , where  $E_L$  is the local field seen by the molecule and  $\mu_p$  is its permanent dipole moment. We can then calculate  $\langle \cos \theta \rangle$  or any other orientation parameter from  $\mu_p E_L / kT$ , again using the Langevin model.

Initially, we compared normal incidence data on poled and unpoled films, and from the change in absorbance, we concluded that we could achieve high polar orientation. As an intended confirmation, we then performed tilted film measurements to determine  $\langle P_2(\cos \theta) \rangle$  from data on the poled films alone and found that there was a significant difference between the results obtained using these two experimental techniques.

This suggested that the local field due to the oriented dipoles had an effect on the extinction coefficient of the infrared bands used in the measurement. We therefore performed measurements on samples subjected to external fields while in the spectrometer to confirm this. These results clearly show that the effects of local fields must be considered when deriving orientation parameters from infrared data for highly polar systems.

## EXPERIMENTAL

The polymer studied was a copolymer of methyl methacrylate with 4-(6-oxypropane)-4'-nitrostilbene methacrylate (MO6ONS) in the proportion MMA/MO6ONS 9:1 (see Fig. 1). The polymer was supplied by Hoechst-Celanese, Robert Mitchell Research Center, Summit, NJ. Films of the copolymer were solvent-cast from a 10% solution in cyclopentanone to give films 5–8  $\mu\text{m}$  thick, suitable for corona poling and for infrared measurements.

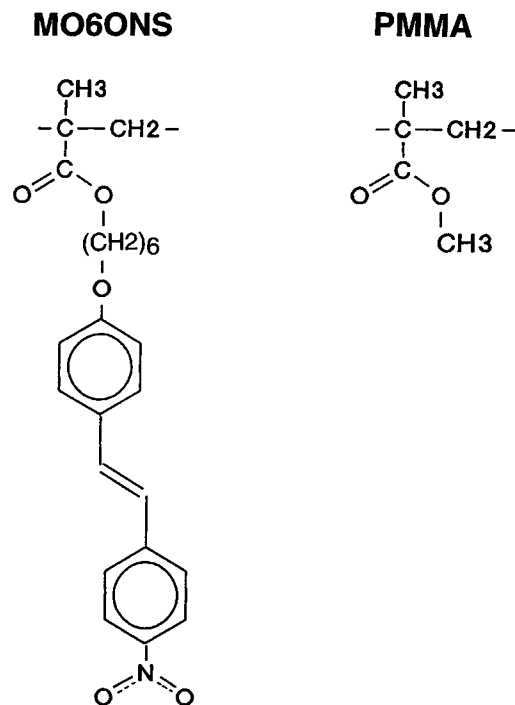
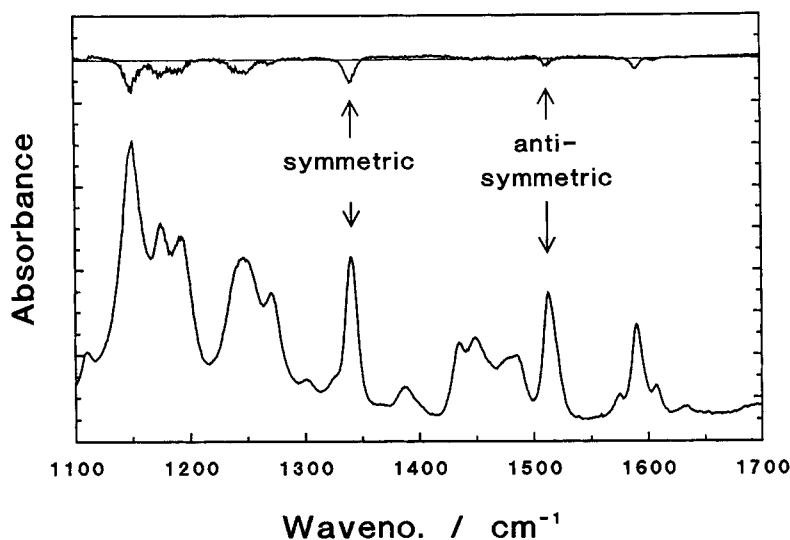


Figure 1 The MO6ONS and PMMA repeat units.

An unpolarized normal incidence infrared spectrum of MMA/MO6ONS from 1100 to 1700  $\text{cm}^{-1}$  is shown in Figure 2. The band at 1341  $\text{cm}^{-1}$  is assigned to the  $\text{NO}_2$  symmetric stretching vibration that has a transition moment essentially parallel to the long axis of the oxynitrostilbene group. The band at 1513  $\text{cm}^{-1}$  is assigned to the  $\text{NO}_2$  antisymmetric stretching vibration with a transition moment essentially perpendicular to the long axis of the oxynitrostilbene group. Either of these  $\text{NO}_2$  absorption peaks could, in principle, be used to characterize orientation. In these experiments, however, only the symmetric stretching band at 1341  $\text{cm}^{-1}$  is considered in detail.

### Experiment 1: Normal Incidence Measurements

In the first series of experiments, a spectrum was obtained for the isotropic film using a Perkin-Elmer 580B spectrometer recording data at 1  $\text{cm}^{-1}$  intervals. The film was then removed from the spectrometer and placed on an earthed heated plate in the corona poling rig. The film temperature was raised to  $T_g$  (111°C) and a high voltage applied to a corona poling needle placed 1 cm above the film. After 2 min, the film was cooled to room temperature at 10°C/min and the field switched off. A second infrared spectrum was then obtained for the poled film.



**Figure 2** The normal incidence absorption spectrum of an MO6ONS/PMMA film. The upper line is the difference between a poled and an unpoled sample.

Needle-to-plate potential differences of 3–10 kV were used to obtain samples of varying degrees of orientation.

Since we could not measure the poling field directly, we measured the pyroelectric coefficient of the poled film as an alternative measure of the degree of polar orientation. This required vacuum deposition of aluminum electrodes on the poled films, and we found that the matching medium normally used for infrared measurements could not be removed from the films well enough to allow successful electrode deposition. It was therefore necessary to perform the infrared measurements on free-standing films, which, consequently, exhibited interference peaks in the spectrum due to their high reflectivity. A separate curve-fitting program was used to remove these interference effects before any further processing. As a small compensation, this correction provided a useful check on film thickness. We are grateful to Dr. I. Karacan of this laboratory for making his program available to us.

The pyroelectric measurements were made as described previously.<sup>6</sup> Since the infrared measurements were made first, a variable delay occurred between poling and the measurement of the pyroelectric coefficient. Prior observations allowed us to correct for the small decay of the pyroelectric coefficient that occurred during this time. Previous measurements have also established a linear relationship between the pyroelectric coefficient and the poling field, obtained by contact poling at accurately known fields. These observations were used to estimate the effective field during corona poling.

The peak at  $1341\text{ cm}^{-1}$  has a small shoulder at about  $1325\text{ cm}^{-1}$ . The infrared spectrum in the narrow range  $1315\text{ to }1370\text{ cm}^{-1}$  was therefore fitted by a background and two Lorentzians to resolve the  $1341\text{ cm}^{-1}$  peak from the  $1325\text{ cm}^{-1}$  peak. Since the film thickness was constant, the orientation parameter was simply calculated from<sup>8</sup>

$$\langle P_2(\cos \theta) \rangle = 1 - \frac{A_p}{A_u} \quad (1)$$

where  $A_p$  and  $A_u$  are the poled and unpoled absorbancies, respectively, for the  $1341\text{ cm}^{-1}$  peak. (Note that in this and subsequent experiments the unique direction from which  $\theta$  is measured is normal to the plane of the film!)

### Experiment 2: Comparison of Normal Incidence and Tilted Film Measurements

A second series of films was then produced using a similar range of corona poling conditions to give samples for a comparison of normal incidence and tilted film measurements. Since it was desirable that matching techniques should be used for tilted film measurements, the pyroelectric coefficient could not be measured because traces of the matching fluid prevented deposition of aluminum electrodes. Tilted film measurements were made at  $45^\circ$  incidence using a polarized beam, KBr prisms, and nujol. Normal incidence measurements were therefore also made using KBr plates and nujol.

In this case, the removal of fringes caused by internal reflections was not required. The procedures for applying a reflectivity and internal field correction described by Cunningham et al.<sup>14</sup> and Jarvis et al.<sup>15</sup> were investigated but found to be unnecessary. The close match between the refractive index of the film (1.55) and that of KBr (1.56) meant that for tilted film measurements it was sufficient to assume that the angle of refraction was 45° for both polarizations, which greatly simplifies the analysis. This simple treatment yields results for  $\langle P_2(\cos \theta) \rangle$  that are only 5% greater than those calculated by a full analysis (assuming a birefringence of about 0.1). In a further simplification, absorbancies were determined using a pseudo-base-line method, since it was found that this gave similar results to Lorentzian curve fitting. For normal incidence measurements, eq. (1) was used to calculate  $\langle P_2(\cos \theta) \rangle$  from the data before and after poling.

In the tilted film case, it is convenient to define the "normalized absorbance"  $a$  as follows:

$$a = \frac{\cos \varphi}{d} \log_{10} \left( \frac{I_0}{I} \right) \quad (2)$$

where  $\varphi$  is the angle of refraction;  $d$ , the sample thickness;  $I$ , the detected intensity, and  $I_0$ , the incident intensity. The measurement with the electric field vector in the plane of the film ( $x$  direction) yields  $a_x$ . The other polarization, in general, gives

$a_\varphi$ , where  $\varphi$  is the angle of refraction and the infrared electric field vector makes an angle of  $90 - \varphi$  with the normal to the film ( $z$  direction). For the special case of  $\varphi = 45^\circ$ , however,  $a_z$  is given by

$$a_z = 2a_\varphi - a_x, \quad (3)$$

and  $\langle P_2(\cos \theta) \rangle$  can simply be calculated from

$$\langle P_2(\cos \theta) \rangle = \frac{a_z - a_x}{a_z + 2a_x} \quad (4)$$

### Experiment 3: Effect of Externally Applied Fields

In view of the discrepancy between the results from the two series of measurements described above, we devised a method of making tilted film infrared measurements on samples subjected to large external fields. It was found that films could be corona poled between two needles, each 1 cm from the film. Two needles were therefore mounted in the infrared spectrometer in a device that allowed films to be mounted normal to or at an angle to the infrared beam as shown in Figure 3. High fields could then be applied across the films at room temperature.

The system was calibrated by using it to pole samples at elevated temperatures (out of the spectrometer) and measuring the resulting pyroelectric coefficient for various voltages applied between the needles. The pyroelectric coefficient was then used as an indicator of the applied field as described above. Unfortunately, the conduction current through the film varies with temperature and, therefore, the high-temperature poling experiments and the experiments in the spectrometer at room temperature are not exactly equivalent. Nevertheless, this allows an estimate of the field seen by the samples in the spectrometer.

A further complication in this experiment is that a prism and matching fluid could not be used since the corona field had to be applied to the film itself. Reflectivity was therefore so high and the detected intensity so low that the incident radiation could not be polarized since the signal-to-noise ratio would then have been too poor. Also, significant refraction occurs in the tilted film case, and even with an angle of incidence of 60°, the angle of refraction was only 34°, not 45° as in experiment 2. In view of these complications, analysis of the IR data in this case is confined to reporting the normalized absorbance as a function of the applied field.

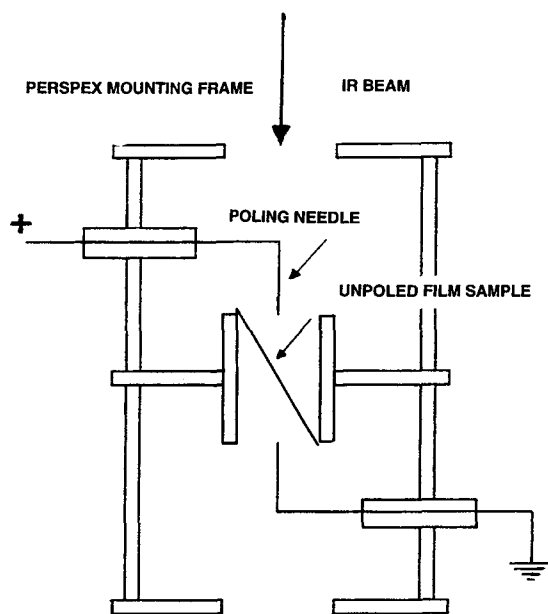


Figure 3 The infrared corona field apparatus.

### Estimation of the Degree of Polar Orientation

To make the link between the infrared measurements of orientation and the pyroelectric coefficient, it is necessary, as discussed in the Introduction, to calculate  $\langle \cos \theta \rangle$  from  $\langle P_2(\cos \theta) \rangle$ . We assume that the polar side groups in this low concentration copolymer behave like a dipolar gas in an electric field. A simple Langevin model is not applicable, however, since the unpoled film shows a slight tendency for the side groups to align perpendicular to the plane of the film. A modified Langevin model was therefore used in which the energy of a dipole is given by  $-\mu_p E_L \cos \theta - bkT \cos^2 \theta$  and the term in  $\cos^2 \theta$  allows for the tendency for dipoles to align perpendicular to the film. Tilted film measurements on unpoled films gave a spread of values of  $\langle P_2(\cos \theta) \rangle$  with a mean of 0.033 and a standard deviation of 0.015. The constant  $b$  was therefore chosen to give a  $\langle P_2(\cos \theta) \rangle$  of 0.033 at zero field. The relationships between  $\langle P_2(\cos \theta) \rangle$  and  $\mu_p E_L/kT$  and  $\langle \cos \theta \rangle$  were then obtained by numerical integration. The extension of this technique to the calculation of any other orientation parameter such as  $\langle \cos^3 \theta \rangle$  is obvious.

### RESULTS AND DISCUSSION

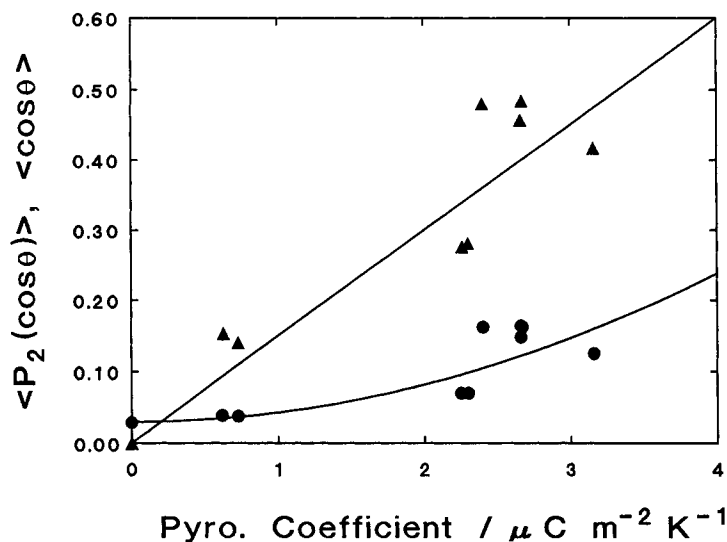
A difference spectrum (poled - unpoled) obtained at the highest fields used in experiment 1 is shown in Figure 2. It can be seen that the absorption at  $1341 \text{ cm}^{-1}$  reduces on poling. Figure 4 shows the

$\langle P_2(\cos \theta) \rangle$  derived from such normal incidence data plotted against the pyroelectric coefficient measured on the poled film. Also shown are the corresponding  $\langle \cos \theta \rangle$  results calculated as described above. The results show a general correlation of  $\langle \cos \theta \rangle$  with the pyroelectric coefficient, the scatter being partly due to the errors in measuring the very small values of  $\langle P_2(\cos \theta) \rangle$  that were obtained but also due to the variable preferential orientation in the unpoled samples.

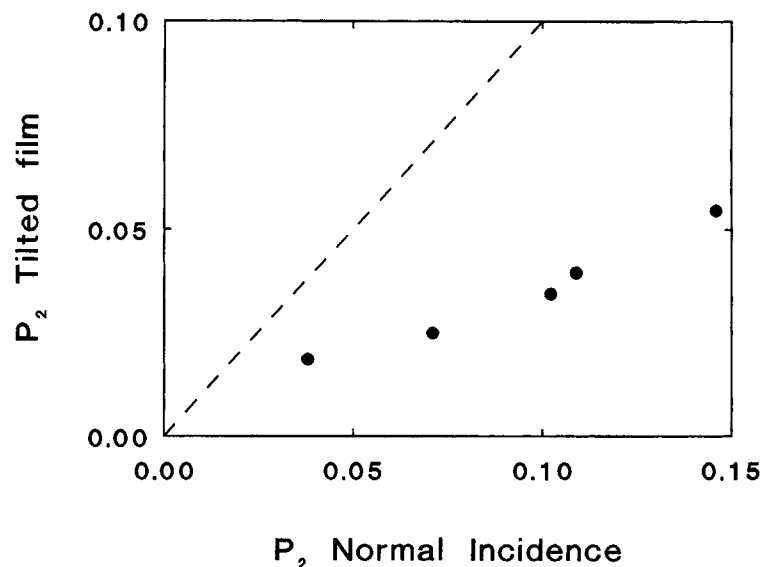
The maximum value of  $\langle \cos \theta \rangle$  of 0.5 is quite high but not unreasonable since the corresponding pyroelectric coefficient of  $3 \mu\text{C m}^{-2} \text{ K}^{-1}$  is close to the highest value that has been obtained for this material. The implication is that there is little chance of substantially improving the polar order in this material. This result is derived from a comparison between poled and unpoled samples, however, and it was thought desirable to check it with a technique that used only the poled film. We therefore embarked on experiment 2 in which we made a new series of films for both normal incidence and tilted film analysis.

The results of experiment 2 are summarized in Figure 5, which shows  $\langle P_2(\cos \theta) \rangle$  derived from polarized tilted film measurements compared with  $\langle P_2(\cos \theta) \rangle$  from unpolarized normal incidence measurements. It is seen that the tilted film method gives much lower values than does the normal incidence method, and it is clear that at least one of the techniques, if not both, is grossly in error.

Both methods assume that the changes in absor-



**Figure 4** The orientation parameters  $\langle P_2(\cos \theta) \rangle$  and  $\langle \cos \theta \rangle$  as a function of pyroelectric coefficient: (●)  $\langle P_2(\cos \theta) \rangle$ ; (▲)  $\langle \cos \theta \rangle$ .



**Figure 5** A comparison of  $\langle P_2(\cos \theta) \rangle$  values deduced by the different methods. The dashed line indicates equal values.

bance are purely due to orientation effects, the molecular polarizability remaining unchanged. We now suggest that this assumption is invalid. Specifically, we propose that the internal field arising from the permanent polarization in a poled sample changes the molecular polarizability, i.e., even when no external field is applied, the local field from the oriented mesogens changes the molecular polarizability, as might be expected for a second-order NLO material. Molecules lying in different orientations will be affected differently since, on average, the local field will be perpendicular to the plane of the film rather than in a given direction with respect to a molecule.

One way to demonstrate that the molecular polarizability is changing is to calculate an equivalent normalized "isotropic" coefficient  $(a_z + 2a_x)/3$  from the tilted film data. As can be seen from the data in Table I, this does appear to decrease with increasing orientation.

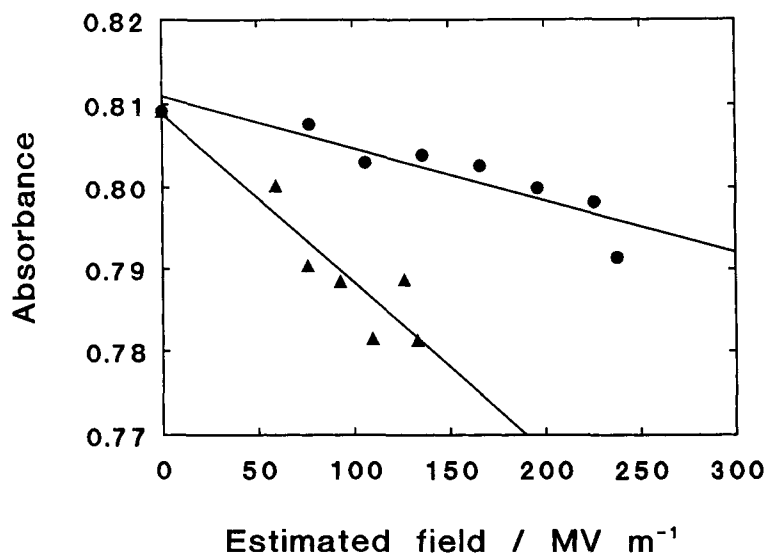
**Table I** The Normalized Equivalent Isotropic Absorbance as a Function of  $\langle P_2(\cos \theta) \rangle$

$\langle P_2(\cos \theta) \rangle$ (Normal Incidence)	$(a_z + 2a_x)/3$
0.038	0.095
0.071	0.074
0.102	0.073
0.142	0.071

An alternative approach is to show a change in absorbance with an externally applied field at such a low temperature that molecular reorientation is unlikely. We therefore performed experiment 3, the results of which are shown in Figure 6. It is seen that the application of an external field reduced the absorbance in both normal incidence and tilted film configurations, but that the effect is much larger in the tilted film case. In considering the implications of this observation, it must be remembered that in both cases unpolarized radiation had to be used. The unpolarized tilted film data therefore yield an average of the in-plane and perpendicular absorption coefficients. By comparison with the normal incidence data where the infrared electric field is always in the plane of the sample, we can readily deduce, however, that the change in the perpendicular absorption coefficient must be much greater than the change in the in-plane coefficient.

It would appear, therefore, that in this instance the local field arising from the permanent polarization causes the greatest change in absorbance for those groups whose transition moment is parallel to the local field. The tilted film method of determining molecular orientation is inappropriate, therefore, since it assumes that the molecules in different orientations have the same polarizability.

The normal incidence method is less subject to error, however, since it compares the in-plane data for poled and unpoled samples and these data are much less sensitive to a field perpendicular to the



**Figure 6** The change in the normalized absorbance of the  $1341\text{ cm}^{-1}$  peak with applied field: (●) normal incidence; (▲) tilted film  $60^\circ$  angle of incidence.

sample. Indeed, if one assumes that, for the most highly poled sample, the local field is comparable with the corona field, then the data of Figure 6 can be used to correct for the change in absorbance due to the local field and corrected orientation coefficients can be estimated. If such a correction is applied, then  $\langle P_2(\cos \theta) \rangle$  is merely reduced from 0.146 to 0.139, suggesting that local fields cause relatively small effects in normal incidence measurements.

Note, however, that it cannot be assumed that normal incidence methods will always give accurate answers. If, for example, we consider the antisymmetric  $\text{NO}_2$  stretching band at  $1513\text{ cm}^{-1}$ , we would expect its absorbance to increase on poling since the transition moment is perpendicular to the permanent dipole moment of the oxynitrostilbene group, and in a perfectly poled sample, the transition moments would be optimally placed to interact with the electric field in a wave entering at normal incidence. What is actually seen, however, is a slight reduction in absorbance on poling that is the opposite to what would be expected. Further experimentation is required to understand this, but, clearly, each case must be considered separately.

## CONCLUSIONS

It is possible, with care, to use infrared dichroism to obtain a measure of the orientation of specific groups in poled films of side-chain polymers. We have shown, however, that the local field due to ori-

ented polar groups must alter the extinction coefficient for the  $\text{NO}_2$  symmetric stretching band. The results obtained in the preliminary experiments suggest that the correction is smaller for the unpolarized normal incidence measurements than for the tilted film measurements and that the data shown for  $\langle P_2(\cos \theta) \rangle$  in Figure 2 are reliable. In general, however, it cannot be assumed that normal incidence measurements will always give reliable results.

The extension of the analysis to obtain from  $\langle P_2(\cos \theta) \rangle$  is speculative but broad correlation with the pyroelectric coefficient has been achieved. The results suggest that the most highly poled samples have  $\langle \cos \theta \rangle$  values approaching 0.5 and, hence, that the pyroelectric coefficient is within a factor of two of its maximum value in a perfectly oriented sample.

We have clearly shown that externally applied fields can produce significant changes in the intensity of bands in the infrared spectrum. More definitive experiments must be performed in which known fields are used so that a more quantitative approach can be developed, ideally covering a number of absorption bands. The feasibility of using interdigitated electrodes and the simplified infrared beam geometry that this allows is currently being investigated.

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