

ARTICLES

Electric Poling of 4-(Dimethylamino)-4'-nitrostilbene in Poly(methyl methacrylate) Studied by Polarized Absorption Spectroscopy**Xuan Cao and Jeanne L. McHale****Department of Chemistry, University of Idaho, Idaho 83843**Received: September 10, 1996; In Final Form: April 24, 1997*®

The inversion symmetry of chromophores doped in thin organic polymer films can be eliminated by electric poling. Polarized absorption spectroscopy (PAS) is used to study the electric poling of a guest–host system of poly(methyl methacrylate) doped with 4-(dimethylamino)-4'-nitrostilbene. Orientational order parameters induced by electric poling are obtained by angle-resolved PAS. The electric field inside the polymer film during poling is estimated from the order parameters obtained. PAS also suggests that there might be another electronic transition in the long wavelength part of the charge-transfer band. The order parameter decay may be fitted by a biexponential function, suggesting two different relaxation mechanisms might exist.

1. Introduction

The nonlinear optical properties of certain organic and polymeric materials have been the subject of numerous investigation in recent years because of their mechanical and electronic properties that facilitate their use in practical devices.^{1–3} In order for a material to have nonlinear second-order properties, such as would be required for frequency doubling or electrooptic modulation, it is necessary to remove the inversion symmetry of the material.^{4–6} Most highly nonlinear organic molecules are charge-transfer molecules, which usually have appreciable static electric dipole moments and hence can be aligned by applying an electric field. This process is known as electric poling. Usually a molecule with large nonlinear susceptibility is doped into an appropriate polymer to form a guest–host system. During the poling process, the polymer is heated to near its glass transition temperature T_g to reduce its viscosity and facilitate molecular rearrangement. A poling field E_p is then applied, and after an equilibration period, the material is cooled in the presence of the field and the orientation of the guest chromophore is frozen in the host polymer matrix.

The efficiency of this procedure depends on the ratio of electrostatic dipole alignment energy to thermal energy. This ratio is represented by the dimensionless parameter u

$$u = \frac{\mu E_p}{kT} \quad (1)$$

where μ is the dipole moment of the species being aligned, k is the Boltzmann constant, and T is the temperature.

The guest–host system after poling has nonlinear optical properties such as second-harmonic generation (SHG) and electrooptic modulation. For ultimate applications, it is important to require that high poled order be achieved and be stable for a considerable time. So the efficiency and persistence of alignment are of great practical interest, and studies of order parameters and their relaxation rates are therefore of considerable interest.

A popular approach to studying the orientational order has been to use the Maker fringe technique to observe the second-harmonic light generated when a laser beam is passed through the sample.^{7–11} The polar orientational order parameters associated with SHG are $\langle P_1(\cos \theta) \rangle$ and $\langle P_3(\cos \theta) \rangle$. Here θ is the angle between the dominant principal axis of the molecular hyperpolarizability tensor and the poling electric field and P_1 and P_3 are Legendre polynomials of order 1 and 3. Goodson et al.¹² studied the decay of the SHG signal of poled 4-(dimethylamino)-4'-nitrostilbene (DANS) in poly(methyl methacrylate) (PMMA), which is expected to follow the relaxation behavior of $\langle P_1(\cos \theta) \rangle$. They found that the decay of the SHG intensity can be better fitted by a biexponential function than by a stretched exponential function. This suggests a two-mode relaxation mechanism for $\langle P_1(\cos \theta) \rangle$. But information about $\langle P_2(\cos \theta) \rangle$ cannot be obtained from SHG experiments, and also SHG experiments are expensive and difficult to carry out. Since the relaxation of the chromophores will generally take a long time, it is also difficult to evaluate the decay time with sufficient accuracy within a practical experimental period of time.

Polarized absorption spectroscopy (PAS) has been a convenient way to study ordered systems such as liquid crystals and has also been used to study the electric poling of guest–host polymer systems.^{11,13,14} But when it is used quantitatively to study the orientation of chromophores in poled polymer films, it usually suffers from disadvantages due to the undetermined sample concentration and film thickness because the chromophores may undergo sublimation or other changes when poled at high temperatures.⁷ Michael et al.¹⁶ recently used PAS to obtain orientational order parameters of some poled films. But the orientational order they obtained for the DANS and PMMA system was poor. For poorly poled systems, it is hard to talk about how the orientational order decays with time. In this paper, we show a simple derivation of order parameters from angle-resolved polarized absorption spectroscopy, which avoids problems due to unknown concentration and film thickness. The method is applied to poled DANS in PMMA films.

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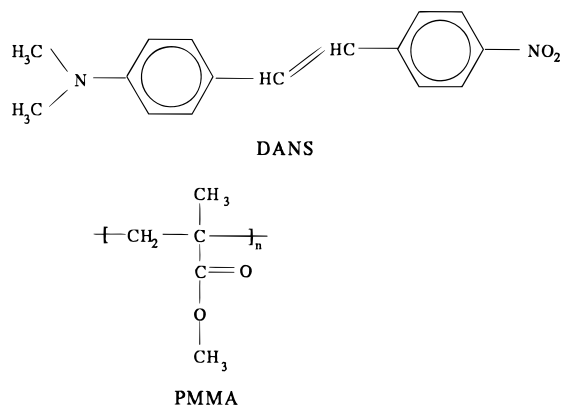


Figure 1. Chemical structures of DANS and PMMA.

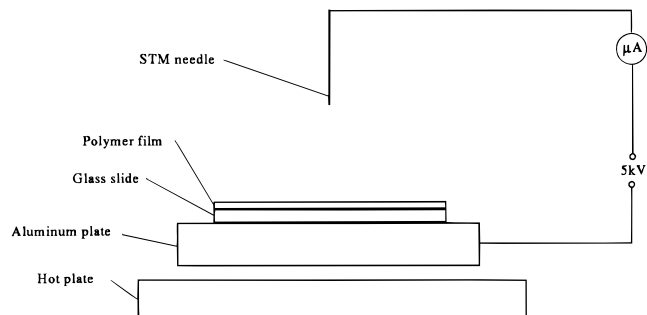


Figure 2. Experimental setup for electric poling.

2. Experimental Section

Chemical structures of the chromophores and polymer host used in this experiment are shown in Figure 1. PMMA films doped with DANS were prepared as follows. A solution of PMMA ($M = 101\,000$, $T_g = 371\text{ K}$) in chlorobenzene doped with DANS was coated onto a 0.17 mm thick transparent microscope slide. The sample was put in a restricted atmosphere at room temperature for 2 days to allow the solvent to evaporate slowly, and then it was baked at 373 K for 10 h to remove residual solvent. The films prepared in this way are visually clear and have uniform surfaces except near the edge. The thickness ranges from 3 to 5 μm . Films of good uniform surface were not obtained by using other solvents with low boiling points. The concentration of DANS in the films was approximately 1–3%. The PMMA–DANS films were poled using electrode configurations as described in Figure 2.¹³

The substrate was placed film side up onto a grounded planar aluminum electrode. The temperature of the film could be raised by a heating plate positioned under the aluminum electrode. The temperature was monitored by placing a thermometer inside the aluminum plate. Temperature measured in this way might be several degrees higher than the actual temperature of the films, but this allows more accurate control of the temperature. First the temperature of the baked films was raised to 383 K, very close to the glass–rubber transition temperature of PMMA. A high positive voltage was applied to the suspended electrode for 10 min. The electric current was typically 2–4 μA . Then, while the voltage was held constant, the temperature of the film was lowered to room temperature. Before the absorption spectral measurements were taken, the surface charge was removed by connecting two opposite surfaces with conductive aluminum sheets.

It is important to let the solvent evaporate slowly when the sample is first coated onto the glass slide to achieve uniform surfaces. It is also necessary to remove all the residual solvent to achieve efficient poling. We noticed that polymer films with

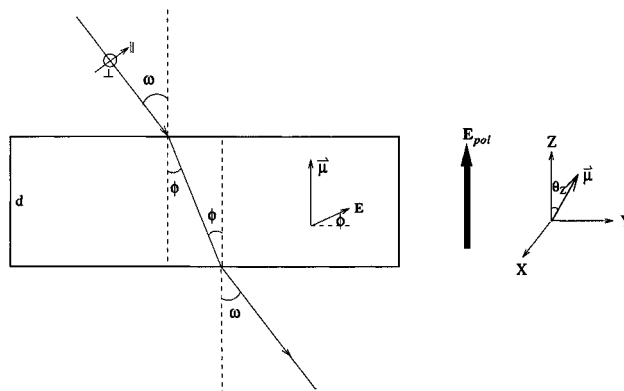


Figure 3. Experimental setup for PAS measurements and coordinate system chosen.

residual solvent are more easily damaged by electric current. A poorly poled film usually has a smoky surface and poor optical clarity. The voltage was adjusted carefully during the poling process to keep electric current around 2–4 μA . The temperature should not be too high since the conductivity of most polymer materials increases dramatically with temperature, to the point of causing damage, without developing a large voltage drop. On the other hand, if the temperature is too low, the viscosity of the material is too high for appreciable molecular reorientation.

The absorption of the film was measured with an absorption spectrometer (Perkin-Elmer Lambda 4B) with the sample configuration described in Figure 3. A polarizer filter is placed in front of the sample allowing the choice of different polarizations of the incident light. The components of the electric field polarization parallel or perpendicular to the incident plane are denoted as \parallel and \perp , respectively. The absorption of the polarizer filter was treated as background, and all the absorption spectra and absorbance measurements shown below have been corrected for this background. ω and ϕ are incident and refraction angles, respectively. The poling direction is parallel to the normal of the film. The coordinate system is chosen to be fixed inside the polymer film with the Z axis parallel to the normal of the film, which can be rotated around the X axis, which is perpendicular to the paper plane. The reflection at the air–polymer surface and glass–air surface is corrected using the Fresnel equation.¹⁷ At the air–polymer interface, the transmittance for the \parallel and \perp polarizations are

$$T_{\parallel} = \frac{n_2 \cos \phi}{n_1 \cos \omega} \left[\frac{2 \sin \phi \cos \omega}{\sin(\omega + \phi) \cos(\omega - \phi)} \right]^2$$

$$T_{\perp} = \frac{n_2 \cos \phi}{n_1 \cos \omega} \left[\frac{2 \sin \phi \cos \omega}{\sin(\omega + \phi)} \right]^2 \quad (2)$$

where n_1 and n_2 are refractive indices of the air and the polymer, respectively. The values we took for this study were $n_1 = 1.00$ and $n_2 = 1.52$ ^{14,18} at 440 nm. The reflection at the glass–polymer interface is neglected since the refractive indices of the polymer and the glass are very close.

Though the thickness of the sample does not need to be known for the investigation of the order parameter in our approach, knowledge of that is helpful to estimate the field strength inside the polymer film during electric poling. To achieve efficient electric poling, the film should be as thin as possible. But the concentration of the dye molecules and the thickness of the film should be appropriate for both electric poling and absorbance measurement. The thickness of the film used in this study was $3.9 \pm 0.2\text{ }\mu\text{m}$ as determined by measuring

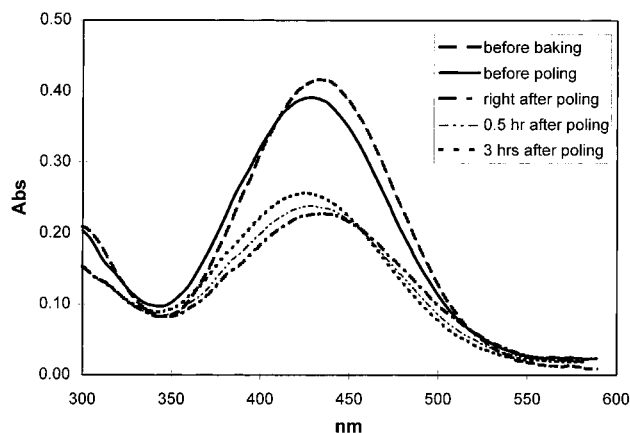


Figure 4. Absorption spectra of DANS in PMMA before and after poling.

the interference fringers in a Bomem MB-100 FT-IR spectrometer. To confirm the uniform thickness of the film, we also used the experimental setup in Figure 3 to measure the absorbance of the polymer film prepared in the same way as described above but without DANS doped in it. Without the absorption of the DANS molecules, the difference in absorbance using different incident angles will only be due to the difference in transmission coefficients of light at the air-sample interface, which should obey the Fresnel equation if the sample surface is uniform. Our experimental results were consistent with what was expected by the Fresnel equation.

3. Results and Discussion

3.1. Poling Process. The spectroscopic properties of the gas-phase DANS molecule were calculated using the semiempirical INDO/S method.^{19–21} It was found that the transition with the largest oscillator strength is that from the ground state to the first excited singlet state, which is also a charge-transfer state. The angle between the permanent dipole moment and the charge-transfer transition dipole moment is about 5°, and the angle between the long inertial axis and the permanent dipole moment is about 3°. So for the DANS molecule, the permanent dipole moment, the charge-transfer transition dipole moment, and the long molecular axis are nearly parallel to each other.

It is known that during corona poling charge accumulates at the surface of the polymer film and opposite charge accumulates at the planar electrode. In this way a large electrostatic field is created in the film and interacts with the dipole moment of the guest molecules. This will be reflected in the absorption spectrum, which is determined by the interaction of the transition dipole moment and the electric field of the incident light. During a poling process, the electrostatic field aligns the permanent dipoles in the direction of the poling field. So, at normal incidence, the transition dipole moment will tend to align in a direction perpendicular to the electric field of incident light after poling. This causes a decrease in the absorbance of the charge-transfer band. A large electrostatic field will also induce a change in the energy interval between the ground and excited states through the Stark effect and thus shift the absorption peaks. Alignment of the chromophores will also change the local environment of the chromophores and affect the interaction among themselves. All these effects will be reflected in the change of the absorption spectra of the chromophores to some extent.

The absorption spectra of DANS in PMMA film before and after poling are shown in Figure 4. These spectra were taken using unpolarized light at normal incidence. The strong 380–500 nm band is assigned as the intramolecular charge-transfer

band. There is a blue shift when the polymer films are baked, probably due to the depletion of the solvent from the polymer films. Immediately after poling a decrease in absorbance as well as a shift toward longer wavelengths was observed. An absorption peak at 434 nm existed before poling. Immediately after poling, the peak absorbance shifted to 444 nm, and during the next a few hours, it shifted back toward 434 nm with a small increase in the peak absorbance. But the absorbance did not recover during the time of experiment. After that, the spectroscopic absorption characteristics remained unchanged for days. While the loss of the absorbance could be due to sublimation of the chromophores during poling, analysis of the relaxation rate of the order parameter suggests that it is more probably due to the very slow rate of relaxation after the initial faster relaxation. This is partially confirmed by the following relaxation analysis. So if the loss of absorbance is not due to sublimation of the chromophores, it is an indication of the high orientational order achieved by electric poling, which is stable for a considerably long time. The shape of the absorption spectrum before and after poling was similar, indicating that no chemical change took place during poling.

3.2. Polarized Absorption Spectroscopy (PAS). E. W. Thurstrup and J. Michl have been the pioneers in applying PAS in the study of stretched polymers.^{22,23} In a stretched polymer, the doped chromophores are parallel to the surface of the film. But in a poled polymer film, chromophores are perpendicular to the surface of the film, so angle-resolved techniques have to be applied in PAS in order to study the orientation of chromophores in a poled polymer. For the coordinate system described in Figure 3, the poling electric field is in the lab Z direction, which is the normal to the film. Under the poling electric field, a molecule in the polymer matrix tends to align its permanent dipole moment in the Z direction. The direction of the permanent dipole moment with respect to the poling field is defined by θ_z . Similarly, θ_x and θ_y are angles of the permanent dipole moment with respect to the X and Y axis, respectively. The alignment of the molecule along a direction is described by Boltzmann statistics. The distribution function along the Z direction is^{13,24}

$$g(\theta_z) = \frac{\exp(-u \cos \theta_z)}{\int_0^\pi \exp(-u \cos \theta_z) \sin \theta_z d\theta_z} \quad (3)$$

where u is defined in eq 1.

Defining

$$\begin{aligned} K_x &= \langle \cos^2 \theta_x \rangle \\ K_y &= \langle \cos^2 \theta_y \rangle \\ K_z &= \langle \cos^2 \theta_z \rangle \end{aligned} \quad (4)$$

to describe the statistically averaged orientation of the transition dipole, then

$$K_x + K_y + K_z = 1 \quad (5)$$

For isotropic media, there is no preference of molecular orientation in space, so

$$K_z = K_x = K_y = 1/3 \quad (6)$$

If the applied electric field is along the Z direction, there will be no preference for alignment along X or Y axis, and thus

$$K_x = K_y = (1 - K_z)/2 \quad (7)$$

Let A_0 be the absorbance measured at a certain wavelength when the molecules are perfectly aligned along the normal of the film and the electric field of the incident light coincides with the electric transition dipole moment of the molecule and the thickness of the film is d . For nonnormal incidence, the optical path length is $d/\cos \phi$, and the absorbances for \perp and \parallel polarizations are:

$$A_{\perp} = A_0 K_x \frac{1}{\cos \phi} = A_0 \frac{1 - K_z}{2} \frac{1}{\cos \phi} \quad (8)$$

$$A_{\parallel} = \left(A_0 K_z + A_0 \frac{1 - 3K_z \cos^2 \phi}{2} \right) \frac{1}{\cos \phi} \quad (9)$$

$$\frac{A_{\parallel}}{A_{\perp}} = \frac{2K_z}{1 - K_z} + \frac{1 - 3K_z}{1 - K_z} \cos^2 \phi \quad (10)$$

where A_{\perp} and A_{\parallel} are absorbances when the incident light is polarized perpendicular and parallel to the incident plane, respectively. ϕ is less than 90° since the refractive index of the film is greater than that of air. In obtaining these equations, we neglected the weak birefringence of the polymers and the contribution to the refractive index from the added chromophores.

From eqs 8–10, when the incident beam is normal to the surface, $\phi = 0$ and $A_{\perp} = A_{\parallel}$. For an unpoled isotropic sample, $A_{\perp} = A_{\parallel}$, since $K_z = 1/3$. For poled anisotropic samples, $A_{\perp} \neq A_{\parallel}$ for $\phi \neq 0$, since $K_z \neq 1/3$ generally.

3.3. Polarized Absorption Spectra of DANS in PMMA.

Since A_{\perp} and A_{\parallel} are different for anisotropic samples, in the following sections, we will show how eqs 8–10 can be used to analyze the orientation of the chromophores in a poled polymer film. The polarization was chosen to be \parallel since for \perp polarization, the electric field due to the light is perpendicular to the poling field and the absorbance change will be only due to path length change when the sample is rotated. When parallel polarization is chosen and the sample is isotropic, eq 9 gives

$$A_{\parallel}^{\text{iso}} = A_0 K_z \frac{1}{\cos \phi} \quad (11)$$

As shown in the following equation, increasing ϕ will increase the optical path length inside the sample and increase the absorbance.

$$\Delta A_{\parallel}^{\text{iso}} = A_0 K_z \frac{\cos \phi - \cos(\phi + \Delta\phi)}{\cos \phi \cos(\phi + \Delta\phi)} > 0 \quad \text{for } \Delta\phi > 0 \quad (12)$$

For a poled sample, $K_z \neq 1/3$. From eq 9, we can see that besides the contribution from the first term as in the case of an isotropic sample, there is a contribution from the second term, which depends on the magnitude of K_z . If $K_z > 1/3$, the second term will be negative, and a smaller absorbance will be observed compared with unpoled isotropic samples. This is the case with DANS since K_z for poled DANS in PMMA is greater than $1/3$. This is what we saw in section 3.1 where a decreased absorbance was observed for poled DANS in PMMA film.

Increasing ϕ will also increase the optical path length inside the sample and increase the absorbance.

$$\Delta A_{\parallel}^{\text{poled}} = \Delta A_{\parallel}^{\text{iso}} + \frac{A_0(1 - 3K_z)}{2} [\cos(\phi + \Delta\phi) - \cos \phi] \quad (13)$$

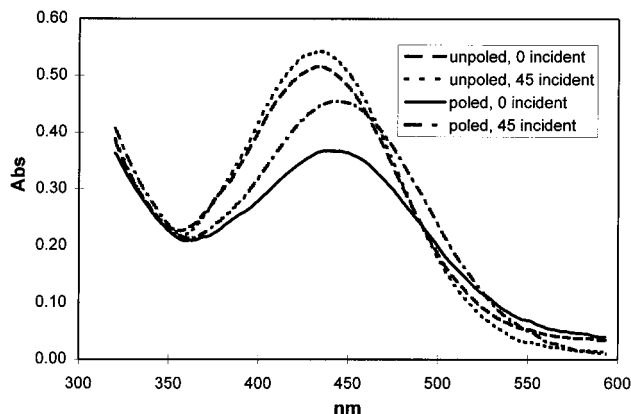


Figure 5. Absorption spectra of DANS in PMMA before and after poling measured using \parallel polarization, 0° and 45° incident angles.

The second term will be positive for $K_z > 1/3$ and $\Delta\phi > 0$. So a large increase in absorbance is expected for the charge-transfer band of the poled DANS in PMMA films.

Figure 5 shows the absorption spectra of DANS in PMMA before and after poling when the electric field of the incident light is in the incident plane and the same incident angle change is used. When the film is tilted from 0° to 45° , the poled film has a much larger increase in absorbance than the unpoled isotropic sample as predicted by eq 13. Intuitively, increasing the incident angle will only change the optical path length in the case of the isotropic sample. But after poling, the transition moment of the chromophores are aligned along the normal of the film and increasing the incident angle will also increase the component of the electric field of light onto the transition dipole moment.

3.4. Obtaining the Order Parameters. The order parameter is usually defined as^{25,26}

$$\Phi = 1/2(3\langle \cos^2 \theta_z \rangle - 1) = 1/2(3K_z - 1) \quad (14)$$

So, to obtain the order parameter Φ , we just need to obtain K_z . In this work, we found it more convenient to use K_z directly to describe the orientational order. From eqs 8–10, there are several ways to obtain K_z .

Using eq 10, we measure A_{\perp} and A_{\parallel} at different rotation angles, plot A_{\parallel}/A_{\perp} versus $\cos^2 \phi$, and from the slope, find K_z . But A_0 cannot be obtained in this way, and the difference of refractive indices in \parallel and \perp polarization inside the polymer films needs to be neglected.

From eq 9, it is obvious that measurement of A_{\parallel} at different incident angles is enough for derivation of order parameters. From eq 9, we have

$$A_{\parallel} \cos \phi = A_0 K_z + A_0 \frac{1 - 3K_z}{2} \cos^2 \phi \quad (15)$$

So plotting $A_{\parallel} \cos \phi$ versus $\cos^2 \phi$ should give us a straight line, and from the slope and the intercept, we can easily find K_z and A_0 . Figure 6 shows the plot of $A_{\parallel} \cos \phi$ versus $\cos^2 \phi$ of unpoled isotropic sample and the sample after poling measured at 440 nm wavelength. These data were fitted by straight lines (with $R^2 > 0.997$).

Equation 9 can also be used directly by applying the nonlinear least-squares fitting procedure to obtain A_0 and K_z simultaneously. The values for K_z and A_0 obtained in this way are the same as those obtained by $A_{\parallel} \cos \phi$ vs $\cos^2 \phi$ plot.

All the absorbances in the following sections were measured at 440 nm, which is the peak absorbance position of DANS in PMMA right after poling. There is no way to obtain A_0

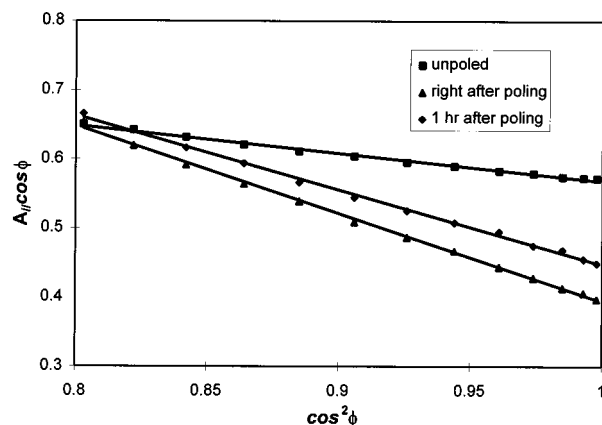


Figure 6. Plot of $A_{\parallel} \cos \phi$ vs $\cos^2 \phi$ fitted with straight lines.

experimentally since a perfectly aligned guest–host system is impossible to obtain. Theoretically, we have $A_0 = 3A_{\text{iso}}$, where A_{iso} is the absorbance of unpoled isotropic sample at normal incidence.

The absorbance of the isotropic sample at normal incidence (A_0^{iso}) before poling was 0.578. From nonlinear least-squares fit of Figure 6, we got $A_0^{\text{iso}} = 1.744 \pm 0.056$ and $K_Z^{\text{iso}} = 0.347 \pm 0.033$ ($\Phi = 0.021$). This is reasonable since A_0^{iso} is about triple the absorbance of the isotropic sample ($3A_{\text{iso}} = 1.734$) and K_Z^{iso} is also close to $1/3$ which is expected for an isotropic sample. We notice that K_Z^{iso} is a little greater than $1/3$ and the fitted straight line in Figure 6 for the unpoled isotropic sample is not strictly flat but has a small slope. This reveals that even in the unpoled isotropic sample there is still some orientational order of the chromophores in the polymer matrix.¹⁶

For the anisotropic sample right after poling, we obtained $A_0^{\text{poled}} = 1.746 \pm 0.053$ and $K_Z^{\text{poled}} = 0.534 \pm 0.034$ ($\Phi = 0.301$). We can see that A_0^{poled} is nearly unchanged and K_Z^{poled} is significantly greater than K_Z^{iso} . This indicates that efficient electric poling has been achieved. We also measured the order parameters at different times after poling. For each set of data at a certain time t , the $A_0^{\text{poled}}(t)$ we obtained is nearly a constant with average 1.749 while $K_Z^{\text{poled}}(t)$ does decay with time. We will deal with this relaxation behavior in section 3.7.

3.5. Transition Dipole Moment of DANS. The order parameter $K_Z = \langle \cos^2 \theta_Z \rangle$ gives the statistically averaged orientation of the transition dipole moment, which is active at the wavelength of measurement. So if we know the direction of this transition dipole moment in the molecular frame, we would know the orientation of the molecule in the lab frame. On the other hand, the order parameter expressed in terms of the orientation of the molecule is unique, independent of transition moment direction. If an absorption band encompasses more than one electronic transition, because of the difference in the directions of transition dipole moments, K_Z will be different for different electronic transitions. Using Snell's law, eq 10 becomes

$$\frac{A_{\parallel}}{A_{\perp}} = 1 + \frac{3K_Z - 1}{1 - K_Z} \frac{\sin^2 \omega}{n^2} \quad (16)$$

where ω is the incident angle and n is the refractive index of the polymer.

So we will have different A_{\parallel}/A_{\perp} for different electronic transitions depending on the magnitude of K_Z . If we measure the absorption spectra using \parallel and \perp polarizations at a fixed incident angle $\omega \neq 0$, then if a band is composed of a single electronic transition, A_{\parallel}/A_{\perp} in that region should be constant.

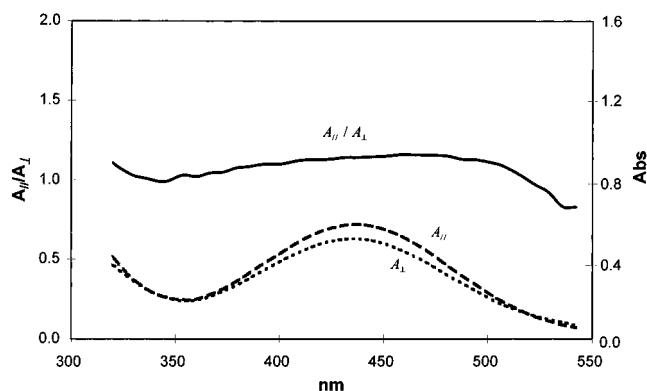


Figure 7. Ratio of two differently polarized absorption spectra of DANS in PMMA after poling.

Otherwise, the inconsistency should be caused by the difference in K_Z . This will suggest that there be two different electronic dipole moments in that region.

Figure 7 shows two absorption spectra of DANS in PMMA using \parallel and \perp polarizations at 45° incident angle and the ratio of these two spectra. It seems that A_{\parallel}/A_{\perp} remains almost as a constant (> 1) in the region of 380–500 nm, which means that there is only a single electronic transition in this region and K_Z is greater than $1/3$. On the right wing of that band, we have $A_{\parallel}/A_{\perp} < 1$, which requires K_Z for that transition dipole moment to be less than $1/3$. This suggests that there might be another electronic transition in the tail region whose direction is different from that of the intramolecular charge-transfer transition dipole moment. But it is hard to tell the exact direction of that electronic transition within the molecular frame just from our present PAS experiment.

3.6. Poling Field and Red Shift of Peak Absorbance.

Poling Field Strength. Looking back at the polarized absorption spectra of DANS in PMMA and using the order parameters obtained in section 3.4, we can make a quantitative estimate of the electric field strength during poling. After poling, the molecules are oriented along the poling field direction described by $K_Z = \langle \cos^2 \theta_Z \rangle$. The quantity $\langle \cos^2 \theta_Z \rangle$ is related to u in eq 1 by the Langevin function, which is defined as

$$L_n(u) = \langle \cos^n \theta_Z \rangle = \frac{\int \cos^n \theta_Z \exp(-u \cos \theta_Z) \sin \theta_Z d\theta_Z}{\int \exp(-u \cos \theta_Z) \sin \theta_Z d\theta_Z} \quad (17)$$

So

$$K_Z = \langle \cos^2 \theta_Z \rangle = L_2(u) = 1 + \frac{2}{u^2} - \frac{2}{u} \coth(u) \quad (18)$$

where u is $24.2\mu E_p/T$ if μ is in D and E_p is in MV/cm.

Taking K_Z to be the initial value of 0.534 would give $u = 2.78$ and $E_p = 3.42$ MV/cm. This corresponds to 1.3 kV across the polymer film taking the thickness of the film as $3.9 \mu\text{m}$. In this study, we neglected the time delay between the actual poling and the absorption spectral measurements and took the initial value of $K_Z = 0.534$ ($\Phi = 0.301$) to be the order parameter achieved during electric poling. But orientational order achieved during poling must be better since there is an initial fast relaxation as shown in section 3.7, and the poling field strength during poling must be greater than 3.42 MV/cm. This is a little surprising, but this field inside the polymer film is due to the accumulated charges on the polymer surface during poling that generate a very strong electric field that aligns the chromophores in the polymer efficiently.

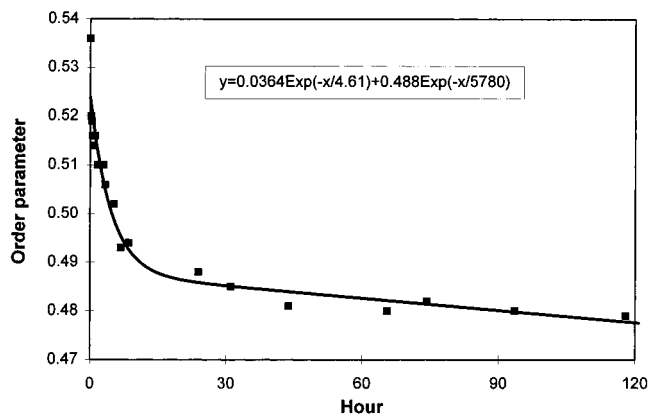


Figure 8. Decay of order parameters of DANS in PMMA after poling fitted with a biexponential function.

Red Shift of Peak Absorbance. Peak absorbance shifts due to electric poling have been observed in several guest–host systems.^{11,13,14} They are usually ascribed to electrochromism, or the Stark effect. In this study, the surface charge was removed intentionally by connecting the two opposite surfaces with an aluminum sheet before the absorption measurements were made. However, an obvious red shift of peak absorbance was still observed for several hours after poling.

One reason might be that the surface charge cannot be completely removed by simply connecting two opposite surfaces because neither of the surfaces are conductive and the surface charge might not be uniformly distributed because of the roughness of the film surface. So there may still be some residual surface charges that cause the peak absorbance shift by the Stark effect. Goodson et al.²⁷ recently reported that these trapped charges can only be removed after heating the film well above the glass transition temperature for an extended period of time.

Song et al.¹¹ recently suggested that the red shift might be due to the interaction among the molecules that depends on the way they are aligned. For two dipole moments oriented side by side, the dipole–dipole interaction energy is positive and the side by side ordering is expected to cause a blue shift. On the other hand, the dipole–dipole interaction energy is negative if two dipoles are oriented head to tail, which gives rise to a red shift. But since DANS molecules are strongly polar in the ground state, they are expected to align side by side under electric field. So this is unlikely to be the cause of the red shift of the peak absorbance of the poled DANS in PMMA. The underlying mechanism needs to be studied further.

3.7. Relaxation of the Chromophores after Poling. Long-term stability of the asymmetric order is essential for application of the guest–host system in real NLO devices. In this section we consider the time decay of the order parameters at room temperature (298 K). Equation 9 was used to determine K_Z from angle dependent PAS at different times after poling up to 120 h. The order parameters obtained are shown as squares in Figures 8 and 9.

SHG has been applied to the analysis of orientational order decay of poled polymer films.^{28,29,30} Two functions are generally used for fitting SHG decay data after removal of the poling field: a biexponential function and a stretched exponential function. The biexponential function has the form

$$K_Z(t) = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \quad (19)$$

where τ_1 , τ_2 are time constants of faster and slower relaxation process, respectively. a_1 , a_2 are constants describing the relative weight of these two relaxation processes. The best fit to the

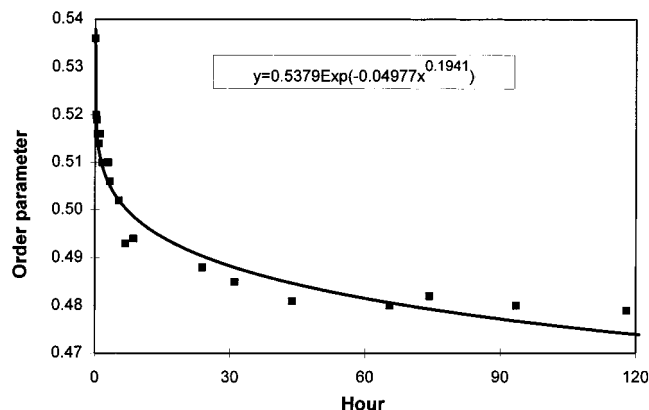


Figure 9. Decay of order parameters of DANS in PMMA after poling fitted with a stretched exponential function.

data using eq 19 is shown as the smooth curve with $\chi^2 = 2.16 \times 10^{-4}$. Values we obtained for these constants are $\tau_1 = 4.61$ h and $\tau_2 = 5780$ h. τ_1 corresponds to a fast relaxation that is completed in a few hours experimentally, while τ_2 is a much slower relaxation process. This means that there might be two different relaxation mechanisms of the chromophores in the polymer matrix. Second-harmonic generation measurements have observed similar decay patterns of second harmonic intensity.^{31,32} One possible explanation is that the fast relaxation is related to the initial orientational relaxation of the dopant chromophores after the poling field is removed, which should be related to properties of the chromophores. The slower relaxation process might be related to orientational diffusion of the chromophores, which is related more closely to the properties of the polymer. It is so slow that no observable absorbance recovery during the experimental period is seen. For practical applications, the slower relaxation process is much more important.

It is also possible to use a stretched exponential function (Kohlrausch–Williams–Watts, KWW) to fit the decay of the order parameters and explain the chromophore relaxation in terms of deviation from a single-exponential decay.^{12,30} The functional form is

$$K_Z(t) = a_0 e^{-(t/\tau)^\beta} \quad (20)$$

where β describes the degree of deviation from single-exponential decay characterized by relaxation time τ . Figure 9 shows the result of fitting the experimental data with a stretched exponential ($\chi^2 = 3.95 \times 10^{-4}$). We obtained $\beta = 0.194$, which is comparable with $\beta = 0.25$ obtained from SHG data for DANS in PMMA.¹² It seems that the sum of two exponentials fits the experimental data slightly better. This supports the two-mode relaxation mechanism. It was found^{12,31,33} that the KWW function is inadequate to describe the relaxational behavior of the second-order NLO susceptibility of corona poled films and the biexponential function better fits the experimental data. Our results seem to support their conclusions. But SHG intensity follows the relaxational behavior of $\langle P_1 \rangle$, while order parameters obtained from PAS are $\langle P_2 \rangle$. The decay patterns of $\langle P_1 \rangle$ and $\langle P_2 \rangle$ seem to follow the same functional form. This suggests that the decay of both $\langle P_1 \rangle$ and $\langle P_2 \rangle$ is dominated by a two-mode relaxation mechanism.

4. Summary

Polarized absorption spectroscopy (PAS) has been used to study the electric poling of DANS in PMMA. The orientational order achieved by electric poling can easily be observed in the

PAS measurement. We have shown a simple method to obtain order parameters from angle-resolved PAS. Efficient chromophore alignment by electric poling is revealed by the PAS measurement. The initial order parameter after poling defined by $\frac{1}{2}(\langle 3 \cos^2 \theta_z - 1 \rangle)$ is about 0.30, which indicates that efficient poling has been achieved. The poling field strength is estimated from measured order parameters to be 3.42 MV/cm, which is typical compared to similar poling experiments in the literature.^{13,14,27}

PAS can also be used to resolve different electronic transitions embedded in an absorption band. This information about a molecule can be obtained for aligned systems using PAS with tilted incident light. It is shown that there might be a different electronic transition on the long wavelength part of the strong electronic transfer band of DANS. To understand these different electronic transitions, it might be better to combine this study with a polarized fluorescence study.^{34,35}

There are several possible explanations for the observed peak absorbance shift. It might be due to the combination of all these causes, and further study is needed to reveal the real mechanism.

The decay pattern of order parameters is found to be better fitted with a biexponential function than with a stretched exponential. This suggests that the orientational order ($\langle P_2 \rangle$) decay is dominated by a two-mode relaxation mechanism. The main advantage of PAS in studying electric poling is its simplicity, availability, and perhaps consistency when used to study long-time relaxation processes.

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