# Quantitative Determination of the Polar Order Induced under High Electric Field in Amorphous PDR1M Azobenzene Polymer Films

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Thin films of amorphous pDR1M azobenzene homopolymer have been wire poled under high-field conditions. All poled films show a very efficient axial and also a strong polar ordering, as shown by polarized UVvisible measurements and SHG experiments. One of the most striking experimental evidences is an increasing new narrow absorption band around 400 nm, which is detected by using p-polarized light under various incidence angles. Such a spectral feature has already been observed in a few azobenzene-containing liquidcrystal polymers. The poled structures are very stable at room temperature: more than one year after poling, 70% of the initial SHG signal is still preserved in films with a thickness larger than 150 nm. The macroscopic polar ordering is nearly destroyed upon heating the poled film at near 80 °C, i.e.,  $\sim$ 45 °C below the T<sub>g</sub> of the starting polymer. A proposed general approach allows the determination of the anisotropic optical constants that simulates nicely all the polarized absorption spectra at several angles of incidence. In particular, the induced birefringence after poling is evaluated as high as  $\sim 0.21$  at 1.064  $\mu$ m, far from any charge-transfer resonance. Finally, from a detailed comparative study of the electronic spectra of a DR1 solution in chloroform and of an unpoled, a poled, and a thermally depoled film, we have shown that the absorption spectra can be nicely deconvoluted into three main bands. Most of the spectroscopic changes upon dc field poling are then qualitatively and quantitatively explained; they come from a significant intensity decrease of the high-energy  $\pi - \pi^*$  transition (-12%) in favor of the low-energy DT band (+12%) and the estimated  $\langle P_2 \rangle$  order parameters for these transitions are quite large ( $\sim$ +0.50), confirming a high degree of ordering.

### Introduction

For the design of materials suited for use in electrooptical devices, nonlinear optical (NLO) chromophores incorporated in amorphous polymers are the subject of intense research activities.<sup>1</sup> Such materials can be produced in large area devices and can be structured more easily in thin film device applications. Interest in organic polymers as second-order NLO materials arises mainly from the fact that the nonlinearity is due to an appropriately arranged collection of relatively independent molecular sources of optical nonlinearity. Most work has been focused on the dipolar nonlinearity that arises from donoracceptor substituted  $\pi$ -electron molecules. A large number of approaches for generating polar materials from molecular systems have already been investigated, and the dc field poling of amorphous polymers is a largely developed technique.<sup>2-4</sup> In this case, NLO chromophores are dispersed in or covalently attached to amorphous polymers. The anisotropy created by the application of a static electric field at high temperature<sup>5</sup> affects both the linear optical (LO) and the NLO properties. On the one hand, the anisotropy of the absorption coefficient can be used as a probe of the degree of orientation,  $\langle \cos^2 \theta \rangle$ , of the molecular polar groups. On the other hand, second harmonic generation (SHG) of light in a Maker fringe experiment is a standard method to measure the overall second-order nonlinearity  $\chi^{(2)}$  and then the extent of the polar orientation,  $\langle \cos \theta \rangle$  and  $\langle \cos^3 \theta \rangle$ , of the molecular groups through the knowledge of their first-order hyperpolarizability,  $\beta$ .

In this paper, we report experimental evidence for a strong polar ordering induced by wire poling under high electric field conditions in the amorphous pDR1M side-chain azobenzene homopolymer. Very strong anisotropic LO and NLO responses are detected in all poled films. Correlatively, unusual enhancements of the absorption coefficient and of the  $d_{33}$  susceptibility coefficient along the poling direction are observed. Although these experimental results are quite unusual for such amorphous systems,<sup>6–10</sup> they are consistent with some previous works where it has been shown, theoretically<sup>11,12</sup> and experimentally in nematic and smectic-A type polymers<sup>13,14</sup> that an already existing axial order favors the enhancement of a field-induced polar ordering: there is thus an increase of the orientational distribution function along the electric field direction.

### **Materials and Methods**

**Sample Preparation.** The monomer was obtained by reacting Disperse Red One (DR1 from Aldrich) with acryloyl chloride, and the homopolymer was synthesized by free radical polymerization of the monomer in dry THF using AIBN as initiator.<sup>15</sup> Gel permeation chromatography (GPC) indicates that the equivalent molecular weight of the resulting polymer pDR1M is ~4000, so that each unit chain contains ~10 monomers (Chart 1). Thin films were typically prepared from solutions containing 80 mg of polymer dissolved in 1–5 mL of chloroform, de-

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Polar Order in PDF1M Azobenzene Polymer Films

CHART 1: Molecular Structure of the Polymer, Poly(4'-((2-(methacryloyloxy)ethyl)ethylamino)-4-nitroazobenzene), Often Called PDR1M





pending on the requested film thickness ranging from  $\sim$ 300 to  $\sim$ 60 nm, respectively. The solutions were spun coated onto standard glass slides (CORNING 2947) and the films were then baked in an oven at 80 °C for at least 1 h to remove any residual solvent.

Wire poling under high field has been carried out using a tungsten wire (25  $\mu$ m diameter) held parallel to and above the films (at a distance as short as 5 mm) applying a dc field of 3.0 kV to ensure an efficient charge injection at the surface of the film.<sup>16</sup> The temperature of the poling process was sufficiently high (~90 °C) to achieve a good stability of the induced NLO properties but significantly below the  $T_g$  of the polymer (~125 °C). The dc field was applied during a 2 h period to achieve an overall structural ordering, and each film was then slowly cooled to room temperature at a rate of 1 °C/min, keeping the dc field on to ensure the freezing of the chromophore orientations.

**UV–Vis and SHG Measurements.** UV–visible absorption measurements were recorded on a double beam spectrometer (SAFAS 190 DES) before and, from time to time, after the poling process. Polarized spectra (in the 350–800 nm range) were obtained at normal and oblique incidences by analyzing the transmitted light using a polaroid film to measure the absorbance of the sample in the vertical (s) and horizontal (p) directions. A glass slide was used as a reference, keeping identical experimental conditions (angle of incidence and polarization).

SHG measurements were performed using the optical setup described in a previous study.<sup>17</sup> Polarized SHG Maker fringe patterns were recorded before and, from time to time, after the poling process, using a 1064 nm Nd:YAG laser operating at very low irradiance (pulse energy  $<50 \ \mu$ J; repetition rate 200 Hz; pulse width 15 ns). A general SHG matrix method applicable to multilayered anisotropic linear/nonlinear media has been applied, allowing experimental determination of the resonance-enhanced NLO coefficients  $d_{ij}$ , as well as the linear absorption coefficients of the harmonic wave (532 nm) in the parallel ( $\alpha_{II}$ ) and perpendicular ( $\alpha_{\perp}$ ) direction with respect to the poling field.

**Figure 1.** Variation of s- (a) and p- (b) polarized absorption spectra of a pDR1M thin film (60 nm), before (dotted lines) and after (full lines) poling, as a function of the incidence angle:  $0^{\circ}$  ( $\bullet$ ),  $15^{\circ}$  ( $\blacksquare$ ),  $30^{\circ}$  ( $\bullet$ ),  $45^{\circ}$  ( $\blacktriangle$ ) and  $60^{\circ}$  ( $\blacktriangledown$ ).

Determination of the Optical Constants. To evaluate the anisotropic optical constants of any thin film in an orthogonal space coordinate system (x, y, z), we have used a calculation procedure that allows a direct determination of the refractive indices and extinction coefficients from experimental UVvisible spectra. The optical constants along the x, y, and zdirections are calculated using an iterative procedure based on the inversion of spectral simulations and, on the Kramers-Krönig analysis.<sup>18</sup> The optical constants in the plane of the layer  $(n_x, k_x)$ and  $n_v, k_v$ ) are determined from polarized normalized absorbance spectra at normal incidence. Then, the optical contants out of the plane of the film  $(n_z, k_z)$  are determined from p-polarized normalized absorbance spectrum at 60° of incidence, with the help of the previously determined in-plane optical constants. This approach offers several advantages: in addition to providing the frequency dependence of the complex refractive indices (nand k), it allows the calculation of the average orientation of the electronic transition moments. Furthermore, from the anisotropic optical constants, one may simulate spectra under various experimental conditions (incidence angle, light polarization). From a comparison of the experimental and simulated spectra, the spectral changes due to any optical effect or to any modification induced in the molecular environment can be distinguished.

## Results

**Linear Optical Responses.** Figure 1 contains a typical set of s- and p-polarized absorption spectra for a thin film (thickness 60 nm), before and after poling, as a function of the external angle of incidence, which varies from 0° to 60° in steps of 15°. The s- and p-polarized spectra before poling display a broad and intense band around 470 nm assigned to  $\pi - \pi^*$  type transitions.<sup>19</sup>

First, we have checked that all the films before poling are isotropic in the plane of the substrate, because s- and p-polarized absorption spectra recorded at normal incidence appear identical within the experimental errors. The isotropic distribution of the chromophores in the plane of the film has been confirmed in numerous samples, and slight discrepancies have been scarcely observed under the spin-coating conditions depicted above. Finally, when recording s- and p-polarized absorption spectra under various angles of incidence, to probe the linear response in the plane and out of the film plane, we did not observe anisotropy because the spectral modifications observed in Figure 1a,b are only due to an increase in the film thickness with the incidence angle.

Then, as expected, all poled films do not reveal any anisotropy in the plane of the film, because s- and p-polarized absorption spectra at normal incidence are again similar. We will therefore assume in this study that the chromophore orientational distribution is uniaxial along the (z) direction of the poling field. Actually, a strong intensity decrease as well as a slight red shift of the band are observed at normal incidence. These results are in agreement with an efficient axial ordering of the chromophores. Indeed, during wire or corona poling, it is well-known that charges accumulate at the surface of the polymer film and opposite charges accumulate at the planar electrode. In this way a strong electrostatic field is created in the film and it may interact with the dipole moment of the chromophores. This is evidenced in the absorption spectrum, which is sensitive to the interactions of the electronic transition moments with the incident light electric field. During a poling process, the electrostatic field tends to align the permanent dipoles in the direction of the poling field, so that many bands are expected to lose intensity at normal incidence after poling. A large electrostatic field also induces a change in the energy interval between the ground and excited states through the Stark's effect<sup>20,21</sup> and, thus, a red shift in the absorption peak maxima. Alignment of the chromophores is also responsible for variations in their local environments and affects their intermolecular interactions. More striking changes are consequently evidenced on spectra recorded at 45° or 60° of incidence: an increasing new narrow band around 400 nm is detected using p-polarized light. Note that a similar spectral feature has already been observed in a few azobenzene-containing liquid-crystal polymer systems.22,23

To get a better insight into these spectral modifications, the anisotropic optical constants of the film were calculated by assuming an uniaxial optical system (i.e.,  $n_x = n_y = n_0$ ,  $k_x = k_y$  $= k_{\rm o}$  and  $n_z = n_{\rm e}$ ,  $k_z = k_{\rm e}$ ). The optical constants in the plane  $(n_0, k_0)$  and out of the plane  $(n_e, k_e)$  of the film were determined from the p-polarized normalized absorbance spectra at 0° and 60° of incidence, respectively. The calculations were performed with the same value of the index of refraction in the UV part of the spectra,  $n_{\infty} = 1.6$ , before and after poling. Looking at the extinction coefficient values reported in Figure 2, one notes before poling that the extinction coefficient is isotropic ( $k_0 =$  $k_{\rm e}$ ) and presents a maximum at 460 nm with a value of 0.74. After poling, a strong anisotropy is observed, because the inplane maximum decreases to 0.32, whereas the out-of-plane maximum increases to 1.0. Also, a red shift is evidenced for both  $k_0$  and  $k_e$  extinction coefficients: the two maxima move up to 480 and 510 nm in the direction perpendicular  $(k_0)$  and parallel  $(k_e)$  to the poling field, respectively. Finally, to validate these determinations of the linear optical constants, p-polarized normalized absorbance spectra at 0° and 60° of incidence were calculated (before and after poling) and compared to the



**Figure 2.** Calculated extinction coefficient spectra,  $k(\lambda)$ , of a pDR1M thin film (60 nm) before poling (full line) and after poling, in the plane  $(n_o, k_o: \bullet)$  and out of the plane  $(n_e, k_e: \bullet)$  of the film. Mean extinction coefficient  $(\langle k \rangle = (2k_o + k_e)/3)$  spectrum (dotted line) after poling is also reported for a better comparison.



**Figure 3.** p-polarized absorption spectra of a pDR1M thin film (60 nm), before and after poling. Comparison of the experimental spectra with an incidence angle of  $0^{\circ}$  ( $\bullet$ ) and  $60^{\circ}$  ( $\bullet$ ) and of the calculated spectra at  $0^{\circ}$  (dotted lines) and  $60^{\circ}$  (full lines).



**Figure 4.** Experimental Maker-fringes of a poled pDR1M thin film (60 nm). The patterns were recorded over the  $[-80^\circ, +80^\circ]$  angular range using various polarizations for the incident and transmitted beams, namely, s (vertical or 90°) and p (horizontal or 0°).

experimental ones. A good agreement between calculated and experimental spectra is observed as inferred in Figure 3. Of course, we have carefully checked that the other experimental polarized absorption spectra reported in Figure 1 can also be correctly simulated and, therefore, consistent with our previous assumptions; i.e., the film is isotropic before poling and keeps a uniaxial symmetry along the applied field after poling.

**Nonlinear SHG Optical Responses.** We have first checked, once more, that all unpoled films are isotropic and do not give rise to a SHG bulk signal. In contrast, typical polarized Maker fringe patterns are detected in thin poled films, as shown in Figure 4: they are consistent with a very efficient polar ordering. Although the wavelength of the harmonic transmitted signal (532 nm) is very close to the maximum of a chromophore electronic



**Figure 5.** Calculated refractive index spectra,  $n(\lambda)$ , of a pDR1M thin film (60 nm) before poling (full line) and after poling, in the plane  $(n_o, k_o: \bullet)$  and out of the plane  $(n_e, k_e: \bullet)$  of the film. Mean refractive index  $(\langle n \rangle = (2n_o + n_e)/3)$  spectrum (dotted line) after poling is also reported for a better comparison. In the near-infrared range, refractive indices extrapolated using Sellmeier's law are also reported.

absorption, the intensity of the p-p polarized SHG responses is several orders of magnitude stronger than that of a quartz plate. The ratio of the maxima of the p-p versus the s-p fringes is known to be dependent on the strength of the applied poling field. It is worth noting that this ratio, nearly equal to 19.0 here, is by far larger than the limit (~9.0) of a low poling field condition.<sup>24</sup> Nevertheless, a careful analysis of the patterns must be undertaken because they are probably perturbed by resonance enhancement effects and by the high number density of chromophores. In particular, it has been evidenced that large discrepancies in the  $d_{ij}$  values may appear when the linear dichroism effects are neglected.<sup>17</sup> Furthermore, we have observed that the SHG responses are stable for a long period of time in all poled samples, particularly in those thicker than ~150 nm.

### Discussion

Analysis of the Macroscopic Susceptibilities: Chromophore Orientation. We have already pointed out that the polarized absorption spectra under normal and oblique incidences as well as the SHG Maker fringes patterns do reflect efficient poling effects to a large extent. They are all consistent with a strong structuration in the film, which tends to align the polar chromophores along the applied field direction. In a first crude approximation, one may describe the axial orientation of the chromophores by the order parameter  $\Phi = 1 - A/A_0$ ,<sup>5</sup> where  $A_0$  and A are respectively the absorbance maxima for the unpoled and poled samples at normal incidence. Using this relation, we obtain  $\Phi = +0.54$ . This order parameter definition holds valid under the assumption that, first, there is no degradation of the chromophores during the poling process and, second, the molecular ordering does not modify the overall characteristics of the band. In fact, it is rather difficult to proove experimentally that the first condition is fulfilled. The second assumption is obviously in contradiction with the large changes that could occur during and after an efficient poling process.

After poling, a very strong anisotropy in the extinction coefficients does appear, a result consistent with a new structural organization of the chromophores in the oriented polymer system. This fact is also nicely illustrated in Figure 5, which shows the variations of the refractive indices in the visible; the variations were extrapolated in the infrared range, far from any charge-transfer resonance, where the birefringence is estimated as large as ~0.21 near 1.064  $\mu$ m. It is thus clearly demonstated that the "narrow band" observed around 400 nm in the

 TABLE 1: Linear Optical Constants in a PDR1M Thin

 Film after Poling, Determined from a Treatment of the

 Absorption Spectra<sup>a</sup>

film thickness:	60 nm		
1064 nm	(fundamental wave)	532 nm	(harmonic wave)
$n_{\rm e} = n_{\rm H} = 1.969$	$n_{\rm o}=n_{\perp}=1.668$	$n_{\rm e} = n_{\rm H} = 2.175$	$n_{\rm o} = n_{\perp} = 1.838$
$\alpha_{\rm e} = \alpha_{\rm H} = 0$	$\alpha_{o} = \alpha_{\perp} = 0$	$\alpha_{\rm e} = \alpha_{\rm H} =$	$\alpha_{o} = \alpha_{\perp} =$
		$112\ 800\ {\rm cm}^{-1}$	$28\ 700\ {\rm cm}^{-1}$

<sup>*a*</sup> The absorption coefficient is defined by  $\alpha_i = 4\pi k_i/\lambda$ .

p-polarized absorption spectra under oblique incidences (see Figure 3) cannot be assigned to a new peak polarized along the poling field. Indeed, no new band appears around 400 nm in the variations of the anisotropic extinction coefficients presented in Figure 2. In fact, this "apparent band" arising from an optical effect is mainly due to the very strong anisotropic dispersion of the refractive indices in this spectral range. This point confirms that the anisotropy in the extinction coefficients obtained through the procedure described in the previous section is really an indication of the degree of orientation,  $\langle \cos^2 \theta \rangle$ , of the molecular polar groups.

Currently, the axial ordering of the chromophores in poled films has been estimated using  $\Phi$  as the order parameter<sup>5,6</sup> and, therefore, this crude approach leads to an overestimation of the ordering, as demonstrated hereafter. Differently, from the anisotropic extinction coefficients it is possible to define precisely an axial order parameter by using the relation  $\langle P_2 \rangle = (k_e - k_e)$  $k_{\rm o}$ /( $k_{\rm e}$  + 2 $k_{\rm o}$ ). This order parameter,  $\langle P_2 \rangle$ , is now adequately defined because it is calculated from only the anisotropic extinction coefficients of the poled film; its value  $\langle P_2 \rangle = +0.43$ is significantly lower than the suggested previous one,  $\Phi =$ +0.54. However, an apparent discrepancy is evidenced when looking carefully at the mean extinction coefficient  $\langle k \rangle = (k_e + k_e)$  $2k_0$ )/3 after poling, as shown in Figure 2. The mean extinction coefficient exhibits a different shape and is markedly less intense than the initial one before poling, particularly in the high-energy part of the spectrum. Similarly, the mean refractive index  $\langle n \rangle$  $= (n_{\rm e} + 2n_{\rm o})/3$  of the poled film in the near-infrared part of the spectrum is also found smaller than the initial one before poling (see Figure 5). All these differences in the optical constants are thus due to perturbations in the molecular interactions, which are induced under poling. Looking now at the anisotropic extinction coefficients, the out-of-plane  $k_{\rm e}(\bar{\nu})$  spectrum clearly exhibits an intense contribution around ~525 nm. In this respect, it is well-known in donor-acceptor azobenzene systems that a net stabilization of the first electronic excited states with increasing polarity is associated with a bathochromic shift of the  $\pi - \pi^*$  absorption band; indeed, a photoexcitation leads to the formation of delocalized excited forms ( $\pi - \pi^*$  transitions), which can be converted into stable charge-transfer (CT) forms (zwitterionic structures), particularly when the surrounding is strongly polar.<sup>25,26</sup> The bathochromic effect observed for the out-of-plane and in-plane extinction coefficient spectra is thus consistent with a stabilization of the charge-transfer state and with an increase in the polarity of the medium; obviously, this effect is predominant for the out-of-plane band, because it coincides with the uniaxial electrical constraint.

A strong breaking of symmetry in the film induced by the poling process, as evidenced in the LO responses, has also been evidenced in the NLO quadratic responses, confirming that the final molecular organization in the poled films is markedly polar. Using the values of LO constants above determined (see Table 1), the p-p and s-p polarized Maker fringe patterns recorded at 1064 nm were analyzed; in thin films (~60 nm thickness)



**Figure 6.** Calculated extinction coefficient spectra,  $k(\lambda)$ , of a pDR1M thin film (60 nm) before poling (full line) and after thermal depoling at 130 °C, in the plane ( $k_0$ : •) and out of the plane ( $k_e$ : I) of the film. Mean extinction coefficient ( $\langle k \rangle = (2k_0 + k_e)/3$ ) spectrum (dotted line) after thermal depoling is also reported for a better comparison.

we have obtained the following parameter values:  $d_{33} = 440$  $\pm$  50 pm/V,  $d_{31} \approx d_{15} = 75 \pm 10$  pm/V (reference quartz  $d_{11}$ = 0.3 pm/V at 1064 nm). One must underline that, during the fitting procedure, the three  $d_{ij}$  coefficients were the only adjustable parameters. It is also important to mention that the SHG signals in most poled samples were always very intense and reproducible, excluding the very thin films ( $\sim 60$  nm) in which the signals were noticeably relaxing with time. Indeed, 2 months after poling only  $\sim 10-20\%$  of the initial NLO responses are detected in the still anisotropic films. In contrast, two major differences were noted in films with a thickness larger than  $\sim 150$  nm: on one hand, the NLO responses are more intense, although the LO responses are slightly less anisotropic; in the second hand, the NLO responses, as well as the LO ones, do not change even 2 months after poling; actually, more than 1 year aged films are still displaying  $\sim$ 70% of the initial SHG responses. More details about all the variations of these properties will be published in a forthcoming paper.

Therefore, it turns out that wire poling under high-field conditions is very promising for electrooptical applications, as far as the process can be generalized to other NLO materials. To date, it is a real challenge to better understand at the molecular level how far the poling may induce a new orientational structure in the pDR1M amorphous polymer system and, also, why no apparent orientational relaxation is observed in the thicker poled films.

From the present study the following question still appears to be open to discussion: are the structural modifications induced during the poling treatment totally reversible? In this respect, it has been recently shown that optical and surface modifications photoinduced in holographic gratings inscribed on pDR1M films are always difficult to erase.<sup>27,28</sup>

As a preliminary answer one must note that upon heating the sample at about 70–80 °C, i.e., close to the poling temperature and ~45 °C below the  $T_g$  of the initial polymer, the SHG signal decreases significantly in time and, finally, vanishes. This indicates that the macroscopic polar properties in the film are lost. At the same time, in the p-polarized absorption spectrum at 60° of incidence the narrow electronic feature near 400 nm disappears, but an anisotropy is remaining. With the aim to erase the remaining ordering in the film, the sample was heated to ~130 °C, i.e., at a temperature very close to the  $T_g$ : any modification in the LO responses was observed, as well as no apparent degradation. This is illustrated in Figure 6, where the imaginary parts of the optical constants obtained after the thermal depoling treatment are reported. After heating,



**Figure 7.** Experimental (points) normalized absorbance spectra of a pDR1M thin film (60 nm) (a) and a solution of DR1 in chloroform  $(10^{-4} \text{ mol/L})$ . The calculated spectra (solid curve) were obtained from a Lorenzian deconvolution into three components (dashed lines: peaks labeled 1-3). A fourth unlabeled background band (dotted dashed lines) has been introduced to account for contributions of the strong higher energy bands.

the extinction coefficients  $k_0$  and  $k_e$  still display a significant anisotropy. The overall shape of the bands in Figure 6 is similar to that observed in Figure 2, but the anisotropy in the extinction coefficients is markedly attenuated. It is also noteworthy that the mean extinction coefficient  $\langle k \rangle$  is now closer, even though weaker, than the initial isotropic extinction coefficient before poling, as quantified by the axial order parameter, which tends to zero ( $\langle P_2 \rangle \approx +0.07$ ): the isotropy in the film is practically restored. It is also worthnoting that, after this depoling process, the mean extinction coefficient still displays a marked red-shifted profile, indicating that the inscribed local ordering is not totally erased. This fact supports the idea that no degradation has occurred in the film during the whole poling process, whereas the apparent overall decrease in the extinction coefficient could come from different amplitudes and contributions of the electronic transitions due to the excited  $\pi - \pi^*$  states. It is also evidenced that the refractive indices indicate the existence of a significant but weaker birefringence ( $\Delta n \sim 0.10$  at 1  $\mu$ m) in the thermally depoled film.

**Detailled Study of the Absorption and Extinction Spectra.** According to Rau's<sup>29</sup> classification, DR1 is a pseudo-stilbene type azobenzene molecule. This means that in the *E* isomer (trans) the high-intensity  $\pi - \pi^*$  transitions overlap a low-intensity  $n - \pi^*$  band and lead to a broad band, the maximum of which is known to be dependent on the solvent polarity.<sup>30</sup> Particularly, Shin and co-workers have found that the absorption maximum of the azo dye 4-nitro-4'-(*N*,*N*-diethylamino)azobenzene shifts by solvatochromic effects from 451 nm in heptane up to 512 nm in DMSO.<sup>31</sup> More recently, Meng et al. have demonstrated that the red shift in pDR1M is less pronounced in solid film (462 nm) than in DMSO solution (483 nm).<sup>32</sup> This

TABLE 2: Comparison of the Spectral Parameters in the Three Peaks Obtained from the Lorentzian Deconvolution of the normalized Absorbance Spectra, of a Thin Unpoled PDR1M Film (60 nm) and of a Solution of DR1 in Chloroform (Concentration  $10^{-4}$  mol/L)

	unpoled pDR1M film	DR1 in chloroform
peak 1: $[\pi - \pi^*]$	$\bar{\nu}_{max} = 22\ 500\ cm^{-1}\ (444\ nm)$ fwhm = 4900 cm <sup>-1</sup> int (%) = 58.0	$\bar{\nu}_{max} = 22\ 100\ cm^{-1}\ (452\ nm)$ fwhm = 4800 cm <sup>-1</sup> int (%) = 63.5
peak 2: $[\pi - \pi^*]$	$\bar{\nu}_{max} = 20\ 200\ cm^{-1}\ (495\ nm)$ fwhm = 3700 cm <sup>-1</sup> int (%) = 23.8	$\bar{\nu}_{max} = 20 \ 400 \ cm^{-1} (490 \ nm)$ fwhm = 3300 cm <sup>-1</sup> int (%) = 28.1
peak 3: CT band	$\bar{\nu}_{max} \approx 18 \ 400 \ \text{cm}^{-1} \ (544 \ \text{nm})$ fwhm = 3600 cm <sup>-1</sup> int (%) = 18.2	$\bar{\nu}_{max} = 19\ 300\ cm^{-1}\ (518\ nm)$ fwhm = 2400 cm <sup>-1</sup> int (%) = 8.4

 $\lambda_{max}$  shift was assigned to the presence of several DR1 groups in close proximity, which not only act as a polar solvent but also favor strong dipolar interactions.

When plotted linearly as a function of energy (i.e., in wavenumbers), the absorption spectrum of a pDR1M film at normal incidence can be deconvoluted into a simple sum of three Lorentzian components, as illustrated in Figure 7a; a similar deconvolution applies for the spectrum of DR1 in chloroform (Figure 7b). Relevant parameter values of these deconvolutions can be compared in Table 2. The two first peaks (labeled 1 and 2) located in the high-energy side of the spectrum are assigned to  $\pi - \pi^*$  type transitions, the transition moments of which are almost collinear to the long molecular axis of the chromophore.<sup>30</sup> The more intense and broad (fwhm  $\sim$ 5000  $cm^{-1}$ ) first peak (1) maximizes at about 22 000  $cm^{-1}$  (~450 nm) and dominates the spectra ( $\sim 60\%$  of the total intensity). A third peak (labeled 3) with a lower intensity appears in the red part of the spectra, at 18 400 cm<sup>-1</sup> (544 nm) in the solid film and at 19 300 cm<sup>-1</sup> (518 nm) in the solution; it is assigned to a CT delocalized transition.<sup>25</sup> Each Lorentzian component results apparently from similar sums of homogeneous and inhomogeous contributions, although their relative proportion differs probably in the amorphous solid matrix and in the chloroform solution.<sup>33</sup> Considering the large width values (fwhm are ranging from 2500 to 5000  $\text{cm}^{-1}$ ), it is clear that a vibronic structure could never be detected whatever the surrounding; therefore, only the relative intensity contributions of the three electronic bands will be significant. Furthermore, in agreement with literature data, we do observe that the CT band maximum is very sensitive to the local polarity of the medium: a red shift of 900 cm<sup>-1</sup>, as well as a relative intensity increase of 10%, takes place in the pDR1M film as compared to the solution. The polarity increase in the pDR1M film seems again to be well correlated with the observed bathochromic and hyperchromic changes<sup>31</sup> and, particularly, it seems that the CT component tends to impose a red shift into the whole absorption spectrum.

However, the observed absorption spectra could in part be affected by special optical effects, as demonstrated in the preceding section. So, in the high-content dye films under study, it is more relevant to concentrate the discussion on the extinction coefficient spectra, which are directly connected to the molecular absorption cross-sections. We have thus performed a similar deconvolution of the spectrum of an unpoled pDR1M thin film (see Figure 8). It is then evidenced that the contribution of the middle component (peak 2) is significantly reduced, whereas the two high- and low-energy components (peaks 1 and 3) remain unaffected (Figure 8); in a first approximation, similar conclusions as above can be drawn.

More information can be obtained from the variations of the three components in a pDR1M film after the poling process (Figure 9) and after the thermal depoling treatment (Figure 10).



**Figure 8.** Experimental (points) extinction coefficient spectrum,  $k(\bar{\nu})$ , of a pDR1M thin film (60 nm) before poling. The calculated spectrum (solid curve) was obtained from a Lorenzian deconvolution into three components (dashed lines: peaks labeled **1–3**). A fourth unlabeled background band (dotted dashed lines) has been introduced to account for contributions of the strong higher energy bands.

The main parameters of the spectral deconvolutions, along and perpendicular to the direction of the poling field, are gathered in Table 3. In-plane results (Figure 9a) show that the main features observed before poling appear unchanged after poling, excluding the drastic intensity decrease in the overall spectrum (note the different ordinate scale in Figure 9a). In contrast, results along the poling direction (Figure 9b) show a drastic intensity increase of the CT band (peak 3) and its maximum becomes comparable to that of peak 1 ( $\pi$ - $\pi$ \* band).

Comparing the results in an absolute intensity scale (in units of wavenumbers, Table 3), it is noteworthy that, upon poling, all parallel (II) and perpendicular  $(\perp)$  intensity figures for each peak display a large increase and decrease, respectively. These observations corroborate the fact that the chromophores have been efficiently aligned along the field direction and that the involved electronic transitions have their transition moment preferentially oriented along the long molecular axis. Under these conditions, it is meaningful to define a second rank order parameter,  $\langle P_2 \rangle$ , whose values are reported in Table 3. We note a very significant and quite similar value of 0.50  $\pm$  0.03 for peaks 1 and 3, whereas a smaller value of 0.35 seems effective for peak 2: these values are consistent with the above proposed average parameter  $\langle P_2 \rangle = +0.43$  (see preceding section), and we can also suggest that electronic transitions 1 and 3 are likely to be coupled. Indeed, it is remarkable that, upon poling, there is a relative integrated intensity decrease of 12% for peak 1 and, concomitantly, a 12% increase for peak 3 (Table 3). At this stage, a complete analysis of the Raman excitation profiles using several exciting laser lines in the contour of the absorption band would give a better insight into the relative contribution and the coupling of the different electronic transitions.33



**Figure 9.** Experimental (points) extinction coefficient spectra,  $k(\bar{\nu})$ , of a pDR1M thin film (60 nm) after poling, perpendicular to (a) and along (b) the poling field direction. The calculated spectra (solid curve) were obtained from a Lorenzian deconvolution into three components (dashed lines: peaks labeled 1–3). A fourth unlabeled background band (dotted dashed lines) has been introduced to account for contributions of the strong higher energy bands. Note that the ordinate scale of Figure 9a has been amplified by a factor of 2.0.

Finally, in the thermally depoled film, the more significant variations are again observed for peaks 1 and 3. Parallel and perpendicular quantities tend to similar values, but a complete isotropy is hardly restored in the film. Indeed, the  $\langle P_2 \rangle$  order parameter for peak 1 is nearly zero (0.04), but for peak 3 it is still equal to 0.17. This suggests that the thermally assisted depoling is not a totally reversible process and that the molecular structural organization in the poled film was thermodynamically rather stable. More experimental works are obviously necessary to gain further information about the possible supramolecular ordering that could occur in such amorphous thin polymer films under high poling field conditions.

### Conclusion

We have demonstrated in this paper that wire poling under high-field conditions is very efficient and induces a stable and strongly polar ordering in films of the side-chain pDR1M homopolymer. The resulting uniaxial polar organization of the chromophores is almost stabilized when the sample is cooled and the field is kept on, provided that the charge injection is intense enough and applied during a long period of time (roughly 2 h). Such an unusual long time poling process seems to be a mandatory condition that allows the formation of an overall macroscopically stable new structure in the polymer films.

Furthermore, from a detailed comparative study of the electronic spectra of a DR1 solution in chloroform and of an unpoled, a poled, and a thermally depoled film, we have shown that the absorption spectra can be nicely deconvoluted into three main bands. Most of the spectroscopic changes upon dc field



**Figure 10.** Experimental (points) extinction coefficient spectra,  $k(\bar{\nu})$ , of a pDR1M thin film (60 nm) after thermal depoling at 130 °C, perpendicular to (a) and along (b) the poling field direction. The calculated spectra (solid curve) were obtained from a Lorenzian deconvolution into three components (dashed lines: peaks labeled 1–3). A fourth unlabeled background band (dotted dashed lines) has been introduced to account for contributions of the strong higher energy bands.

TABLE 3: Variation of the Integrated Intensities of the Three Peaks Obtained from the Lorentzian Deconvolution of the Extinction Coefficient Spectra of a Thin PDR1M Film (60 nm), before Poling, after Poling and after a Thermal Depoling at 130 °C<sup>a</sup>

	unpoled film	poled film	depoled film
peak 1: $[\pi - \pi^*]$			
$\bar{\nu}_{\rm max} \approx 22 \ 300 \ {\rm cm}^{-1}$	$int = 872 \text{ cm}^{-1}$	$int_{\perp} = 304 \text{ cm}^{-1}$	$int_{\perp} = 692 \text{ cm}^{-1}$
(448 nm)	% = 69.2	% = 56.4	% = 66.9
		$int_{  } = 1139 \text{ cm}^{-1}$	$int_{  } = 788 \text{ cm}^{-1}$
		% = 57.0	% = 55.9
	$\langle P_2 \rangle = 0$	$\langle P_2 \rangle = 0.48$	$\langle P_2 \rangle = 0.04$
peak 2: $[\pi - \pi^*]$			
$\bar{\nu}_{\rm max} \approx 20\ 200\ {\rm cm}^{-1}$	$int = 156 \text{ cm}^{-1}$	$int_{\perp} = 96 \text{ cm}^{-1}$	$int_{\perp} = 128 \text{ cm}^{-1}$
(495 nm)			
$fwhm \approx 3500 \text{ cm}^{-1}$	% = 12.4	% = 17.9	% = 12.4
		$int_{  } = 252 \text{ cm}^{-1}$	$int_{  } = 274 \text{ cm}^{-1}$
		% = 12.6	% = 19.4
	$\langle P_2 \rangle = 0$	$\langle P_2 \rangle = 0.35$	$\langle P_2 \rangle = 0.28$
peak 3: CT band			
$1 \bar{\nu}_{\rm max} \approx 18\ 900\ {\rm cm}^{-1}$	$int = 232 \text{ cm}^{-1}$	$int_{\perp} = 139 \text{ cm}^{-1}$	$int_{\perp} = 214 \text{ cm}^{-1}$
(529 nm)			
$fwhm \approx 3000 \text{ cm}^{-1}$	% = 18.4	% = 25.7	% = 20.7
		$int_{  } = 606 \text{ cm}^{-1}$	$int_{  } = 348 \text{ cm}^{-1}$
		% = 30.3	% = 24.7
	$\langle P_2 \rangle = 0.17$	$\langle P_2 \rangle = 0.53$	$\langle P_2 \rangle = 0.17$

 $^a$  Corresponding values of the axial order parameter,  $\langle P_2\rangle$ , are reported for each component.

poling are then qualitatively and quantitatively explained. They come from a significant intensity decrease of the high-energy  $\pi - \pi^*$  transition (-12%) in favor of the low-energy CT band (+12%); the estimated  $\langle P_2 \rangle$  order parameters for these transitions are quite large (~+0.50) and confirm a high degree of ordering.

Polar Order in PDF1M Azobenzene Polymer Films

An important next challenge will thus be to elucidate the local structuration of the chromophores, and their most probable supramolecular arrangement. Such works are in progress and encouraging circular dichroism results demonstrating the formation of an optically active molecular structure were recently obtained; they will be published in due course.

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