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Dynamics of Photoinduced Orientational Order of Azo-dyes in Polymer Films

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SUMMARY: Dynamical and spectral behavior of photoassisted electrical poling and photoinduced anisotropy are studied in films of DR1-doped PMMA, DR1-PMMA copolymer and new DR1-Polyimide copolymer. The orientational mobility of DR1 is characterized both in ordering processes (angularly selective trans-cis photoisomerization) and in disordering relaxation processes. Mobility is increased by the photoisomerization and decreases slowly with time, after the end of optical pumping. The transient dichroism recorded simultaneously on six probe wavelengths shows a spectral inhomogeneity of the absorption band of DR1 and of the photoinduced anisotropy (particularly in polyimide films).

Introduction

Many optoelectronic applications of linear and nonlinear optical properties of dye-doped polymers need some special ordering of anisotropic or polar active molecules. Three optical methods developed for ordering chromophores are based on the resonant excitation of photoisomerizable molecules:

- The photoinduced anisotropy (PIA), or Weigert effect, is known for a long time: birefringence and dichroism are induced by a polarized resonant light.
- The photoassisted electrical poling (PAEP) has been demonstrated in our laboratory six years ago1). Optical pumping increases the mobility of molecules which can be oriented by the field.
- The all-optical poling (AOP) is the most recent method2): The material is coherently pumped by the fundamental and the second harmonic of a laser. A $\chi^{(2)}$ can be created with non polar molecules (octupolar molecules) and different macroscopic symmetries can be induced3).

These three techniques need an optically induced rotation of molecules. They are particularly efficient when photoisomerization occurs. The trans⇔cis photoisomerization of azobenzenes is by far the most frequently used mechanism, because of its efficiency and of the good stability of azo-dyes, which can be included in many chemical compounds. We use Dispersed Red 1 (DR1) as a model molecule. In another paper we present complementary results obtained with spiropyran ⇔ merocyanine photoisomerization4).

The three ordering methods can be understood and modelized with a common formalism5,6). An angularly selective optical pumping depletes the population of the trans state. This Angular Hole

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Burning (AHB) has the axial symmetry of the polarized light, in PIA and in PAEP, but a polar or an octupolar symmetry in the case of AOP. The reversible photoisomerization produces a more or less random rotation of molecules: this Angular Redistribution (AR) is an isotropic process in PIA and AOP, but in PEAP, it is driven by the torque induced by the field on the molecular dipole. The resulting macroscopic symmetry is governed by the pumping light, in PIA and in AOP, and by the electric field in PEAP.

Many molecular and environmental parameters are involved in the model. The comparison of experiments with a set of simulations highlights the rôle of some parameters. We have shown the influence of the average rotation in each isomerization process[6] and that of reverse photoisomerization[4]. In spite of very good qualitative simulations, it is never possible to fit theoretical curves to experimental results because of the non exponential behavior of all relaxation processes in polymers. In this paper we discuss the angular mobility of azo-dye molecules, both in ordering (PIA and PAEP) and disordering processes (angular relaxation). We also present new spectroscopic studies showing some spectral inhomogeneity and irreversibility of the photoisomerization.

Experimental

Samples. Three types of materials have been used. 1) guest-host mixtures of Disperse Red 1 (DR1, Aldrich) in polymethylmethacrylate (PMMA). 2) PMMA with DR1 side chains (25% m/m; Fig. 1B). 3) a new polyimide with DR1 side chains (32% m/m; Fig. 1A)[7]. For dichroism experiments, microscope glass plates are spin-coated in order to get films of optical density less than 1. Samples are baked at 90 °C during half an hour. For ATR experiments, thin gold layers (≈ 35 nm) are evaporated on glass plates before and after the deposition of polymer films (1- 2 μm).

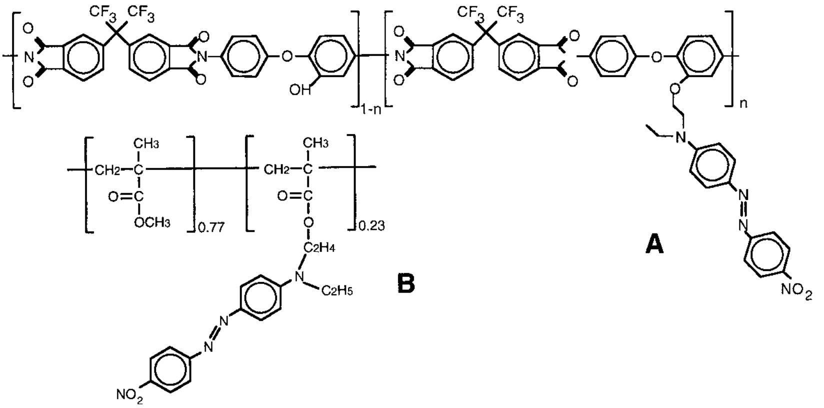

Figure 1. (A) DR1-polyimide copolymer (Synthesis: J. Chauvin[7]).(B) DR1-PMMA copolymer.

Multiwavelength dichroism measurements. For recording transient dichroism simultaneously on several wavelengths, without pumping samples with a too strong probe beam, we built a new experimental setup: the entrance slit of a monochromator has been replaced by six slits, illuminated by a Xe arc lamp, through a rotating wheel with narrow slits. The image of the output slit is formed on the sample at the center of the spot illuminated by the pumping beam. The probe beam is a periodic succession of pulses (≈1ms) of different colors. A computer synchronized with the slit-wheel, records the signal from two photodiodes placed behind a Wollaston prism and from a reference photodiode. The linearly polarized pump beam is produced by an UV Hg arc lamp with a 365 nm filter, or by an Ar laser (514 or 488 nm) or by a dye laser (≈ 585 nm). For each probe wavelength, optical densities, $DO_{//}$ and $DO_{\perp}$, are calculated (polarizations parallel and perpendicular to that of the pump), by comparison with a bare glass plate. Time variations can be recorded during several hours (best resolution ≈ 50 ms). In photostationary states, the spectrum can be scanned manually. The average optical density, S_0, its relative variation, P_0, the absolute anisotropy, S_2, and the relative anisotropy, P_2 (or P'_2), are built:

$$S_{0,\lambda} = \tfrac{1}{3}\left(DO_{//} + 2DO_{\perp}\right) = N_T\bar{\sigma}_T(\lambda) + N_C\bar{\sigma}_C(\lambda) \quad (1)$$

$$P_{0,\lambda}(t) = \left[S_{0,\lambda}(t) - S_{0,\lambda}(0)\right]/S_{0,\lambda}(0) = \left(\bar{\sigma}_C(\lambda) - \bar{\sigma}_T(\lambda)\right)N_C(t)/\left(\bar{\sigma}_T(\lambda)N\right) \quad (2)$$

$$S_{2,\lambda} = \tfrac{1}{3}\left(DO_{//} - DO_{\perp}\right) = N_T\,\bar{\sigma}_T(\lambda)a_T(\lambda) < P_2 >_T + N_C\,\bar{\sigma}_C(\lambda)a_C(\lambda) < P_2 >_C \quad (3)$$

$$P_{2,\lambda}(t) = S_{2,\lambda}(t)/S_{0,\lambda}(0) \qquad \text{or} \qquad P'_{2,\lambda}(t) = S_{2,\lambda}(t)/S_{0,\lambda}(t) \quad (4)$$

For X=T (Trans) or X=C (Cis), N_X is the number of molecules per unit of area of the film and $< P_2 >_X$ the order parameter *i.e.* the projection of the angular distribution on the Legendre polynomial $P_2(\cos\theta)$, where θ is the angle between the axis of the molecule and the symmetry axis defined by the polarization of the pumping light. (2) is valid if $N_C+N_T=N$ is constant, *i.e.* if the population of excited levels is negligible. Both isomers are assumed to have an axial symmetry. For each, we define the average absorption cross section and the anisotropy:

$$\bar{\sigma} = (\sigma_{//} + 2\sigma_{\perp})/3 \qquad ; \qquad a = (\sigma_{//} - \sigma_{\perp})/(\sigma_{//} + 2\sigma_{\perp}) \quad (5)$$

Attenuated Total Reflection (ATR)[6,8]. The sample is a glass slide coated with a polymer film between two semitransparent gold layers. The glass face is put in optical contact with a half sphere. The IR reflectivity (830 nm) is measured through the half sphere as a function of the incidence angle. The angular positions of the Fabry-Perot dips, with TE and TM polarizations, give the three components of the index of refraction and the thickness of films. Electrooptic coefficients can be measured by applying a modulated voltage on the gold electrodes (field $E_1 \cos\Omega t$) and by using a lock-in detection. The electrodes can also be used for applying a DC field for poling (E_0 =50 V/µm). They are transparent enough to allow optical pumping of chromophores. The time variations of n_Z (index perpendicular to the sample) and of r_{33} (or $\chi^{(2)}_{zzz}$) are reconstructed from the shift and the modulations of the angular position of the TM mode of largest incidence.

$$
\begin{aligned}
2n_z\Delta n_z &= \Delta\chi^{(1)}_{zz} + \chi^{(2)}_{zzz}(E_0 + E_1\cos\Omega t) + \chi^{(3)}_{zzzz}(E_0 + E_1\cos\Omega t)^2 \\
&= \Delta\chi^{(1)}_{zz} + \chi^{(2)}_{zzz}E_0 + \chi^{(3)}_{zzzz}(E_0^2 + \frac{1}{2}E_1^2) + \left[\chi^{(2)}_{zzz} + 2\chi^{(3)}_{zzzz}E_0\right]E_1\cos\Omega t + \frac{1}{2}\chi^{(3)}_{zzzz}E_1\cos 2\Omega t \\
&= 2n_z\left(\Delta n_z^{(0)} + \Delta n_z^{(\Omega)} + \Delta n_z^{(2\Omega)}\right) \qquad (6)
\end{aligned}
$$

In $\Delta n_z^{(0)}$ ($\rightarrow$ angular shift) the electrooptic contributions are negligible compared to the variation of birefringence, $\Delta\chi^{(1)}_{zz}$, induced by the rotation of molecules. When there is a DC field, the signal at frequency Ω ($\propto r_{33}$) contains a contribution from Kerr effect ($2E_0\chi^{(3)}$) which is measured with the modulation at 2Ω.

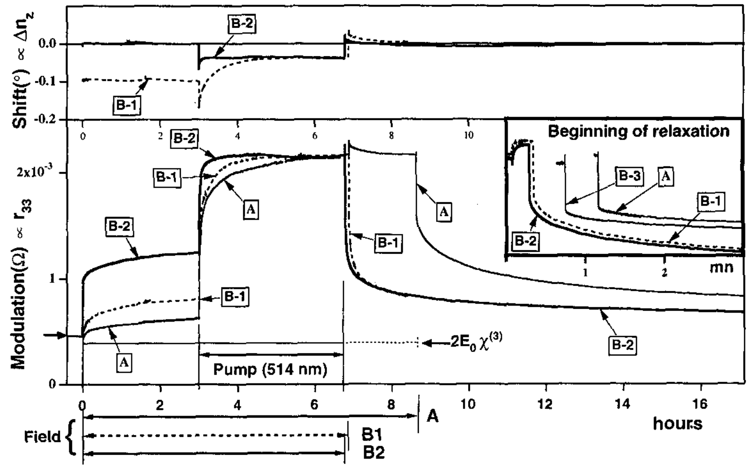

Figure 2. Time variations of n_z and of the electrooptic coefficient r_{33} in a DR1-PMMA guest-host film. The DC field is switched on at t=0,. After 3 hours a circularly polarized pump is applied during 4 hours. Then the field is removed immediately (B-1, B-2) or after 2 hours (A, B-3). A and B-1 are fresh samples (no modulation at t=0). B-2 is the same sample as B-1 after one week in dark: its modulation starts as indicated by an arrow. B-3 has been recorded one day after B-2. The horizontal line ($2E_0\chi^{(3)}$) is the contribution of Kerr effect: the Pockels effect is measured above this base line.

Orientational mobility of DR1 in poling experiments (ATR)

The inhomogeneity of the molecular mobility is illustrated by Figure 2 (in guest-host DR1-PMMA films). When the DC field (E_0) is applied to sample B-1, a small Pockels effect ($\chi^{(2)}$) is observed on the modulation signal at frequency Ω. It indicates that some molecules are free to rotate. At t=3 h, the pump is switched on and PAEP orients many other molecules. When the pump and the field are removed the drop in the modulation is due to the instantaneous fall of Kerr effect and to the angular relaxation of free molecules. Other molecules relax slowly. After one week (starting of curve B-2) some Pockels modulation remains. When the field is applied again, the rise of B-2 is exactly identical to that of B-1 because of free molecules. On the contrary when the pump is turned on, the dynamics is faster since 'slowest' molecules are

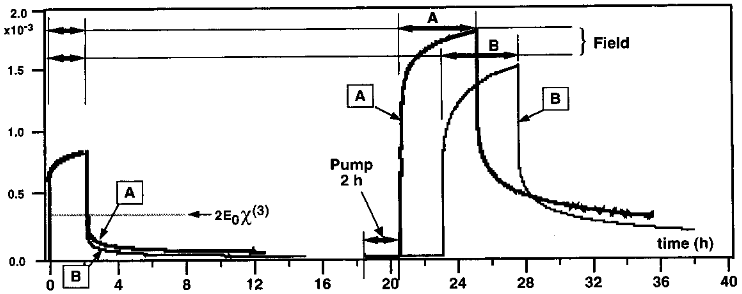

Figure 3. Pockels EO modulation induced by the DC field alone, before and after pumping. A and B are two different spots on the same guest-host film.

already oriented. The steady state level and the relaxation behavior are identical for B-1 and B-2. Roughly speaking, we distinguished free molecules which rotate spontaneously, weekly linked molecules which are oriented by optical pumping but relax in a few hours and strongly linked molecules remaining oriented after one week. This arbitrary distinction depends on the chosen experimental time scales and on many parameters, as illustrated by the difference between A and B-1 (Probably, B-1 has been accidentally illuminated before the experiment).

Time variations of n_Z indicates (upper graph in Fig. 2):

1) A negligible variation of $\Delta n_z^{(0)} \propto < P_2 >$, by the action of E_0 alone. In agreement with the Langevin theory, if $<P_1>$ is small, $<P_2>$ is of second order.

2) A fast drop of the trans population (AHB) when the pump is switched on (IR probe is sensitive to Trans) and a slow increase of $<P_2>$, due to the angular redistribution of molecules in the z direction (perpendicular to the pump circular polarization and parallel to the field).

3) A fast rise when the pump is switched off (Cis→Trans relaxation);

4) A clear difference between B-1 and B-2 proving that a part of $<P_2>$ doesn't relax in 1 week.

Time variations of the orientational mobility. By comparing the modulation signal of A and B-3 experiments with that of B-1 and B-2 (Inset in Fig. 2), it is clear that the orientational relaxation is slower when the field is maintained 2 hours after the pump removal. The same behavior has been observed with thermoassisted poling[9)] and was interpreted as a slow relaxation of the polymer structure after cooling. Here, the structure perturbation is due to photoisomerization of azo-dyes. To prove this variation of mobility we applied the DC field alone, before and after pumping without field. The modulation at Ω is shown in figure 3. As expected, the mobility of DR1 is larger after pumping than before and it is smaller in experiment B (2 hours after pumping) than in experiment A (immediately after pumping). Similar results have been obtained with Spiropyran.[10)]

PAEP in polymers with DR1 side chains. With DR1 side chains on Polyimide (Figure 4) or on PMMA (Figure 5), there are almost no free chromophores. The long term stability is better with polyimide, as one could expect from the higher T_g and from the massive structure of the polymer chain. Nevertheless, the maximum r_{33} is smaller in polyimide than in PMMA, probably because the mass proportion of DR1 is smaller (16% instead of ≈45%) and also because the poling time (1 h) was too short. We couldn't repeat the experiment since we got only one sample, because of the difficulty to obtain films of good optical quality with polyimide (up to now the solvents used for spin coating lead to a poor roughness of the surface and to many short circuits). The same polyimide-DR1 material has been used successfully for second harmonic generation7) (optical quality requirements are much less constraining for SHG than for ATR).

In Fig. 5, PAEP is compared for three different pump wavelengths, in PMMA-DR1 copolymer (23% mol ≈ 45% w/w). We expected a better efficiency with 580 nm and with UV, since for both, the optical density is approximately 9 times smaller than with 514 nm (the optical density is ≈ 3 μm^{-1} at 514 nm). The final efficiency is the same with 580 nm and 514 nm, but the pumping is faster with 580 nm, because all the thickness of the sample is immediately pumped (1.3 μm: unsaturated OD ≈ 0.46) and pump power is higher. With 514 nm (0.84 μm: unsaturated OD ≈ 2.6) only 3 10^{-3} of the intensity reaches the back layer of the sample (with saturation it could increase to $\approx 10^{-2}$). Probably, in a very thin film (≈0.3 μm) the final r_{33} should be better with 514 nm.

With UV pump the building of r_{33} is slow but more efficient. This cannot be explained only by the penetration length. From simulations, it is possible to show that the larger cross section of the cis state increases the number of cycles of photoisomerization, which is favorable to PAEP. In addition it is likely to remark that the higher energy of UV photons produces a higher vibronic excitation of molecules, which could increase more efficiently their angular mobility. Furthermore, in spite of a larger photodegradation, the poling appears to be more stable (4% loss between t_{relax}=1h and 15 h, instead of 8% with 580 nm), probably because the rearrangement of the polymer around chromophores is more efficient.

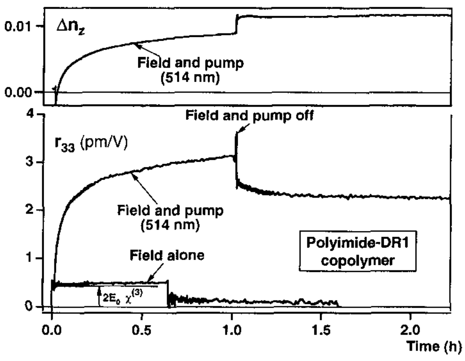

Figure 4. Photoassisted poling of DR1-side chains on Polyimide.

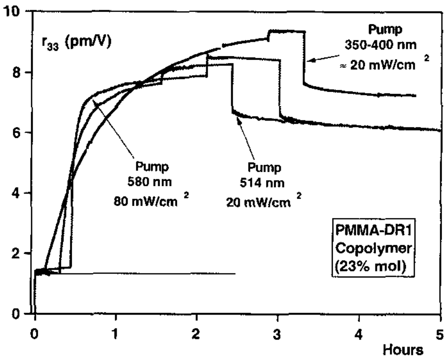

Figure 5. Photoassisted poling of DR1-side chains on PMMA, with different pump wavelengths.

Spectral and transient behavior of photoinduced dichroism

These experiments are performed with the multiwavelength experimental setup, with a linearly polarized pump. Our purpose was: (1) To characterize the dyes mobility with a method (PIA) much easier than ATR (electric short circuits and films roughness are major problems in ATR). (2) To distinguish both isomers by a spectral analysis. (3) To get a better estimation of quantum yields of photoisomerization, by introducing polarization in the Fisher-Rau method, which needs to pump and probe on two different wavelengths, with extrapolation to infinite pump power.11)

The distinction between Cis and Trans states is clear on Figure 6: In the upper graphs, the normalized average optical density (P_0) increases at 360 nm, where absorption is larger for cis than for trans, while it decreases at 485 nm (more sensitive to Trans). The nomalized anisotropy (P_2) is shown in the lower graphs: at the beginning of pumping, the anisotropy is positive at 360 nm, but immediately strongly negative in the visible. This is a proof of AHB: Cis molecules, resulting from the first excitation of Trans molecules parallel to the pump polarization ($\cos^2\theta$), are parallel to that direction. Furthermore their transition dipole moment is

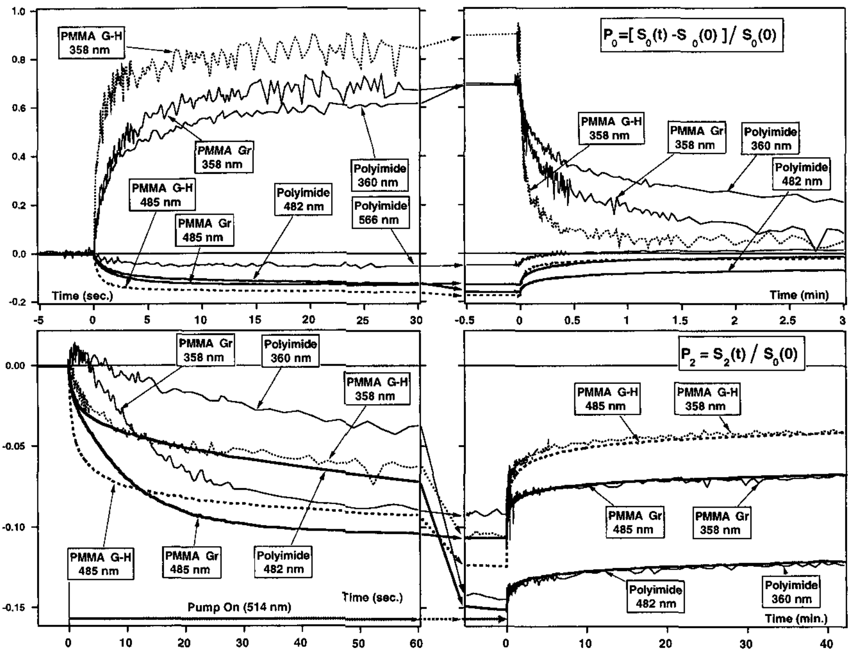

Figure 6. Relative variations of the mean optical density (P_0) and of the anisotropy (P_2) with blue and UV probe wavelengths, for guest-host DR1-PMMA (PMMA G-H; pump: 40 mW/cm^2, 35 mn), grafted DR1 side chains on PMMA (PMMA Gr; pump: 20 mW/cm^2, 12 mn) and on Polyimide (pump: 20 mW/cm^2, 30 mn). At 360 nm, for polyimide, we approximately took into account the main chain absorption, while normalizing.

approximately parallel to that of the trans state before its excitation. After a time varying from 0.2 s (for guest-host) to 8 s (for polyimide) the anisotropy at 360 nm becomes negative, since $<P_2>_C$ decreases, according to the theory of angular redistribution. Then the negative trans anisotropy dominates.

The comparison of samples shows that (as expected) the mobility is higher in guest-host PMMA-DR1 than in the copolymer (faster transients, lower long term stability of anisotropy). When chromophores are grafted to the polymer, their rotation necessarily distort the main chain: the rotation is more difficult but more irreversible. Even the lifetime of Cis is longer in the copolymer (upper right graph in fig. 6). In polyimide the angular redistribution is still much slower than in PMMA-DR1 copolymer, but very efficient after a long pumping time and the orientational order is more stable (low mobility). This is a consequence of the higher value of the glass transition temperature of polyimide (≈260°C instead of ≈120°C). The mass of each monomer and the rigidity of the chain make it difficult to move.

Photodegradation and spectral inhomogeneity. Apparently, the Cis state does not relax completely, particularly in polyimide. In fact it is more complicated. According to (2), P_0 should be proportional to $(\sigma_C - \sigma_T)N_C(t)$, so that its variations should be proportional to each other, at all wavelengths. The discrepancy to this rule is much larger with polyimide than with other materials: as shown in Fig. 6, at 566 nm, P_0 changes of sign. This is due to a modification of the absorption spectrum of molecules which is more than a simple cis-trans photoisomerization.

This discrepancy is quite evident on spectra in Figure 7b and 7c (for Polyimide). According to (2), all differential spectra should be proportional to $\sigma_C(\lambda) - \sigma_T(\lambda)$: they appear to vary with pumping time and with power and wavelength of the pump. Probably, some photodegradation occurs, particularly with UV pumping. It could be responsible for the large remaining spectral modification, after one hour in dark (decrease of absorption in the visible spectrum and an increase in UV). But the more striking effect, in figures 6, is the spectral inhomogeneity: the photoinduced variation of absorption spectra is very different with different pump wavelengths. A spectral hole appears on the long wavelengths side with a yellow pump and on the short wavelengths side with an UV pump. Furthermore we observe a red shift of the hole (blue shift of the spectrum) when increasing pumping time or power, particularly with UV pump . This shift could be understood as a change in the interaction between chromophores and their environment (modification of Stark effect) induced by photoisomerization cycles (geometrical rearrangement). But this effect appears more like a spectral redistribution (population decrease in the pump spectral neighborhood and is redistributed in other spectral regions). Spectral redistribution could also explain the irreversible variation of spectrum observed with low power green and yellow pumps, after relaxation in dark.

With PMMA-DR1 copolymer, the spectral inhomogeneity is smaller (Fig 8 b) and the remaining spectral modification is very small, one hour after the end of pumping (Fig 8 c). With PMMA-

DR1 guest-host films, the spectral inhomogeneity is comparable to that of Polyimide, but the reversibility is better.

The normalized photoinduced anisotropy is shown in Fig. 7d and 8d, during optical pumping and after relaxation in dark. An homogeneous line, with a constant anisotropy $a_T(\lambda)$ (Cf. eq. 3) should give a flat signal, at least during relaxation period, when $N_C = 0$. Clearly, the inhomogeneity appears in polyimide, more than in PMMA.

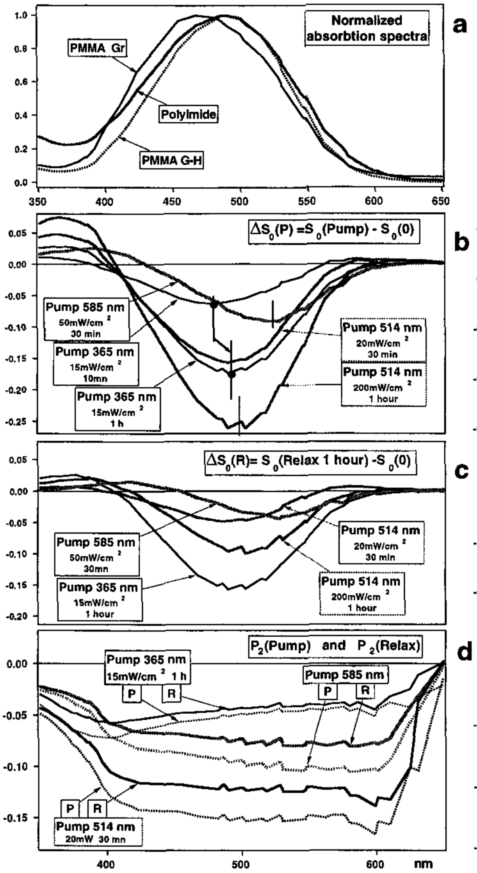

Figure 7. a: Normalized absorption spectra of fresh samples. **b:** $\Delta S_0(P)$: Photoinduced variations of absorption spectra **in Polyimide** just before the end of pumping. **c:** $\Delta S_0(R)$: after relaxation in dark (1 hour) **d:** P_2: Normalized photoinduced anisotropy in polyimide. For each pump wavelength, the label P corresponds to the end of pumping and the label R to 1 hour relaxation.

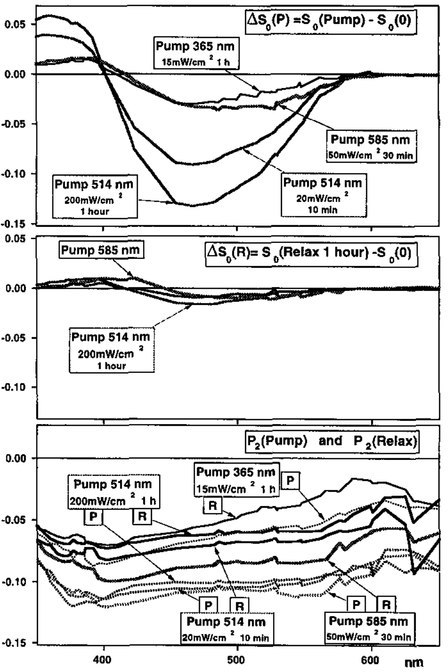

Figure 8. Results with **PMMA-DR1 copolymer.** b, c and d represent the same experiments as the corresponding ones in fig. 7. The initial optical density (at maximum) was 0.65 in PMMA and 1 in Polyimide.

Conclusion

Different methods of characterization of the orientational mobility of azo-dyes have been shown. The dynamical measurement of photoinduced dichroism, simultaneously at different probe wavelengths, is much easier than ATR: the angular redistribution associated with photoisomerization and the angular free mobility (stability of orientation) of chromophores in different polymers can be compared and the results can be used for choosing materials for PIA, PAEP and all-optical poling. In addition, this method permits to follow the variations of the population and of the anisotropy of both isomeric states. We confirmed that angular mobility is larger in guest-host DR1-PMMA films than in the copolymer. The orientational stability is maximum in DR1-Polyimide copolymer. It has been shown that angular mobility of chromophores depends on the site to site variations of the environment and on the time delay after the photoisomerizing optical pumping. Irreversibility and spectral inhomogeneity of absorption appear, particularly in DR1-polyimide: it impede any improvement of quantum yield measurements by the Fisher-Rau method.

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