# Photoinduced orientation of azo dye in various polymer matrices

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Photoinduced dichroism in various polymers containing the same azo dye has been studied. "Angular hole burning" and molecular reorientation have been identified by analysis of dichroism dynamics at various probe wavelengths. The glass-transition temperature $T_g$ is of major relevance for the reorientation of optically active molecules. For low $T_g$ (below ambient temperature) thermal diffusion impedes anisotropy buildup. For higher $T_g$ the angular distribution induced by the polarized pump beam is frozen. We propose a simple model based on diffusion rates in *trans* and *cis* molecules.   © 1999 Optical Society of America

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Interest in azo dyes has been emphasized in the past few years because of the ability of these dyes to record optical information.[1–3] This ability comes from the *trans−cis* photoisomerization that modifies the molecular dipolar momentum and thus the refractive index as well as the absorption of the material. By using polarized light, one can also induce anisotropy that leads to birefringence and dichroism.[4,5] The optimization of this property is important for optical recording, since modulations achieved in this way are very high. Our aim in this Letter is to understand the role of the interactions between the dye and the polymer matrix during photoinduced anisotropy. We show the predominant importance of the glass-transition temperature ($T_g$). In polymers containing azo dye, anisotropy arises from several contrasting mechanisms[6,7]: First, optical pumping preferentially isomerizes *trans* molecules with their transition axes oriented along the light polarization. This phenomenon is called "angular hole burning" (AHB). The second mechanism is angular redistribution (AR) of molecules when they relax from *cis* to *trans*. As there is no torque applied to the dye molecules, reorientation arises randomly. Since molecules that are perpendicular to the pump polarization are no longer pumped, AR associated with multiple isomerization cycles will tend to accumulate molecules in that direction. The third mechanism is angular diffusion (AD) owing to thermal agitation, which tries to restore the isotropic thermodynamic equilibrium.

We have used three compounds containing the same dye. The first is poly($N$-vinyl carbazole) (PVK) doped with 10-wt. % 2,5-dimethyl-4-($p$-nitrophenylazo) anisole [DMNPAA (Azo)] and 30-wt. % $N$-ethyl-carbazole plasticizer (ECZ, the PVK monomer). The two other materials are copolymers composed of [$\omega$-($N$-carbazolyl)alkylmethacrylate] and [4-(11-methacryloylalkyloxy)-2,5-dimethylphenyl](4-nitrophenyl) diazene, where the lengths of the alkyl spacers have

been set to be hexyl and undecyl for C6-C11-Azo and undecyl and hexyl for C11-C6-Azo. The chemical structures are presented in Fig. 1. The polymers and dye synthesis can be found in Ref. 8. $T_g$ for the compounds is 15 °C for PVK:Azo, 56 °C for C6-C11-Azo, and −20 °C for C11-C6-Azo. Samples were made by hot pressing of polymer between two glass plates.

To induce dichroism in these polymers we use a 514-nm linearly polarized laser beam (20 mW/cm²). A probe beam propagating nearly parallel to the pump is realized by use of a broad-spectrum source and a monochromator. In this way the latter has been modified and has five entrance slits behind a rotating wheel with narrow slits. The monochromator successively and periodically selects the analysis wavelengths. We have verified that the pumping effect of the probe beam is unobservable. Behind the sample, a Wollaston prism splits the probe beam into two polarization components that are parallel and perpendicular to the pump polarization. This setup is detailed in Ref. 9.

Figure 2 shows the evolution of the parallel and the perpendicular components of the optical density (OD) during pumping and after the pump has been switched off. The dynamics of the OD's are very
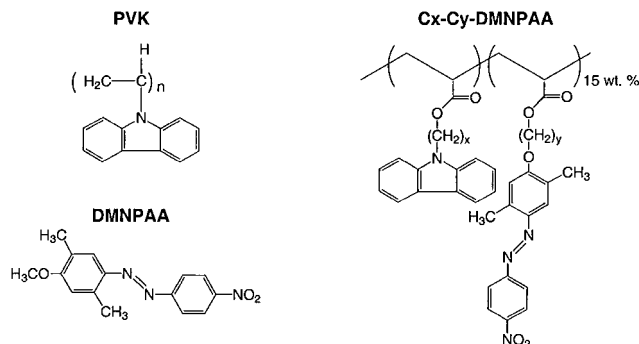


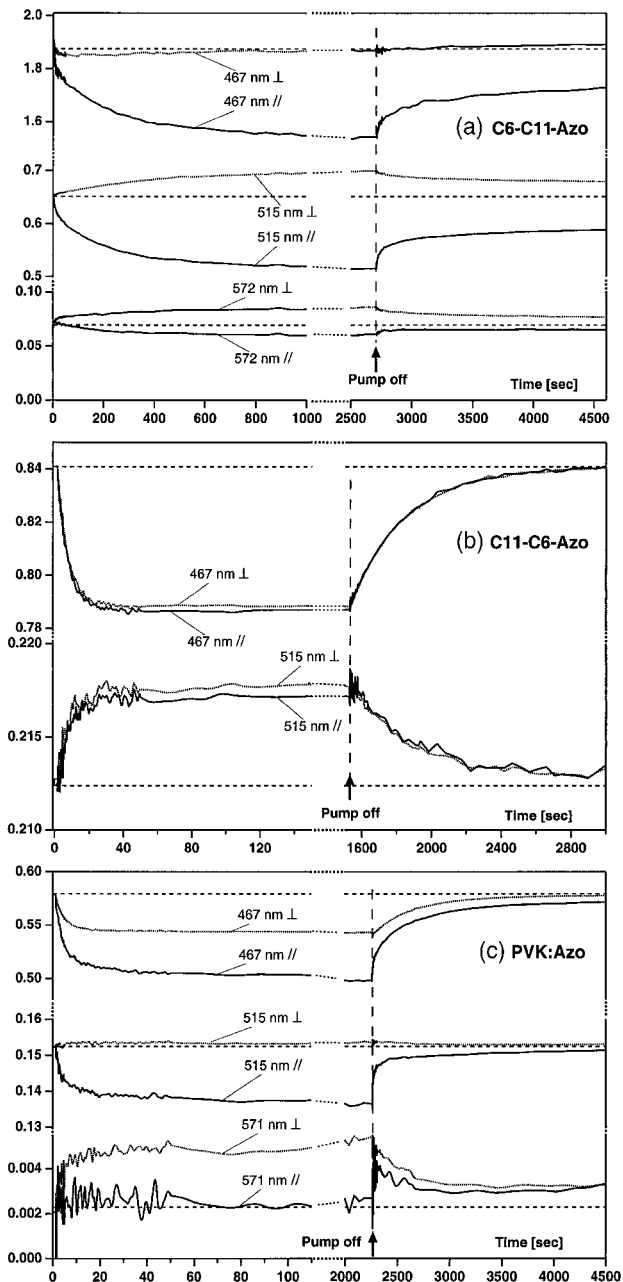Fig. 1.   Molecular structure of the three compounds.

Fig. 2.  OD dynamics:  Optical pumping is switched on at $t = 0$.  The probe wavelengths and polarizations with respect to the pump polarization are noted.  The dotted lines are the isotropic OD before pumping.  C11-C6-Azo exhibits the same behavior at 572 nm and at 515 nm.

different for the three polymers and for the various probe wavelengths.

We first discuss the evolution of the OD's in C6-C11-Azo [Fig. 2(a)] and PVK-Azo [Fig. 2(c)].  In both materials $OD_\perp$ at 515 nm increases above the initial isotropic value.  This increase is a typical behavior when AR accumulates *trans* molecules in the perpendicular direction.  However, this is not sufficient proof of the existence of AR.  Indeed, AHB alone can produce this kind of behavior when the probe is simultaneously sensitive to *cis* and *trans* states (515 nm is near the isobestic point).  To prove unequivocally the presence

of AR, we note that a careful study of the shape of OD transients and the use of different probe wavelengths are necessary, since the relative absorbance of *cis* and *trans* molecules varies with wavelength.

In C6-C11-Azo, the large remaining anisotropy 30 min after pump removal is an indication of AR. Nevertheless, the relaxation of molecules back to the *trans* state is not complete:  $S_0 = (OD_\parallel + 2OD_\perp)/3$ does not recover its initial value, either because of an incomplete *cis–trans* relaxation or because of some photochemical modification.  More convincing are the two following arguments:  (1) The relative anisotropy, $S_2 = (OD_\parallel - OD_\perp)$, grows and relaxes more slowly than the average OD, $S_0$ (Fig. 3).  (2) At 467 nm, $OD_\perp$ first decreases (0−100 s) and then increases.

Both observations indicate the existence of opposite phenomena acting in the media.  In the first 100 s of pumping, AHB reduces the *trans* population and the 467-nm OD for both polarizations, since this wavelength is more sensitive to *trans* than to *cis* orientation. After some time, AR accumulates *trans* molecules in the perpendicular direction, slowly increasing $OD_\perp$ and anistropy.[10]

In the case of PVK-Azo the situation is not so clear. Reversal of $OD_\perp$ variations is not observed.  $S_2$ variations indicate that AR exists, but for the majority of molecules the thermal orientational diffusion in the *trans* state is very fast.  Few of them remain aligned 30 min after pump removal (according to the research reported in Ref. 9 the angular mobility is very inhomogeneous in polymers).  In addition, a careful study of $S_0$ shows that its variations cannot be explained with only two states.  A third state has a nonnegligible population during optical pumping (triplet state, or charge transfer complex with PVK).

With C11-C6-Azo [Fig. 2(b)], for any wavelength, parallel and perpendicular components reach a plateau within 50 s.  The pumping process maintains a very low dichroism that vanishes immediately after the pump beam has been switched off.  This sample remains quite isotropic at any time.  Since the sample is a viscous liquid at room temperature ($T_g = -20\,°C$), the thermal diffusion shuffles the angular distribution
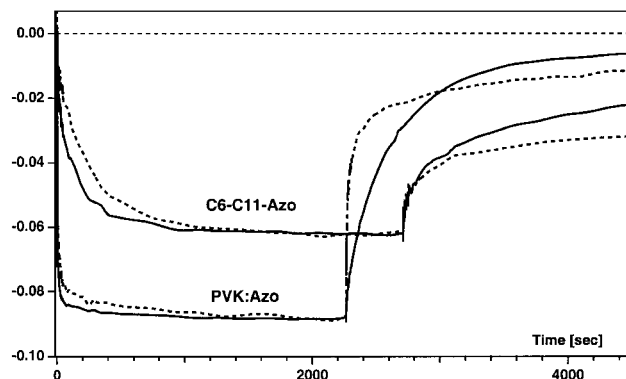


Fig. 3.  Comparison of the time evolution of the anisotropy, $OD_\parallel - OD_\perp$ (dotted curves), with that of the mean OD, $[S_0(t) - S_0(0)]/S_0(0)$ (solid curves), for two compounds. The anisotropy has been normalized to the value of the mean OD on the photostationary plateau.
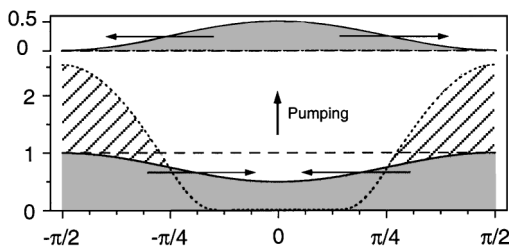
Fig. 4.   Angular distribution of the ground state, i.e., the *trans* (bottom) and the excited states, i.e., the *cis* and the other possible excited states (top).   Horizontal dashed line, distribution before pumping; solid curves, AHB at the beginning of pumping ($\cos^2 \theta$); arrows, tendency of diffusion spreading in each level; dotted curve, resulting anisotropy after the end of pumping and full relaxation to the *trans* state if the diffusion is negligible in the *trans* state.

of *cis* and *trans* molecules faster than the AHB can produce anisotropy.   Chromophores are free to rotate in spite of the C6 chemical bound.   The variations of OD at 467 and 515 nm have opposite signs:   These wavelengths are on opposite sides of the isobestic point.

In Ref. 11, different mechanisms of AR are discussed.   Here we show that photoinduced anisotropy can be discussed phenomenologically in terms of diffusion rates in the angular distributions of the ground state and the excited state.   We understand excited state to mean molecules that are in the *cis* form.   We also include all intermediate states in the photoisomerization and the relaxation processes (as vibrational states of *trans* a short time after its relaxation from *cis*).   Then, the ground state holds only chromophores that have not absorbed any photons for a short time. The AD of the ground state is due only to the thermal reorientation, which is usually represented by Brownian motion.   In the excited state energy is supplied by photon absorption and the following nonradiative relaxation (this is the AR process).

The competition between these diffusion processes and optical pumping is intuitively illustrated in Fig. 4. Before pumping, the angular distribution $n_{\text{trans}}(\theta, \varphi)$ is flat.   When the pump is switched on, AHB excites *trans* isomers with a $\cos^2 \theta$ law with respect to the pump polarization.   Then, AD rotates molecules in both states to flatten distributions.   A moment later, the excited molecules return to their ground state. Since their angular distribution has changed, these molecules increase the shoulder of the ground distribution.   After multiple excitation–relaxation cycles, three extreme cases can be distinguished:

1.   Diffusion processes in both states are negligible:   This is the pure AHB case, without AR.   When the pump is switched on, the anisotropy grows but then decreases if the transition is saturated.   When the pump is switched off, the anisotropy disappears at the same rate as the population of the excited state. This is not the case for our polymers.

2.   AD of the excited level (AR) is faster than that of the ground level.   The anisotropy grows and, when the pump is switched off, distribution of the ground state is distorted as shown in Fig. 4.   This is

the case for C6-C11-Azo, which has the highest $T_g$. Without diffusion in the ground state, the photoinduced anisotropy is large and permanent (as observed in very high-$T_g$ polymers[9]).

3.   AD in both states is faster than AHB. Anisotropy is very small during pumping and disappears immediately when the pump is removed (anisotropy $S_2$ relaxes faster than $S_0$, the excited population).   This is the case for C11-C6-Azo in its viscous phase.

PVK-Azo is intermediate between cases 2 and 3.   $T_g$ for this case is included between those of C11-C6-Azo and C6-C11-Azo.   The AD rate in both states also governs the rate of growth of anisotropy at the beginning of pumping, as shown in Fig. 4 by comparison of PVK:Azo and C6-C11-Azo.   A more-precise model should include reversed *cis*−*trans* optical pumping.[9,11]

In summary, we have performed multiwavelength experiments of photoinduced dichroism on three different polymers containing the same azo dye.   The results show that grafting the DMNPAA onto the polymer backbone leaves it free to rotate during isomerization−relaxation cycles.   This ability seems to be more related to the compounds' $T_g$ than to the stabilization of the dye by chemical bonding.   So if there is no anisotropy observed in C11-C6-Azo, this is due not to the immobilization of the chromophores according to their grafting but to the too-high mobility of both the *trans* and the *cis* isomers, because of the low $T_g$ of this polymer.   So the highest anisotropy is obtained with C6-C11-Azo, which possesses the highest $T_g$, although the length of the spacers is greater than with C11-C6-Azo.   High $T_g$ prevents thermal relaxation in *trans* molecules but does not impede AR in the photoisomerization cycle.

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