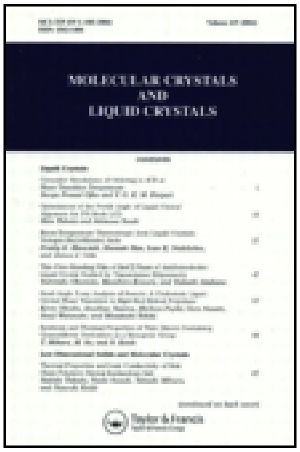

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M. P. Fontana [a], C. Paris [a] & M. Polli [a]

[a] Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materia, University of Parma, Parma, Italy

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MOLECULAR REORIENTATIONS AND RELAXATION IN PHOTOSENSITIVE LCP'S: INDUCED BIREFRINGENCE AND POLARIZED MICRO-RAMAN SPECTROSCOPY

M.P. Fontana, C. Paris, M. Polli
Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materìa,
University of Parma, Parma, Italy

Abstract The liquid crystalline side chain polymer azopolyacrylate (PA4) has interesting photoisomerization effects upon absorption of light by the azo-group in the side chain. The material also easily forms a glassy structure, with $T_g \sim 20$ °C. In this work we show that upon illumination with polarized blue laser light the molecules reorient perpendicularly to the polarization direction of the incident light. We demonstrate this on the microscopic scale by polarized micro-Raman spectroscopy of the illuminated zone. The reorientation process was followed in time as a function of incident light power and at different temperatures in the neighborhood of T_g, by monitoring the induced birefringence. Thus we were able to study molecular relaxation and its behavior in the neighborhood of the glass transition in this fragile glass, using light to take the system out of equilibrium.

INTRODUCTION

One of the most interesting characteristics of liquid crystals is the possibility of controlling molecular alignment of the mesophase by external means, such as for instance electric fields. In low molecular weight LC's however, molecular alignment is lost when the external field is turned off. Thus such materials cannot be used for optical information storage. Furthermore their liquid state requires them to be held in special cells. Liquid crystalline polymers (LCP) on the other hand feature both the molecular self-organization characteristics of LC's and the complexity of structure and molecular conformational dynamics of polymers.[1] This gives rise to new effects or strongly modifies the dynamics of old ones. In particular for instance the molecular relaxation times after the external perturbation is turned off might be expected to be much longer in the case of LCP's, or even lead to stationary metastable states. Furthermore most LCP's easily form glassy phases, which however retain much of the molecular orientational mobility of the liquid crystalline mesophase. Thus "solid" LC's are possible, and this means great simplification in producing devices, due to the ease of machining and good mechanical properties of polymers. In fact such systems have great potential in applications as high density memory devices, ferroelectric and piezoelectric systems and non-linear optical materials.

Particularly interesting are recently synthesized photosensitive side chain LCP's, in which a mesogenic moiety is attached via a flexible methylene spacer chain to the polymeric backbone.[2] In such and similar materials reversible optical storage has already been demonstrated.[3] Among several possible photoeffects, photoisomerization has been shown to be particularly efficient in inducing molecular realignment in the illuminated area. In some cases the photoinduced trans-cis transition will destroy the pre-existing liquid crystalline order; in others it may facilitate molecular realignment in a specific direction. The information thus stored may be preserved for a long time (e.g. years) if the alignment is performed in the glassy state of the LCP.[4]

It is thus important to determine the dynamics of photoinduced effects at or near the glass transition temperature T_g. Such studies have additional interest since they allow to probe the molecular dynamics near the glass transition, a subject of much current interest.[5] In this paper we correlate macroscopic effects due to photoisomerization in a side chain LCP with the light- induced microscopic molecular realignment processes. We do this by measurements of photoinduced birefringence and polarized micro-Raman spectroscopy over the same illuminated area. The material we have chosen for our study is PA4, a polyacrylate with an azobenzene moiety attached to the backbone via a flexible spacer.[6] Our results show quite efficient molecular realignment due to photoisomerization in the azo-chain. Furthermore, in the slowed-down time scale of the glassy structure of the polymeric network, we were able to follow easily the molecular relaxation kinetics and determine its behavior as a function of temperature and incident laser pump power.

MATERIALS AND EXPERIMENTAL PROCEDURES

PA4 (poly [[4-pentyloxy-3'-methyl-4'-(6- acryloyloxyexyloxy)] azobenzene]) is a side chain LCP, with a melting point of 83 °C and a nematic-isotropic clearing point of 96 °C. Upon cooling it shows evidence of a nematic-pseudo-smectic transition at about 65 °C, before going through a transition to a glassy state, with a T_g of $\sim$ 20 °C.[7] This last feature makes it particularly interesting to study molecular relaxation mechanisms at the glass transition. The azobenzene moiety is attached to a carbonyl group off the backbone via a 6 member methylene spacer. Finally a [4+1] carbon alkyl tail is substituted at the 4 position of the second phenolic ring.

A small amount of the material is placed in a cell made of two thin glass plates and a spacer of 5 to 10 μm thickness. The glass plates were not treated to induce any alignment. The cell was placed under the objective of a polarizing microscope in a micro-Raman spectrometer. The sample could be illuminated both by the microscope lamp and by an Argon laser light beam coupled to the objective through a semi-reflecting plate. Thus the Argon laser beam could be used as a pump beam to modify the molecular alignment, and the resulting changes in the sample birefringence could be monitored by a TV camera looking at the microscope image. The argon laser beam could also be used to excite the Raman spectrum from the sample; the Raman light emitted in the backscattering configuration was collected by the microscope objective and focussed onto the entrance slit of a triplemate SPEX spectrometer; it was finally detected with photon counting and the data stored in the computer which controlled the spectrometer. Micro-Raman measurements were also performed using a DILOR X-Y optical multichannel spectrometer,[8] which allowed the spectra to be taken at much lower incident power levels for a given signal-to-noise ratio, and using also the Krypton lasing wavelengths. This was very useful to obtain the intrinsic Raman spectra, i.e. spectra in which the polarization characteristics of the Raman lines were not influenced by the excitation light itself.

The temperature dependence of the molecular relaxation following optically induced molecular realignment was studied in a pump-probe configuration: a small He-Ne laser beam was passed through the sample cell in a crossed polarizers configuration. An Argon laser beam with calibrated variable power could also illuminate collinearly the sample area crossed by the He-Ne laser beam. The transmitted intensity at 633 nm was filtered by the monochromator and detected with photon counting. At the same time a small fraction of the incident He-Ne beam was detected with a photodiode for normalization of the transmitted light signal. In performing studies of transmission of light in the crossed polarizers configuration, care must be given to minimize the spurious effects due to light scattering (either static scattering in a polydomain birefringent medium, or dynamic scattering connected with director fluctuations in a nematic phase). It is not sufficient to use small thicknesses. We used spatial filtering of the transmitted light, by focussing it onto the entrance slit of the monochromator which was set at a width of 100 μm, after passing it through two pinholes (2000 μm and 500 μm diameter, separated by about 15 cm). Using this arrangement the scattering signal was almost totally eliminated, so we could measure reproducibly the induced birefringence effects. Finally, the sample cell was placed in a small optical oven, in which temperature could be controlled within 0.1 °C.

THE DEPOLARIZED RAMAN SCATTERING EXPERIMENT[9]

The power spectrum of the Raman scattered light is related to the Fourier Transform of the correlation function of the molecular Raman polarizability tensor:

$$I_{ij}^{\nu}(\omega) = FT < \alpha_{ij}^{\nu}(t)\alpha_{ij}^{\nu}(0) >< Q^{\nu}(t)Q^{\nu}(0) > \qquad (1)$$

where $i, j = x, y, z$ refer to the components of the tensor α^{ν} in the molecular frame, where

$$\alpha^{\nu} = \left(\frac{\partial\alpha}{\partial Q^{\nu}}\right)_0$$

and Q^{ν} is the normal coordinate of the Raman mode. The polarizability tensor for a totally symmetric vibration can be decomposed into a sum of two terms:

$$\{\alpha\} = \frac{1}{3}Tr\{\alpha\}\{I\} \pm \{\beta\} \tag{2}$$

where $\{I\}$ is the unit tensor and $\{\beta\}$ is the traceless, anisotropic part of the polarizability ($\mathrm{Tr}\{\alpha\} = 0$ for a non symmetric vibration). The first term of Equation (2) is independent of the orientation of the molecule so we can split the scattering correlation function into an isotropic part and into an angle-dependent term containing $\{\beta\}$. Experimentally we obtain that decomposition using the so- called VV-VH experiment in which the Raman light is collected through an analyzer oriented in parallel (VV) and normal (VH) directions relative to the polarization of the field incident on the sample. We must average over all the molecular orientations and, for an isotropic system we have:

$$< I^{\nu}_{iso}(\omega) >= \frac{1}{9}Tr\{\alpha\} =< I^{\nu}_{VV}(\omega) > -\frac{4}{3} < I^{\nu}_{VH}(\omega) >$$

$$< I^{\nu}_{ani}(\omega) >=< I^{\nu}_{VH}(\omega) > \tag{3}$$

In strongly anisotropic systems such as nematic liquid crystals, the orientational average will involve the angular distribution function $f(\cos\theta)$ of the molecules, where θ is the angle between the main axis of the molecule and the nematic director, assuming a monodomain sample. In the laboratory frame of reference X, Y, Z the incident laser propagates in the X direction and it is Z-polarized. We observe the scattered light in backscattering mode by analysing the depolarization ratio beetween the intensity of the Y-polarized scattered light (I_Y) versus the Z-polarized one (I_Z). Depending on the molecular distribution, I_Y, I_Z and their depolarization ratio R assume different values. In an isotropic system it easy to see that:

$$R = \frac{I_Y}{I_Z} = \frac{3\gamma^2}{45\alpha^2 + 4\gamma^2}. \tag{4}$$

having defined the anisotropy parameter $\gamma = (\alpha^{\nu}_{z} - \alpha^{\nu}_{x})$ and $\alpha = 1/3(Tr\{\alpha\})$.

The value of R yields information on molecular symmetry and, since we are dealing with *polarizability* fluctuations R will depend also on the local ordering around a given molecule.

Now let us examine a mesogenic system in which the nematic director is parallel to the Z axis of the laboratory frame. In this case it is possible to find an expression for R in terms of α, γ and the order parameters $< P_2 >$ and $< P_4 >$.

In the isotropic phase, where $< P_2 > = < P_4 > = 0$, such an expression reduces to Equation (4), but at the clearing point R jumps discontinously to a value connected to the establishment of long range order.

In a monodomain oriented nematic, following Jen *et al*[10] we can define the three depolarization ratios

$$R_1 \propto \frac{<\left(\alpha^{\nu}_{yz}\right)^2>}{<\left(\alpha^{\nu}_{zz}\right)^2>}, R_2 \propto \frac{<\left(\alpha^{\nu}_{zy}\right)^2>}{<\left(\alpha^{\nu}_{yy}\right)^2>}, R_3 \propto \frac{<\left(\alpha^{\nu}_{yx}\right)^2>}{<\left(\alpha^{\nu}_{xx}\right)^2>} \qquad (5)$$

A measurement of these three ratios is in principle necessary to completely determine the system. This implies that three separate experiments must be performed, using both homogeneous and homeotropic alignment. However, for a strongly uniaxial Raman tensor, the order parameters $< P_2 >$ and $< P_4 >$ can be obtained by determining only R_1 and R_2. For good homogeneous alignment, generally $R_1 \cong 0.1$ and $R_2 \cong 2 \div 3$ at the low end of the nematic temperature range.[10]

RESULTS

Raman spectroscopy

Since the main purpose of this work is the study of photoinduced effects on molecular orientation and their temperature dependence, it is crucial to establish some procedure to quantify the level of laser-induced heating in our PA4 sample. This is particularly important in the region close to the glass transition. In order to do this we chose what we believe to be a fairly new procedure[11], which uses the expected behavior of the degree of depolarization of a totally symmetric vibration at the nematic-isotropic transition temperature of a low molecular weigh LC. In most nematic mesogens in their isotropic phase, $R = 0.3 \div 0.4$. At the clearing point T_c, R should jump discontinuously to the totally depolarized value of unity, as expected for a polydomain, non-aligned birefringent sample. This jump is our internal temperature sensor. At incident powers of 10 mW (cylindrical focussing), the

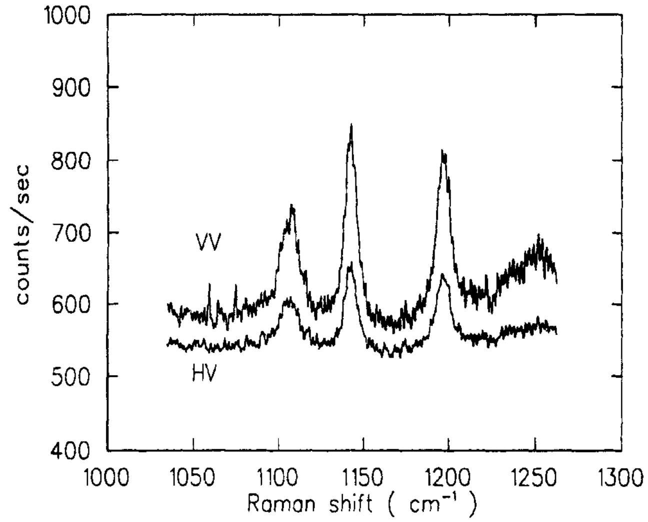

Figure 1: Polarized Micro-Raman spectra of PA4 in the aromatic ring deformation mode range. Incident power < 0.5 mW, integration time 20 s, $\lambda = 674$ nm

transition takes place at the proper temperature and is reasonably sharp. From this we deduce that the real sample temperature is close (within 1 °C) to the measured temperature.

In fig. 1 we show a typical Raman spectrum of PA4 in the spectral region of the C-H aromatic ring deformation modes in the two polarizations VV and HV. The spectrum was obtained using the 674 nm krypton line which is spectrally far from the range where photoisomerization processes may be active. Thus such spectra should not be modified by the excitation beam. The spectra were found to be fairly independent of temperature and phase.[12] Their polarization characteristics depended strongly on position in the sample: we found values for R ranging from 0.3 to 0.7 in a virgin sample, i.e. a sample which had not been illuminated with the Argon laser pump beam. We want to focus our attention on the central peak at 1140 cm^{-1}; it has a clean, nearly lorentzian lineshape, and we have used it in the following analysis. The peak corresponds to a totally symmetric vibration in the aromatic rings of the azobenzene side chain; thus its degree of depolarization can yield information on the degree of ordering and eventual reorientations of such chain.

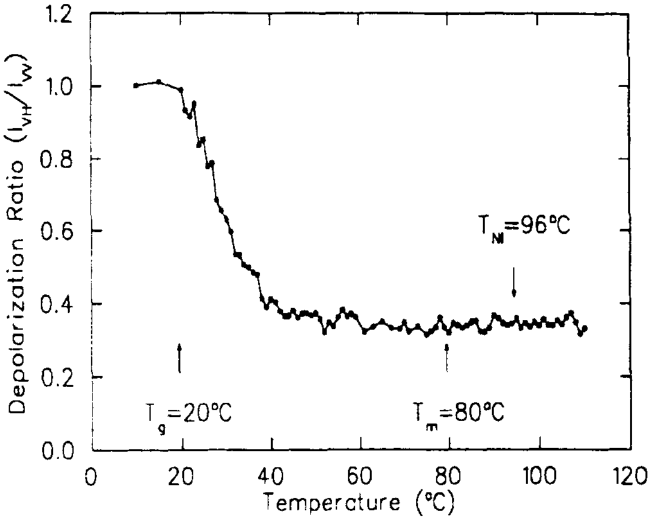

Figure 2: Behavior of the Raman depolarizarion ratio of the peak at 1140 cm^{-1} as a function of temperature.

In the isotropic phase, we found, independently of excitation power and wavelength, that the degree of depolarization was constant at the value of 0.34. From this value, assuming uniaxiality for the corresponding Raman tensor element, we could obtain the value **a** = 0.03 for the diagonal elements xx and yy (i.e. corresponding to a polarizability modulation in the plane perpendicular to the main symmetry axis of the molecule). With such small value of **a** only two geometries are necessary to determine the order parameters $< P_2 >$ and $< P_4 >$ in the aligned mesophase or glassy phase, namely those in which we measure the depolarization ratios R_1 and R_2. If the Raman depolarization ratio is measured using the 488 nm excitation, we may expect some effects on R due to the eventual laser induced molecular reorientation processes.

In fig. 2 we report the behavior of the degree of depolarization exhibited by the 1140 cm^{-1} mode of PA4 as a function of temperature.

Clearly there is no trace of the expected discontinuity at $T=T_c$: The degree of depolarization seems to ignore the phase transition, and keeps its isotropic phase value until about T_g + 20 °C, whereupon it starts to grow till it reaches the value

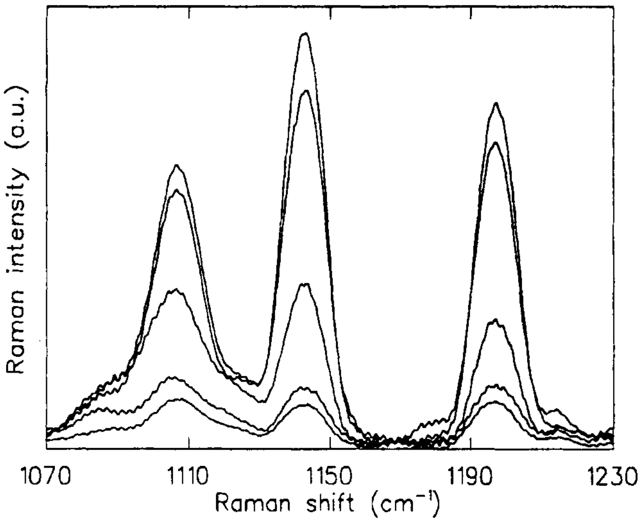

Figure 3: VV spectra taken at different sample angles: θ increases from 0° to 90° as the intensity grows

of about unity. Upon heating the curve is reproduced. This behavior is clearly anomalous and totally different from what was observed in low molecular weigh LC's.[11] As we shall see in the following paragraph, it is to be attributed to molecular reorientation induced by the excitation laser beam, coupled with changing molecular relaxation times upon approach of the glass transition.

If the 488 nm beam can influence molecular reorientation, the effect can be studied more specifically in a pump-probe experiment, by exciting the Raman spectrum using the 674 nm Krypton line and looking for changes in R due to excitation with the polarized pump light in the blue-violet spectrum.

We found that R could be strongly altered by the pump beam, and that the effect depended on the relative orientation of the molecular symmetry axis and the polarization vector of the pump beam.

In figs. 3 and 4 we show some results, obtained by rotating the sample about the direction of propagation of the pump beam, after exposure to z-polarized 476.5 nm light (300 mW/cm^2 estimated power density, 60 s exposure, T = 22 °C). The rotation angle is defined relatively to the direction of polarization of the pump beam.

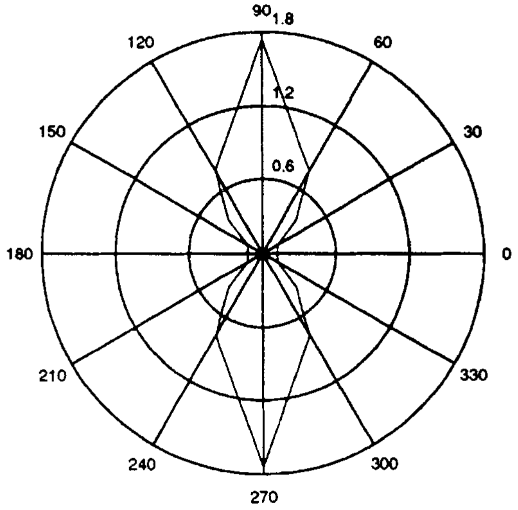

Figure 5: Polar diagram of the Raman spectra of figs. 3 and 4

function of pump light excitation power and temperature, by monitoring the induced changes in the 633 nm light of a small He-Ne laser transmitted by the sample in the crossed polarizers configuration. In what follows we shall give a brief summary of some of our results (a more complete report is in preparation).

We have studied the transmission changes upon excitation with 488 nm light in two different configurations of the crossed polarizers: configuration a, in which the polarization vector of the pump light was at 45° relatively to the crossed polarizers; b, in which it was at 90°.

In order to interpret the polarization behavior of the Raman data of fig. 2, we have first verified the effect of the pump light on sample birefringency as a function of temperature. We found substantial effects both on the value of the clearing point temperature T_c, and on the mesoscopic structure of the phases. For no pumping, the intensity of transmitted light increased sharply at T_c, but it did not remain constant as the temperature was lowered throughout the nematic phase, indicating some changes on the mesoscopic level in the temperature range (~ 60 °C) where anomalies in the specific heat had been observed.[7] The transmission versus temperature behavior changed dramatically upon switching the pump light on.

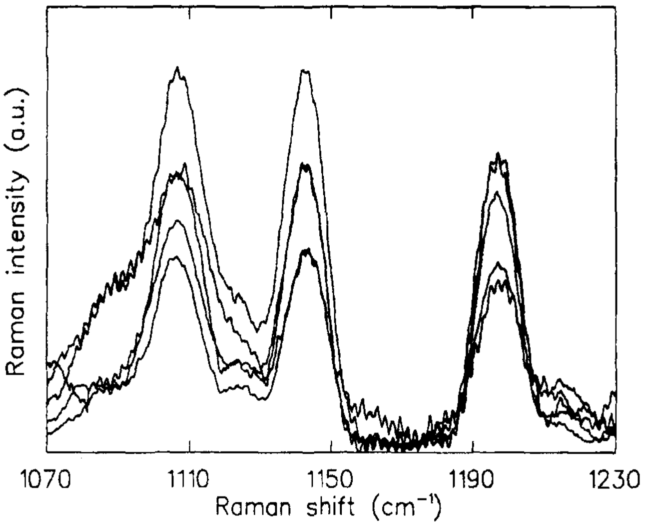

Figure 4: HV spectra: here θ increases from 0° to 90° as intensity decreases.

The degree of depolarization R varies considerably as the sample is rotated, indicating strong molecular alignement, typical of a well aligned, monodomain sample.

The effect can be better visualized in the polar diagram of fig. 5, where it is apparent that the pump beam induces a molecular reorientation perpendicular to its polarization direction. Since for $\theta = 0°$ we are measuring the R_1 depolarization ratio, and for $\theta = 90°$ we measure the R_2 ratio, from the obtained values we can calculate the order parameters $< P_2 >$ and $< P_4 >$ for the molecular alignment induced in the sample area illuminated by the pump beam. The obtained values are 0.68 and 0.17 respectively. Thus the pump beam at 488 nm can quite efficiently produce a homogenous monodomain aligned zone in the glassy LCP.

Induced Birefringence

On a macroscopic level, the alignment effects can be easily observed with a polarizing microscope. As the pump 488 nm light is turned on, the polydomain, birefringent domain patterns quickly disappear, to yield a homogenous dark area in the crossed polarizers configuration. We have studied these effects more quantitatively as a

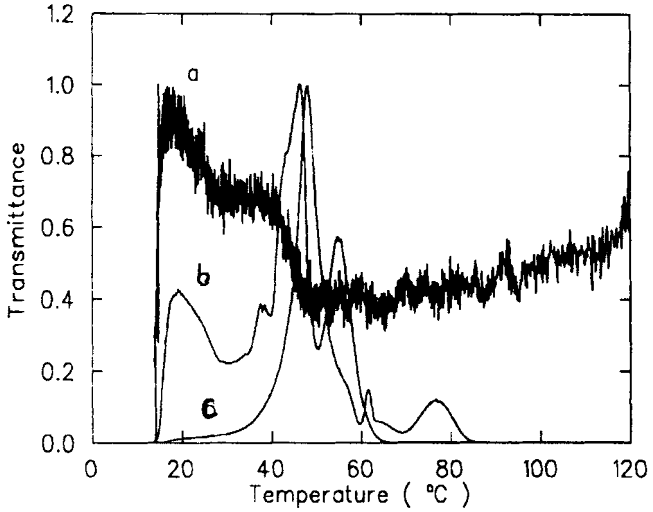

Figure 6: Transmittance vs. temperature for three different optical pumping powers a) 1500 mW/cm^2, x 10^3; b) 300 mW/cm^2; c) 120 mW/cm^2.

In fig. 6 we show the data for three different pump power levels. The first effect is the lowering of the clearing point temperature, i.e. under the action of the pump light the sample remains isotropic well into what should be the nematic phase. The other effect is the different temperature dependence of the birefringency, which seems to be mainly determined by the external perturbation. We have observed that two different types of effects determine the value of the transmittance at a given temperature and pump level: one is the already reported depolarization of the incident probe light; this is the main effect observed in configuration b. In configuration a, besides this effect we also note a rotation of the plane of polarization of the incident probe beam, i.e. the sample behaves as a retardation phase plate. The competition of these two effects probably determines the oscillatory behavior in the transmittance observed at low pump levels. We have followed the pump light effects up to power densities of about 1600 mW/cm^2. The transition temperature Tc steadily decreases with increasing power, until the glass transition temperature is reached. Thus with a sufficient pump power the nematic phase is frustrated over the whole temperature range, down to the glass transition range.

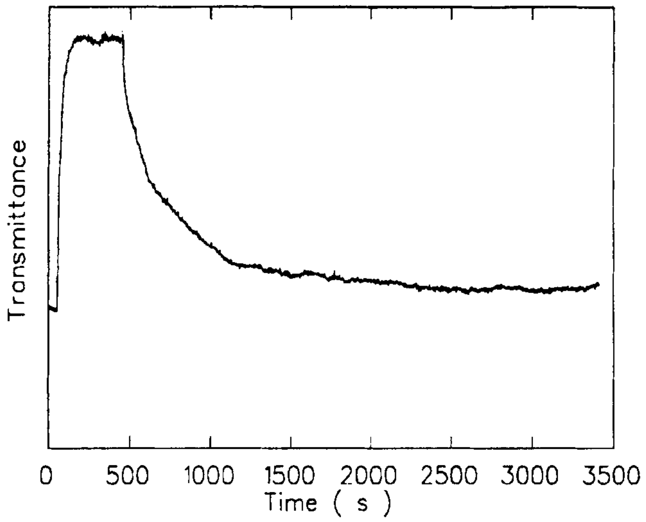

Figure 7: Transmittance change vs time caused by pumping at 488 nm and 270 mW/cm^2; on at 50 s off at 450 s; T= 26°.

Such results are also confirmed by our studies of the time behavior of induced birefringence at different pump powers. In fig. 7 we show the time behavior of the transmission in configuration a, obtained at T= 26°. Note the large change in transmittance caused by the pump light,which actually we found to be even larger, depending on the initial value, which varied according to thermal and optical history of the sample. Actually the overall behavior depends strongly on the history of the sample, the power density and the temperature. We should also note that the overall change of transmittance seems to be more related to the pumping *energy*, altough the time dependence varies strongly with the power density. We shall coonclude by discussing very briefly the temperature behavior of the relaxation times when the laser pump is turned off. Firstly, let us note that the signal does not go back to the original value, but instead saturates at a level which increases with decreasing temperature. For $T < T_g$, such metastable state is of long duration (no quantitative upper limit has been established yet, but writing on our samples was preserved for weeks). This makes this material a good candidate for optical memory devices, especially if modified so that its glass transition temperature is increased somewhat.

Another noteworthy feature we observe is the divergence of the relaxation time as $T \rightarrow T_g$. Our temperature resolution was not sufficient to probe the critical behavior at the glass transition, but our results indicate that this may be a simple method to study the dynamics of the glass transition in fragile glass forming systems.

CONCLUSIONS

In this paper we have shown that photoisomerization in the azo-side chain can be quite an efficient method to control molecular alignment on the microscopic and macroscopic scales. In the PA4 molecule the pump light can control the mesogenic potential and the interplay between light-induced effects and the dynamics of the glass transition causes many technologically interesting optical effects .

Our data explain the previosly puzzling behavior of the degree of depolarization of fig.2; R does not change because under the influence of the excitation light at 488 nm, always at much higher power densities than 400 nW/cm^2, the nematic phase is frustrated all the way down to the glass transition. At this point the dynamics of the glass transition changes the equilibrium between the isotropizing effect of the light and the nematogenic tendency of the azo-chains. Theresults could be either the formation of disordered birifringent domains, or the formation of an oriented monodomain structure. This would depend on the pump power level. In either case R should increase considerably as T_g is approached.

When the Raman spectra are excited in the red, where the photo-isomerization processes responsible for molecular re-alignment cannot take place, these is no influence of the excitation light on the spectrum. Under the action of the blue-violet pump light, the molecules in the glassy phase reorient perpendicularly to the pump polarization vector. If the pump power is sufficiently strong, this realignment forces the separate birefringent domains to align also, so that a monodomain zone is formed. In such area the method of Jen et al[10] may be applied; in our case we obtained R_1 and R_2 by simply rotating the sample relatively to the propagation axis of the pump light (which was coaxial with the probe light).

Finally, the behavior of the induced birefringence relaxation upon approach of the glass transition indicates a divergence in the relaxation time. This may make glassy PA4 a very efficient system to study optical memory effects, certainly on the micron scale, and possibly down to the nanoscale using proximal field optical pumps.

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