

# Optical control of structural morphology in azobenzene containing polymeric liquid crystals

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We present a study of photoinduced transitions occurring in a low  $T_G$  liquid crystalline polymer containing the azobenzene group in the side chain. The structural phase of this material can be optically switched between the glassy, nematic and isotropic states. We show the equivalence of light and temperature in causing these effects, promoting this material as a tool in the investigation of structural relaxation at transitions in confined geometry and fast temperature variation as in the case of the optically induced quenching that we report. The results allow us to propose also alternative writing methods for the application of these materials to high density optical memories.

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## I. INTRODUCTION

Azobenzene containing polymers have been the subject of intense research for many years now, especially due to their potential applications to recording systems and high density re-writable optical memories [1]. The azobenzene moiety and its *trans-cis*-photoisomerization cycle have been found to yield a bewildering variety of interesting optical, mechanical, and structural effects (for most of the relevant literature up to 2002, see [2]), most of which with the potential to be used in concrete applications. In this framework of particular interest are side chain polymers containing the azobenzene moiety in the side chain. These systems are often mesogenic, and the resulting interplay between the photoinduced effects and the mesogenic intermolecular potential with its long range orientational ordering characteristics both increases the number of photoinduced effects and amplifies the optical response, yielding materials with extremely high sensitivity to optical writing. The azobenzene group orientation and shape in turn influence the local main chain conformation, whose dynamics takes place over a longer time scale, leading to useful memory effects. Finally these materials are glass formers, and many have glass transition temperatures close to ambient temperature. All this yields systems of high complexity, with a phenomenology which depends on many parameters and is also history dependent; this may explain why after so many years the literature abounds of quantitative and often repetitive experimental work and modeling, but applications rarely go beyond the demonstration stage.

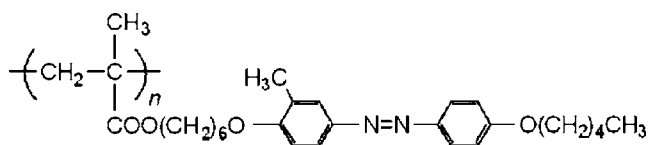
In any case most of the photoinduced effects which are interesting for applications are well understood by now on the qualitative level. Azobenzene containing polymers exhibit two effects applicable in optical data storage: photoinduced birefringence (PIB) and photoinduced isotropic phase transition (PIPT). Photoinduced birefringence has been widely investigated (see, for example, [3], and references therein): such a phenomenon is obtained by a selective excitation with polarized light which isomerizes all chro-

mophores oriented along the pump beam polarization direction. The result of the anisotropic optical pump is an overall molecular reorientation perpendicular to the polarization direction, with specific differences in behavior depending on the excitation power and wavelength. The resulting order is effectively in-plane uniaxial; however we should remark that, although most of the attention has been given to the in-plane reorientation phenomena, PIB involved also out of plane reorientation, yielding sometimes strongly biaxial systems [4–6]. Another interesting effect is the photoorientation due to pumping with unpolarized light, again with differences depending on the wavelength [7]. There is also evidence that the reorientation process when analyzed more closely reveals sometimes unexpected complexities. For example, we have shown [8] that under the action of the pump light the system first passes through a local isotropic phase before going to the photoinduced birefringent phase; subsequently this locally induced phase expands spontaneously (i.e., after the pump light has been turned off). This indicates the important role played by the lowering of local viscosity and/or the increase of the available volume which accompanies the *cis-trans-cis* photoinduced cycling, and the amplification role due to the nematic potential.

While PIB has been extensively studied PIPT has attracted less attention. The second phenomenon is due to the change in size and shape of the azobenzene group undergoing the *trans* → *cis* isomerization. The presence of the smaller and nonmesogenic *cis* isomer reduces the nematic potential and this may result in the frustration of the liquid crystalline phase [3,9,10]. While PIB is studied particularly in high  $T_G$  polymers, which are deemed to ensure the stability of stored information, PIPT is observable in low  $T_G$  azo polymers which exhibit a liquid crystalline behavior. In this latter class molecular dynamics is ruled by an interplay between its liquid crystalline and polymeric nature, and their viscosity and mechanical properties are very sensitive to the action of light [3].

Independently of its potential applications PIPT is also of some fundamental interest. It provides one of the few examples of optically induced phase transitions, which is of some general interest since in this case the transition takes place isothermally, without any modification of the chemical

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FIG. 1. Molecular structure of *Pma4*.

composition of the material (contrary, for example, to the case of lyotropic systems).

Their photosensitivity allows the study of relaxation processes in the neighborhood of the glass transition isothermally, with a variety of probes which correspond to the many photoinduced effects related to the *trans-cis*-photoisomerization, and which can cover quite a large range in the space-time correlators related to the structure and dynamics of these glass formers (for some examples, see [11]). These matters are particularly important when the extension to the nanoscale is of interest, both fundamentally to study complex molecular systems in restricted geometries [12,13], and for applications to very high density optical memories [14]. For instance, how does the role of the mesogenic potential change when the system size becomes smaller than the liquid crystalline coherence length? Or again, when will the nematic potential cease to be an amplification factor, and become an obstacle, for the writing efficiency if nanometric spatial resolution is the goal? In order to answer these questions it is important to study in detail the light temperature *phase* diagram (for brevity we shall denote the out of equilibrium morphology with the word *phase*), using a subset of the many effects due to photoisomerization which may be particularly relevant to probe the molecular order and its changes, in a reference material system which can be prepared in a well defined and reproducible initial state. For this

we studied a low  $T_G$  azo-LCP (liquid crystalline polymer) which we prepared in the standard fashion, but also, in the isotropic glassy phase obtained by a very fast quench in liquid nitrogen. We found this glassy azo-LCP a particularly good reference system for our studies of the light temperature phase diagram and the associated slow relaxation dynamics.

## II. MATERIAL AND METHODS

We focused our attention on an azo-methacrylate having a glass transition at room temperature whose chemical structure is shown in Fig. 1, referred henceforth with the acronym *Pma4*. Such material belongs to the well studied family of azo-polymers which present a general similar behavior, with some interesting differences connected to the specific chemical formula [15].

According to differential scanning calorimetry measurements [15], the material undergoes a glass transition at  $T_g \approx 21^\circ\text{C}$  followed at a higher temperature by the appearance of a nematic phase which persists up to the clearing temperature  $T_c$  observed at approximately  $84^\circ\text{C}$ . *Pma4* was found to yield a photoinduced birefringence with high stability and sensitivity [14,16] even on a nanometric scale. We prepared samples with different thickness: thin films (40–100 nm) using the Langmuir Shaeffer technique [17] and bulk samples (1–3  $\mu\text{m}$ ) made by sandwiching a drop of material, formed by the melt of the polymer powder, between two glass slides. However, after the preliminary measurements, we restricted our study to a fixed sample thickness, since we found that the photoinduced molecular dynamics, in those thickness ranges, rescales approximately with the optical absorption, i.e., with a Lambert Beer behavior as a function of sample thickness.

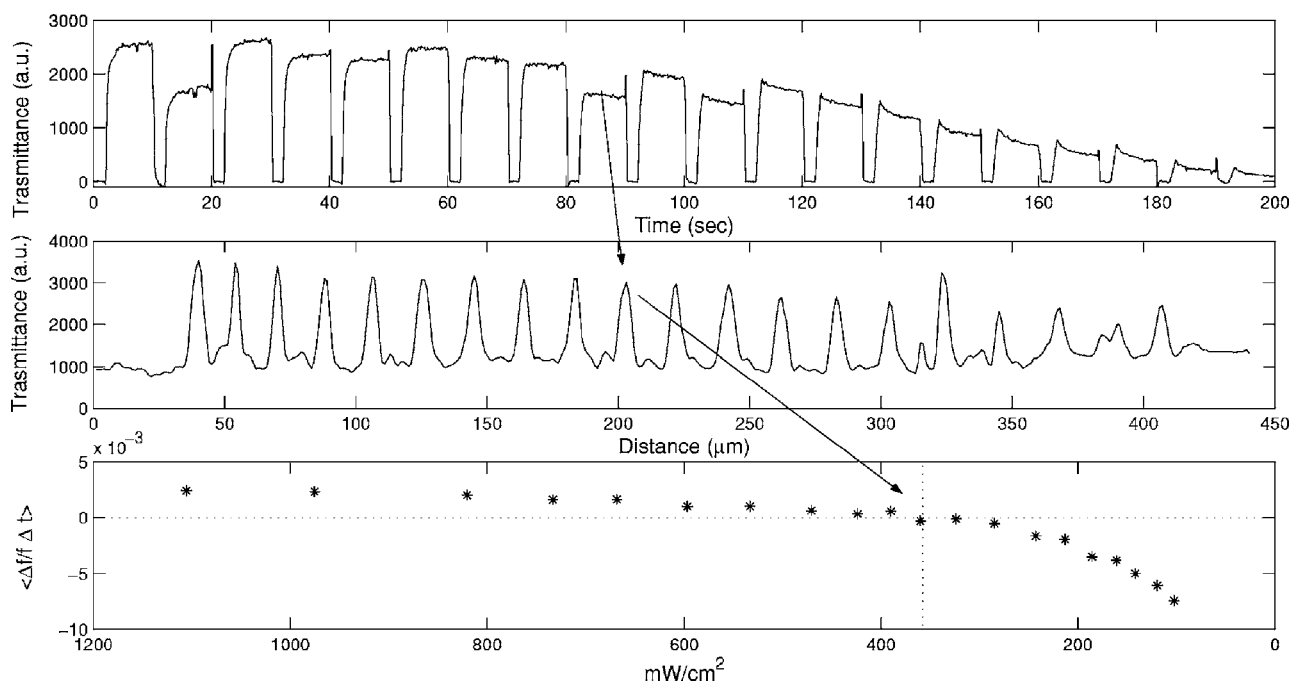


FIG. 2. Upper plot pump probe birefringence measurements at room temperature, spots profiles, and means of the logarithmic derivative of relaxation.

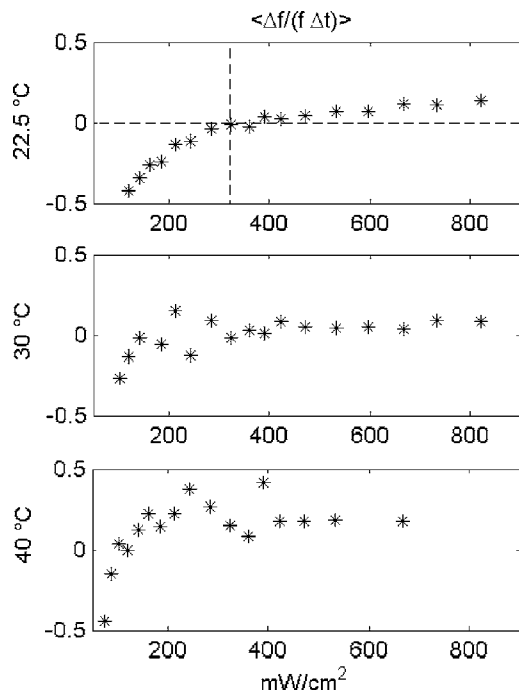


FIG. 3. Slopes of birefringence signals as function of pump energy at different temperatures.

The study was finally carried out on the bulk samples since the higher thickness amplifies the birefringence signal improving the measurements contrast and avoids and/or minimizes possible effects due to the surface.

Photoinduced birefringence measurements were performed with an experimental set up based on a polarizing optical microscope. The use of a microscope to probe the photoinduced effects is an important characteristic of our experimental set-up; such a choice was made so that a careful

analysis of the spatial homogeneity of the samples and of the photoinduced effects could be performed. The complexity of the material, in fact, leads to irreproducibilities which are connected both to the thermal history of the sample and to the morphology of the liquid crystalline phases. Thus a quantitative study requires a sufficient space resolution to identify what in the sample response is due to the intrinsic behavior and what might be due to morphological and history dependent inhomogeneities on the mesoscale. The experiments were made using a pump-probe configuration, with the writing and reading beams being provided, respectively, by the 488 and the 633 nm lines of Ar<sup>+</sup> and He-Ne lasers. The beams were made collinear using a semireflecting plate and were focused on the sample through the 40x microscope objective. A confocal geometry was employed in order to clean and reduce the Gaussian profile of laser beams up to a beam-size of FWHM  $\sim 0.5 \mu\text{m}$  by focusing the beams on a  $25 \mu\text{m}$  size pin hole placed in the image plane. Both laser beams were controlled by acousto-optic modulators, to control intensity and exposure time of pump laser and to acquire the probe signal with lock-in techniques. Birefringence was measured in the transmission mode by the measurement of the depolarization ratio of the probe laser whose plane of polarization was rotated by  $45^\circ$  with respect to that of the polarized writing beam in order to maximize the birefringence signal. A band pass filter (550–800 nm) was inserted after the analyzer to remove the pump light from photodetector. The experimental setup also contained a highly sensitive charge coupling device camera for imaging and a motorized XY stage with  $\mu\text{m}$  spatial resolution.

### III. PUMP-PROBE EXPERIMENTS

The pump-probe experiments were made as a function of temperature and writing beam intensity on a sample previ-

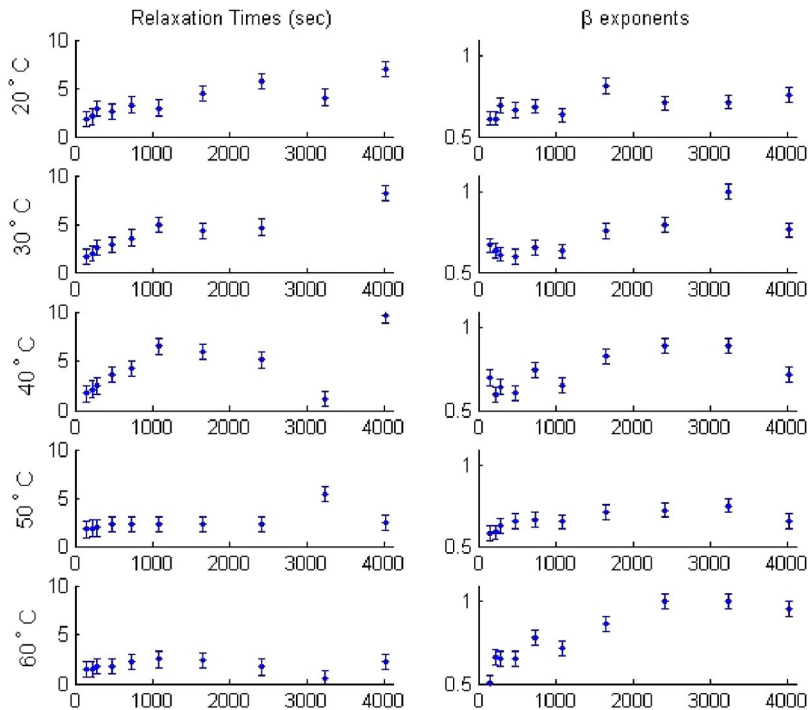


FIG. 4. (Color online) Exponent  $\beta$  and relaxation time  $\tau$  as function of pump energy at different temperature. The error bars were estimated as the average standard deviation observed in the reproducibility tests. These errors arise from the spatial inhomogeneity of the sample and are greater than those obtained from data fitting (therefore not shown).

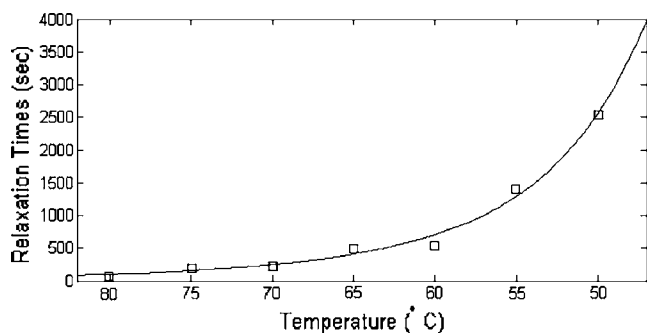


FIG. 5. Relaxation times of nematic recovery as function of temperature (square points) and best fit with the Vogel Fulcher function  $\tau = \tau_0 \exp(T_a / (T - T_0))$  (solid line) with parameters  $T_a = 1150$  K and  $T_0 = 235$  K.

ously treated by thermal quenching. The thermal quenching induces a vitrification of the material without a passing thought to the nematic phase which was found to be a source of spatial inhomogeneity and irreproducibility in the data. The adopted thermal protocol consisted of an annealing of the sample at  $T = 120^\circ\text{C}$  ( $40^\circ\text{C}$  over clearing point) for 10 min and a subsequent immersion in liquid nitrogen at  $-196^\circ\text{C}$ . After the quenching the sample is left to thermalize at room temperature and then studied. The material, observed with crossed polarizers in a polarizing microscope, appears black and without the usual nematic textures.

Optically written spots of  $\approx 5 \mu\text{m}$  diameter were produced with different laser intensity and the birefringence signal was acquired during and after the optical pump. The profiles of written points were then measured by a back scan. In Fig. 2 we show in the upper graph the plot of the birefringence signal acquired during write action, each time interval 20 sec corresponding to a one-point measure; after that the sample is moved to a new position. The pump light is switched on after 2 sec with a fixed exposure of 1 s as the power density is varied from 100 to 1000  $\text{mW}/\text{cm}^2$ . The middle panel displays the achieved optical profile obtained after 10 points. The data show that the material has a qualitatively different response at high and low pump power. When the sample is pumped with high power densities the birefringence signal continues to increase after the pump is switched off while it decreases in the other case. This behavior has been visualized by measuring the slope of the signal after the optical pumping. This parameter, reported as a function of writing energy density in the lower panel of Fig. 2, was calculated by averaging the logarithmic derivative of the curves.

An energy density threshold  $E_{TH} = 250 \text{ mJ}/\text{cm}^2$  could be defined as the one corresponding to a null slope. It appears that the photoinduced orientation process, produced with energy  $E > E_{TH}$ , has a sort of inertia: the system continues the alignment by itself. Such phenomenon can be only explained by a jump of the system into the nematic phase. Since the pump wavelength (488 nm) is in the spectral range the *trans-cis-trans* isomerization cycles take place with high efficiency; we can infer from our results that such cycles induce a temperaturelike fluidification effect which allows a transition to the lower energy nematic phase, previously frustrated

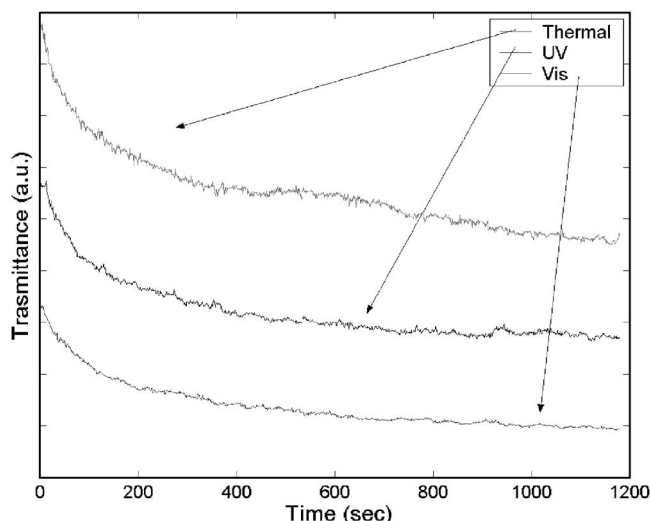


FIG. 6. Transmittance during nematic recovery in the case of thermal, UV, and visible treatments.

by the high viscosity of the glassy phase. The measured energy threshold can be seen as an energy barrier between quenched glassy and nematic molecular configurations. In order to support this assumption the quenched samples were also illuminated with circularly polarized light. Such illumination is supposed to induce no preferential molecular orientation and above the identified energy threshold should be able to provide the system with the required mobility to reach the nematic phase. As a matter of fact we found that exposure to circular polarized light above the energy threshold produces birefringent spots while it has no effect at the lower intensity. The nematic axis directions in the written spots were found to be randomly oriented.

The energy threshold was studied as a function of temperature by heating the sample and using the same measurements protocol. The slopes of birefringence signals are reported in Fig. 3 at different temperatures as a function of pump energy. The energy threshold decreases with increasing temperature as expected. We already stated that the nematic recovery from quenched glassy configuration is allowed by the fluidification that can be obtained both by illumination or high temperature. However, even if the energy threshold decreases its quantitative trend versus temperature was not clearly identifiable. At a higher temperature, as can be deduced from the scattering of data, the slope of the signal does not change sign at a well defined energy density. While below the glass transition the threshold energy is well defined at a higher temperature, the energy barrier and the nematic phase can be overcome both by heating and illumination, i.e., the material is approximately described as an undercooled fluid in the proximity of the glass transition as it should since here  $T > T_G$ . At lower pump energy further differences in the molecular relaxation dynamics can be identified. The system seems to change its nearly glassy character as the pump energy approaches the energy threshold. This is evidenced by the functional behavior with the time of the birefringence signals, which can be interpolated with a stretched exponential function. Series of photoinduced birefringence experiments as a function of optical pump energy (as those shown

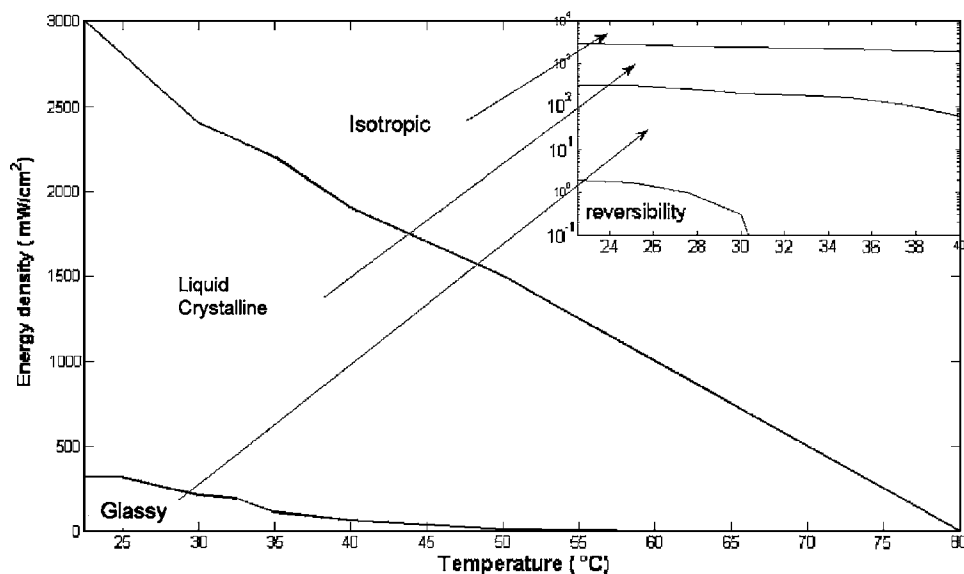


FIG. 7. Phase diagram reporting illumination energy thresholds corresponding to phase transitions, in the upper right corner part of the same diagram is plotted on a logarithmic scale in order to show the reversibility threshold.

in Fig. 2 at room temperature) has been performed at different temperatures. The relaxations of birefringence signals after the optical pump have been fitted with the stretched exponential function ( $I = I_0 e^{-(t/\tau)^\beta}$ ), which yields to the values of the exponent  $\beta$  reported in Fig. 4 as a function of temperature and pump energy. We find  $\beta = 0.66$  at low pump power and temperature (typical of fragile glasses  $\beta \approx 0.4 - 0.6$  [18,19]) while for higher temperatures or pump powers such exponents approach the value 1 typical of a more homogeneous system.

This result together with the previous studies [10] on the photoinduced isotropic transition shows a temperature-light equivalence and the ability of control of the structural morphology of the material by external illumination.

#### IV. LIGHT QUENCHING

In the previous section we showed how illumination of the *Pma4* sample corresponds to a heating process. The photoinduced fluidification decreases its phase transition temperatures and when their value reaches the actual sample temperature an isothermal phase transition takes place. By decreasing or removing the pump light action the system reversibly tends to recover its equilibrium phase at that temperature, which may be seen in this case as a cooling.

Such an effect allows us to explore the possibility of an optical quenching of the material, since light action can be varied much faster than the temperature. Thus, a photoinduced phase transition was induced on the sample and its behavior after the removal of the optical pump was studied and compared with that observed after thermal quenching. The sample after thermal quenching shows no birefringence because the disordered molecular configuration is frozen in the isotropic phase and the liquid crystalline phase is frustrated. However, if the sample is heated above glass transition temperature the molecular mobility increases allowing a system rearrangement, i.e., a recovery of the nematic phase with the appearance of the liquid crystalline texture normally

obtained by a slower cooling. Such an isothermal transition between the isotropic and nematic phase could be observed by the change of the transparency of samples since the quenched sample is transparent while in the nematic phase it appears opaque. The trend of transmittance  $I$  versus time  $t$  in such a process is well fitted by a stretched exponential  $I = I_0 e^{-(t/\tau)^\beta}$  with the parameter  $\beta = 0.66$  characteristic of the polymeric system near the glass transition. The characteristic times  $\tau$  of the nematic recovery, extrapolated by fitting transmittance curves at different temperatures, shows a Vogel Fulcher functional behavior [ $\tau = \tau_0 \exp(T_a/(T - T_0))$ ] implying a divergence as the temperature approaches the glass transition as plotted in Fig. 5. The value of the Vogel Fulcher parameters  $T_a = 1150$  K and  $T_0 = 235$  K agrees with those obtained in our material with different techniques such rheology [20] and Raman and quartz nanobalance [10], and the parameters correspond to a fragility index of about 4.9.

In order to obtain the isotropic phase of the sample more efficiently, we used unpolarized light both in the VIS and UV. Unpolarized light allows us to excite equally the molecules in all orientations while UV light, at the *trans*-molecule absorption peak, increases the *cis*-isomer concentration that is the cause of the fluidification effect. We compared the nematic recovery dynamics in samples disordered both by thermal quenching and by illumination. In the latter case the treatments were performed with an unpolarized light in UV and visible spectral regions. The two photoquenchings were made by first exposing the sample, respectively, to the 360 nm line of a 150 W Hg lamp and to a tungsten filament 150 W lamp for the time necessary to observe sample transparency ( $\approx 20$  min in both cases), and then turning the optical pump off. The sample irradiated with visible light, differently from UV, has a negligible *cis*-isomer concentration as indicated by the absence of the characteristic peak at 450 nm in the absorption spectrum. Figure 6 shows the plots of the sample transparency with time at 80 °C after each treatment. The characteristic times of the three plots are the same indicating that the initial configurations are equivalent. In the first part of the plot (during thermalization at 80 °C, not shown in figure) the sample treated

with UV presented, however, some difference. This discrepancy may be caused by the considerable presence of *cis*-isomers that are absent in the other two cases.

## V. CONCLUDING REMARKS

In this paper we demonstrated how, in low  $T_G$  azo polymers, the optical pumping may be equivalent to the temperature, making these materials interesting for fundamental studies on polymeric systems. Such interest arises from the two main advantages of the use of the light instead of the temperature action: it can be varied faster (up to  $10^6 \text{ sec}^{-1}$ ) and it can be confined in a diffraction limited region or in an even smaller range using near-field optical microscopy. The first point allowed us to obtain an optically induced quenching while the second could permit in the future the investigation of phase transitions in confined and easily controllable geometry.

The phase diagram, shown in Fig. 7, reflecting light-temperature equivalence, has been determined and, in particular, we measured the energy threshold to obtain a transi-

tion from the undercooled glass to the liquid crystalline state.

This transition could be important in the prospective of an application of the materials in optical data storage since it represents a new writing mechanism. The advantage of such a method lies in the sensitivity, since the process has a low energy cost. As pointed out in the paper the quenched glassy state has a higher energy than the liquid crystalline one, therefore the writing process requires just the energy which allows the system to go to its natural ordered phase (it could even be tuned by the quenching rate). The choice of studying rapidly quenched samples, initially because of improved spatial homogeneity and reproducibility reasons, was also found to increase sensitivity and reduce response time. Moreover rewritable data storage can also be obtained from an optical melting-quenching cycle, which erases the photoinduced information. Our future work, however, will be addressed more on the fundamental aspect, since the external control of the structural phase offers some interesting possibilities for the study of polymeric glasses, such as aging processes studied as a function of illumination history or confined phase transitions on different spatial scales.

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