Mol. Cryst. Liq. Cryst., 1999, Vol. 329, pp. 329-337
Reprints available directly from the publisher
Photocopying permitted by license only

Light Induced Polarized Splitting of the Absorption Band of Mesogenic Azo-Polymer

O.V. YAROSHCHUK[a*], L.I. SHANSKII[a], J. LINDAU[b]
and A.G. TERESHCHENKO[a]

[a]*Institute of Physics, NASci. of Ukraine, Prospect Nauki 46, Kyiv, UA-252022, Ukraine and* [b]*Institut fuer phys. Chemie, Martin-Luther-Universitaet, Halle(Saale) 06108, Germany*

It is showed that light induced anisotropy in the azo-polymer films can become apparent in dichroism of the polarized spectra as well as in the polarization depended shift of the absorption bands. The rate of the shift depends on the order parameters of the light induced structure. The highest shift (about 30 nm) for the uniaxial structure induced with non-polarized collimated light was observed. Temperature stability of the value of the shift was studied. It allowed to estimate the activation energy E_a=35 kT$_{\text{room}}$ of polymer's main-chains.

Keywords: light induced anisotropy; azo-polymer; polarization spectroscopy

INTRODUCTION

It is well known that some optically isotropic photosensitive materials acquire anisotropic properties under pumping with collimated polarized and non-polarized light, that are expressed in dichroic absorption and birefringence [1]. Effect of photoinduced anisotropy is wide used for practical purposes

---

* Corresponding author. E-mail: olegyar@marion.iop.kiev.ua

(information recording, LC orientation and others).

As materials that are successfully used for these purposes azo-dye containing polymers are shown up [1-5]. Azobenzene derivatives play the role of absorbing centers. As a rule, they are placed in side chains of polymer molecules. Azo-dye containing polymers are characterized with a high efficiency of anisotropy induction. Light induced birefringence in this materials reaches values as much as 10^{-1} [6].

Anisotropy induction in films of azo-dye containing polymers is associated with orientational alignment of azobenzene derivatives under absorption of collimated light. Azobenzene molecules are strongly dichroic. Direction of an optical dipole moment of azobenzene is approximately coincided with the long axis of the molecule [2]. According to the principle of minimal absorption, in stationary state that is reached under irradiation, azobenzene fragments are oriented perpendicular to the direction of a polarization of the light. This is observed in spectra of the films as polarization of the absorption bands. Besides, the absorption bands can be shifted with respect to their position for non-oriented films. A reason of this phenomena could be effective (for example, dipole-dipole) interaction of the ordered azobenzene fragments leading to the shift of their electron levels and, as a result, to the change of the position of absorption bands. Shift of absorption bands at a direction of the testing light polarization coincided with the direction of azobenzene fragments ordering is much greater then in case of their mutually perpendicular orientation. In this sense, it is said about polarized splitting of absorption band. Such effect was previously observed in LB films of azobenzene derivative [7]. The aim of this work was to investigate the effect of polarized splitting of absorption bands in the spectra of photoaligned structures.

EXPERIMENTAL PART AND DISCUSSION

Structural formula of the used azo-polymer is **[-O-CO-CH(Sp-M)-CO-O-$(CH_2)_8$-]**, where Sp-M is side-chain with spacer **Sp=-$(CH_2)_6$-O-** and azo-dye mesogen **M=-Ar-N=N-Ar-NO_2**. Synthesis is described elsewhere [8]. Photosensitive azobenzene fragment is attached to main chain through the flexible alkyl spacer $(CH_2)_6$, due to which main-chain fragments are capable to change freely its position in space under light absorption and conformational transitions. Strong polar group NO_2 is attached to the end of azobenzene fragment, due to that effective dipole-dipole interaction of azobenzene fragments occurs. Using the methods of DSC, X-ray scattering and polarized microscopy it was found that this polymer has mesomorphic properties at the temperature within 42°-55°C (**Cr** 42°C **Sm_A** 52°C **N** 55°C **I**). At T_c=55°C phase transition from nematic into isotropic state takes place.

Polymer was dissolved in dichloroethane and then spincoated on quartz plate and dried at room conditions during one day. Thickness of the polymer films obtained was 0.05-0.3 μm. As an activation light, irradiation of the high pressure Hg-lamp was used. A parallel beam of light was formed by means of quartz lens in focus of which the source of irradiation was located. This beam was directed perpendicular to a plane of sample. Intensity of irradiation was 5 mWt/cm^2 and time of irradiation was about 10 min. Polarization of light was performed by means of a Glan prism. As a source of testing light low-powered deuterium lamp was used. Spectra were recorded with automated monochromator MDR-12 (LOMO, St. Petersburg, Russia).

An absorption spectrum of a non-irradiated film is presented in Fig.1, curve 1. A band at λ_{max}=375 nm is owing to π-electron excitation in the N=N group of the azobenzene fragments. This band was not changed at a changing of polarization of testing light that was evidence of optically isotropic properties of a non-irradiated film. Curves 2 and 3 in Fig.1 present absorption spectra of the same film irradiated with polarized light. Polarization of a testing beam was respectively parallel or perpendicular to the direction of azobenzene fragments alignment (which is perpendicular to the vector ***E*** of the exciting light). In this case an effective polarization of the band with λ_{max} =375 nm was observed. The ratio of the optical densities of the film for testing beam polarized respectively parallel or perpendicular to the direction of azobenzene fragments alignment was $D_{//}/D_{\perp} \approx 8$. In addition, polarized splitting of the absorption band takes place. The value of splitting is higher for the $D_{//}$ component and is about 5 nm (350 cm^{-1}).

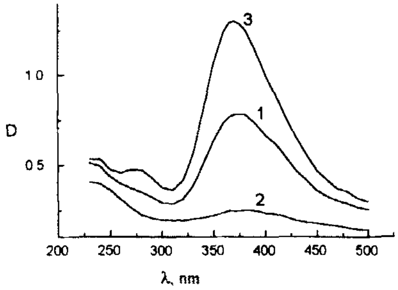

FIGURE 1 Absorption spectra of the azo-polymer film: **1** - non-irradiated; **2, 3** - after irradiation with polarized light, polarization of the testing beam is parallel (**2**) or perpendicular (**3**) to polarization of the irradiating beam.

In Fig.2 absorption spectrum of a non-irradiated film (curve 1) and spectra of the same film irradiated with non-polarized light, when testing beam was polarized in the plane of its incidence (curve 2) and perpendicular to it (curve 3). An exciting beam was falling perpendicularly to the plane of the film, while angle of a testing beam incidence was 45°. It is shown that polarized splitting of the band is very strong in this case. The value of splitting is about 30 nm (2000 cm^{-1}).

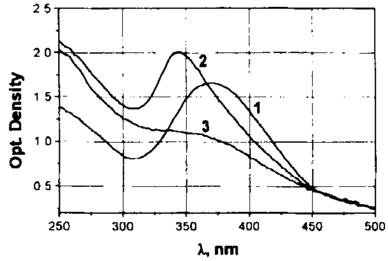

FIGURE 2 Absorption spectra of (1) non-irradiated film and irradiated by non-polarized light: linearly polarized testing beam is (2) in plane of incidence and (3) perpendicular to it. For (2) and (3) angle of testing beam incidence is 45^0.

It is possible to explain the observed large difference of the band splitting under irradiation with polarized and non-polarized light in the next way. It was said above that azobenzene fragments trend to align perpendicular to the direction of polarization of an exciting light. Due to it, different structures with polarized and non-polarized light should be induced. Under the *polarized* light action the double axes structure in the general case should appear. Indeed, here is endless variety of directions perpendicular to vector ***E*** of the light. All they lie in the plane which is perpendicular to the plane of the film and direction of exciting beam polarization (plane α in Fig.3a). In the real case all this directions are not realized with the equal probability. Conditions of the films preparation, state of substrate surface and some other factors are also very important. Due to their influence, isotropy of the distribution of azobenzene fragments in α plane is broken. Nevertheless, aligning of azobenzene fragments in *l*-direction (see Fig.3) is apparently not effective.

This leads to the decreasing of the efficiency of dipole-dipole interaction and, consequently, reduces the rate of the displacement of the absorption band. In the case of irradiation with *non-polarized collimated* light uniaxial structure in polymer film should be induced, because exclusively possible direction l perpendicular to the directions of exciting light polarizations is the direction of the light incidence. Azobenzene fragments have to be aligned in this direction with high ordering efficiency (Fig.3b) providing effective dipole-dipole interaction that results in significant displacement of the maximum of the absorption band.

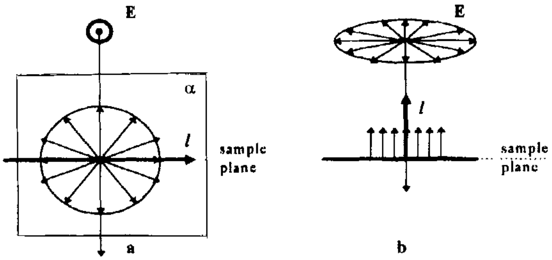

FIGURE 3 Angle distribution of azobenzene fragments under irradiation with polarized (**a**) and non-polarized light (**b**).

Value of frequency splitting depends on phase state of the film. Position of the absorption maximum of an anisotropic film at different temperatures is showed in Fig. 4. In this case anisotropy was induced with polarized light and polarization of a testing beam was coincided with direction of azobenzene fragments ordering. It is seen that position of the maximum in smectic phase weakly differ from that one observed in solid phase. On the contrary, in the nematic phase shift of the absorption band increases. It is evidence of an amplification of azobenzene fragments ordering in a direction which is defined by irradiation. At film heating above T_c polarized splitting disappears.

After short time holding of the film at temperatures a little elevating T_c and the following cooling to the room temperature the polarized splitting of a spectrum was recovered. It showed on memory properties of a medium. After long time treatment of a film in isotropic phase subsequent cooling below T_c did not result in reproduction of polarized splitting effect (see Fig.4).

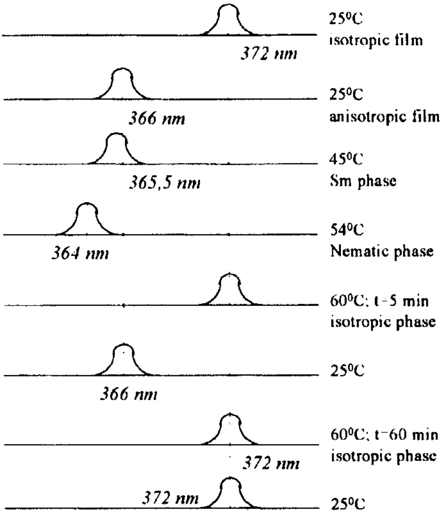

FIGURE 4 Dependence of the value of frequency splitting on phase state of the film.

As more film was heated as less time was needed for erasing of a light induced polarized splitting. The holding time τ_T necessary to reduce in e times the value of the frequency shift for a number of temperatures of isotropic phase was measured. The dependence of this time on the temperature of an isotropic phase is presented in Fig. 5. This curve satisfies well the Arrenius law. On the basis of this curve an activation energy E_a=35 kT_{room} was estimated.

Some microscopic mechanisms may be responsible for observed memory effect. Analogous effect in low-molecular LCs is bound with adsorption of oriented LC monolayer on the substrate surface. This monolayer is regarded to align bulk after cooling of LC cell from isotropic phase[9]. Such mechanism of memory effect in anisotropic films of LC polymers is hardly possible. It is known that aligning of polymer layers with a help of anisotropic substrates is not effective because of a high viscosity. Besides, estimated value of activation energy E_a=35 kT_{room} substantially differs from the value of E_a=70 kT_{room} in case of mechanism of adsorption on substrate surface[9]. More probable is mechanism based on ordering of main-chain fragments. It is described in detail in[10]. Indeed, when film heated above T_c, disordering of the mesogenic azobenzene fragments takes place. In contrast to it, partially aligned macro-chains having a low mobility are capable to keep during some time its orientation. If the film was cooled before destruction of macro-chains ordering, than ordering of azobenzene fragments will be recovered. In the other case aligned state will be fully erased. Estimated activation energy could be assigned to the thermostability of the orientation of main-chain fragments.

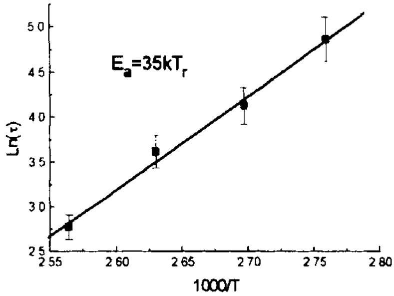

FIGURE 5 The dependence of anisotropy erasure time on the temperature of an isotropic phase of the polymer film.

CONCLUSIONS

In conclusion, induction of anisotropic structures in films of azobenzene containing polymers by means of collimated beams of polarized or non-polarized light leads to polarization of absorption spectra. In addition to difference in intensities, spectra in two orthogonal polarizations differ in spectral position of maximum of absorption band. The greatest shift of absorption band is reached under anisotropy induction by non-polarized light, because in this case ultimate (uniaxial) ordering of azobenzene fragments in selected direction may be obtained. As result, intermolecular interaction between azo-fragments increases leading to electron levels deformation and absorption band shift. Temperature stability of light induced structures may be explained by thermostability of ordered macrochain fragments. Their activation energy is evaluated as E_a=35kT$_{room}$.

References

[1] M. Dumont, S. Hosotte, G. Froc and Z. Sekkat. *SPIE,* **2042,** 2 (1994).

[2] S. Hvilsted, F. Andruzzi and P.S. Ramanujam. *Opt. Lett.*, **17,** 1234 (1992).

[3] J. Stumpe, L. Laesker, Th. Fischer, M. Rutloh, S. Kostromin and R. Ruhmann. *Thin solid films,* **284–285,** 252 (1996).

[4] K. Ichimura, S. Morino, T. Huxur, S. Furumi and H. Akiyama. *Proceedings of IDW'97,* **359** (1997).

[5] W. M. Gibbons, T. Kosa, P. Palffy-Muhoray, P.J. Shannon and S.T. Sun. *Nature,* **377,** N7, 43(1995).

[6] A. Tereshchenko, L. Shanskii, O. Yaroshchuk and Yu. Lindau. *Optics and spectroscopy,* **83,** N5, 808 (1997).

[7] L. Blinov, N. Dubinin, V. Rumyantsev and S. Yudin. *Sov. Opt. i spektroskopiya,* **55,** N4, 679 (1983).

[8] A. Bohme, E. Novotna. H. Kresse, F. Kuschel and J. Lindau, *Makromol. Chem.,* **194,** 3341 (1993).

[9] Y. Ouchi, M.B. Feller, T. Moses and Y.R. Shen. *Phys. Rev. Lett.*, **68,** N20, 3040(1992).

[10] G. Puchkovs'ka, V. Reshetnyak, A. Tereshchenko, O. Yaroshchuk and J. Lindau. *Mol. Cryst. Liq. Cryst.,* 1998 (Accepted for publication).