



Investigation of Photoinduced Dichroism in Polymeric Poly(Methyl Methacrylate) Doped Sudan II Thin Films

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Abstract: Photoinduced dichroism in polymeric poly(methyl methacrylate) doped Sudan II thin films was investigated. Transmitted intensities in both parallel and perpendicular polarization state of the probe beam was recorded using pump-probe technique. Dichroism at different pump beam powers was calculated. Results showed that the transmitted probe beam intensity in the case of parallel polarization state is greater than that of the perpendicular polarization state. The dynamic behavior of the dichroism showed that it increases rapidly when the pump beam is switched on, saturates and then decreases when the pump beam is switched off. The behavior of the dichroism as a function of the pump beam power showed that it increases, reaching a maximum and then decreases with increasing of the pump beam power.

Keywords : Dichroism, Sudan II, Photoinduced.

Introduction and Experimental

Photoinduced *trans-cis* isomerization, molecular reorientation and non-linear optical properties of azobenzene containing systems make them suitable for many optical applications¹. Azobenzene and their derivatives have been extensively studied in the area of nonlinear optical properties, including second-order phenomena such as photoinduced poling and frequency doubling and in third-order phenomena such as degenerate four-wave mixing and photorefractivity². A number of groups have reported on the possibility of azobenzene materials in the areas of photonics and nanotechnology³⁻⁵. The importance of organic and polymeric nonlinear optical (NLO) materials for applications in nonlinear optics is widely recognized⁶. In this regard, and because of their potential utility for optical data storage, azo-chromophore containing polymeric films have attracted much attention. There is considerable interest in initiating and controlling changes in chromophore/polymer compound properties by the use of photoinduced molecular rearrangements of the chromophore molecules which are incorporated in a guest-host system². The phenomenon of anisotropic absorption of light or dichroism was discovered and named by Abbe Haüy, and was described subsequently in greater detail by Brewster⁷. Dichroism is a measure of the orientation of the nonlinear optical chromophore molecules in the host polymer⁸. The phenomenon was soon realized to be related to a combination of the intrinsic dichroism of chromophore molecules and the state of orientation existing in the polymer which leads to oriented absorption of chromophore molecules⁷. An equally important application of linear dichroism (LD) is the determination of sample or molecular structures. To a large extent, the sample structure determines the result of a LD experiment; and this is what makes it possible to extract structural information from a LD experiment⁹. The optical nonlinearities (NLO) of polymer films, that contain azo-compound, have been studied extensively¹⁰⁻¹⁵. To the best of our knowledge, linear dichroism of poly(methyl methacrylate), PMMA, thin films using Sudan II chromophore has never been studied before. In this work, the dichroic behavior of Sudan II/PMMA thin films chromophore was investigated. The relationship between the chromophore chemical structure and dichroism was examined.

Guest-host polymeric samples were prepared from PMMA (MW: 36000) from Acros Organics, and Sudan II (95% chromophore content), from Aldrich. 4gr of PMMA was dissolved in 40ml of tetrahydrofuran

(THF, C_4H_8O) and Ethanol(CH_3CH_2OH) with a molar ratio of (1:1). Sudan II (equivalent to 3 % of PMMA by weight) was then added to the clear dissolved solution of PMMA. The mixture was stirred for 6 hours until the chromophore molecules were fully dissolved. Thin films were dip-coated on transparent glass substrates. Samples were baked in an oven and held at 70 °C for one hour in order to eliminate the residual solvent. Film thicknesses were measured by the Prism Coupling technique and were of the order of 1 μ m. Finally, samples were kept in a desiccator at 22 °C in a dark environment for later investigation.

Absorption spectrum of the Sudan II/ PMMA thin films were measured by a UV-visible spectrophotometer (Photodiode Array Photospectrometer (PDA) Specord S100, Analytik Jena).Fig. 1 shows that the absorption maximum of Sudan II in PMMA prepared samples was at 483 nm.This wavelength is particularly attractive because it lies out of the absorption band for PMMA matrix. Moreover, this absorption wavelength lies within the maximum absorption band of the chromophore in the visible range. Therefore, a laser line at 488 nm provided by an argon-ion laser is quite suitable for our investigation, which provides the most suitable pumping wavelength.

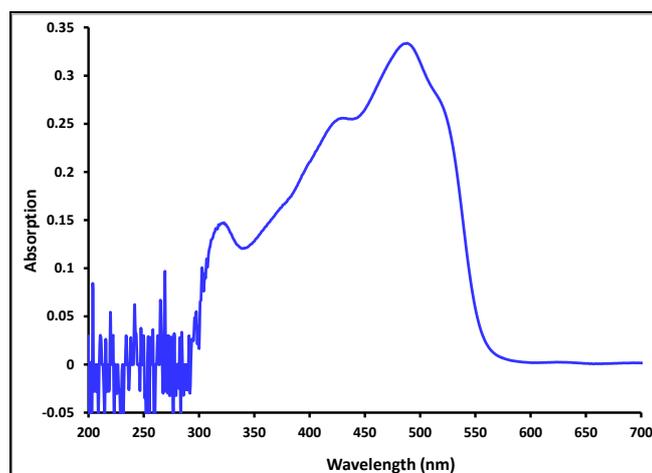


Fig. 1: UV-visible absorption spectrum of Sudan II / PMMA thin film

The photoinduced linear dichroism of the Sudan II / PMMA sample can be measured with the setup in Fig. 2. This set up contains a multi-line Ar-ion laser (543-MAP-A02, MellesGriot) adjusted at $\lambda=488$ nm. Linear dichroism studies require to pump and probe the samples with laser wavelengths identical or close to the maximum absorption of the chromophore and out of the absorption range of the PMMA matrix to eliminate the influence of the laser on the polymeric network. The probe beam linearly polarized passes through the Sudan II / PMMA sample while it is being subject to the pump beam. The power of the probe beam was kept at about 0.3% of the pump beam and (1mm-diameter spot).

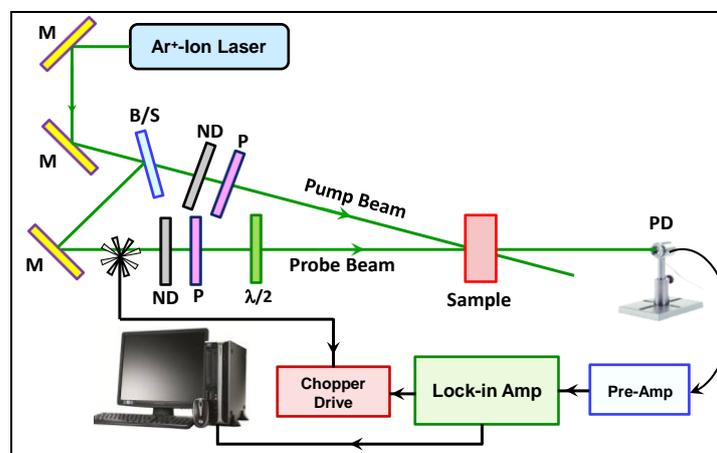


Fig. 2 Experimental set up of the dichroism measurements of the Sudan II / PMMA samples. M: Mirror, P: polarizer, ND: neutral density filter, B/S: beam splitter, $\lambda/2$: half-wave plate, and PD: photodiode.

It is important to use a very weak probe beam where changes in the absorption will be greatest, without influencing the pumping effect of the sample. The polarization of the probe beam was controlled with a half-wave plate and a polarizer. The probe signal of the beam falling on the Sudan II/ PMMA sample and

subsequently on a photodiode is fed to a personal computer through a low noise current preamplifier (SR570, Stanford Research Systems), and a DSP lock-in amplifier (SR850, Stanford Research Systems). An IEEE 488.2 GPIB (National Instruments) card was used to control and record the experimental data along with a special program written in Borland C++.

The chromophore molecules are characterized by anisotropic polarizability and absorption. When they are oriented parallel and perpendicularly to the polarization of the pump light through photoisomerization and molecular reorientation, Sudan II / PMMA thin film becomes dichroic¹. The linear dichroism (LD) of Sudan II / PMMA thin film is defined as the change in absorbance that occurs when the electric vector of the light beam is rotated 90°⁹, and is computed from¹⁶:

$$D = A_{//} - A_{\perp} \quad (1)$$

Where $A_{//}$ and A_{\perp} are the probe beam absorbance parallel and perpendicular to the electric vector of the pump beam, respectively and calculated from [8]:

$$A_{//} = -\log\left(\frac{I_{//}}{I_0}\right) \quad (2)$$

and

$$A_{\perp} = -\log\left(\frac{I_{\perp}}{I_0}\right) \quad (3)$$

Where I_0 is the intensity of the probe beam when there is no sample, and $I_{//}$ & I_{\perp} are the intensities of the probe beam transmitted through the sample when it is polarized parallel and perpendicular to the pump beam polarization, respectively.

Results and Discussion

Linear dichroism

Dichroism measurements were performed by irradiating Sudan II / PMMA with linearly polarized light, while performing *in situ* transmittance measurements with a probe light polarized either parallel ($A_{//}$) or perpendicular (A_{\perp}) to the initial irradiating light polarization. The transmitted parallel and perpendicular components were detected with a detector and a lock-in amplifier electronic apparatus as illustrated in Fig. 2. Finally they were recorded and monitored on a PC.

Photoinduced changes in the transmitted probe beam intensity spectra of Sudan II / PMMA thin films at different parallel polarized laser intensities of the probe beam are plotted in Fig. 3. This figure shows the increasing of transmitted light intensity as a function of the pump intensity.

The transmitted probe beam intensity spectra of Sudan II / PMMA at different perpendicular polarized laser intensities have a similar trend and shown in Fig. 4. Figs. 3 and 4 show that the intensities of the transmitted light are increasing rapidly when the pump beam is switched on.

A saturation state reached after a little increasing. The intensity decreases dramatically when the pump beam is switched off. The isotropic state, which takes a long time, is reached by smooth decreasing. On the other hand, Figs. 3 and 4 show that the intensities of the transmitted parallel polarized laser light are greater than those of the transmitted perpendicular polarized laser light. This may be attributed to the contribution of the dipole moments of the chromophore molecules upon orientation. This contribution is largely affected by the laser light polarization state, in which parallel laser light induces a stronger polar order in the samples in the direction perpendicular to it.

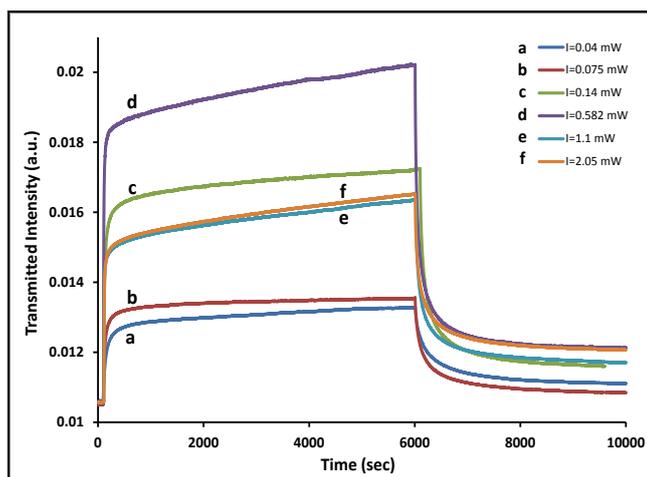


Fig. 3: Transmitted spectra of Sudan II / PMMA thin films at different parallel polarized laser pump intensities ((a): 0.04, (b): 0.075, (c): 0.14, (d): 0.582, (e): 1.1 and (f): 2.05 mW).

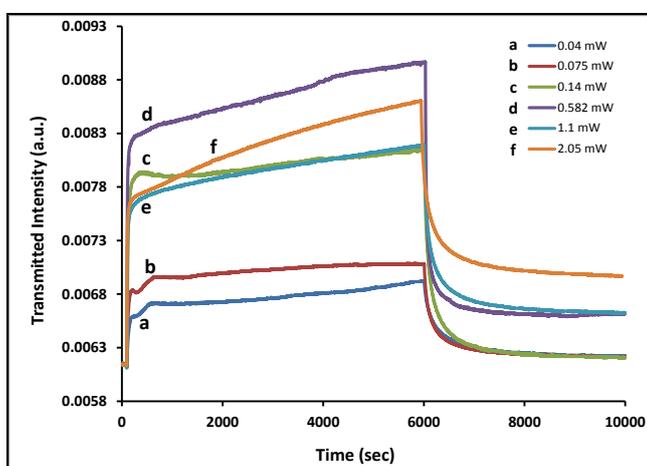


Fig. 4: Transmitted spectra of Sudan II / PMMA thin films at different perpendicular polarized pump laser intensities ((a): 0.04, (b): 0.075, (c): 0.14, (d): 0.582, (e): 1.1 and (f): 2.05 mW).

This leads progressively to a greater increase in the transmitted probe light with parallel polarization. Similarly, a smaller increase in the transmitted probe light with perpendicular polarization is also recorded.

Linear dichroism of Sudan II / PMMA was calculated using Eq.1 over the whole irradiation period (0 ~10000 s) at different laser light intensities: 0.04, 0.075, 0.14, 0.582, 1.1 and 2.05 mW; at 22 °C. The relationship between the dichroism of Sudan II / PMMA thin film and the pump beam intensity is shown in Fig.5.

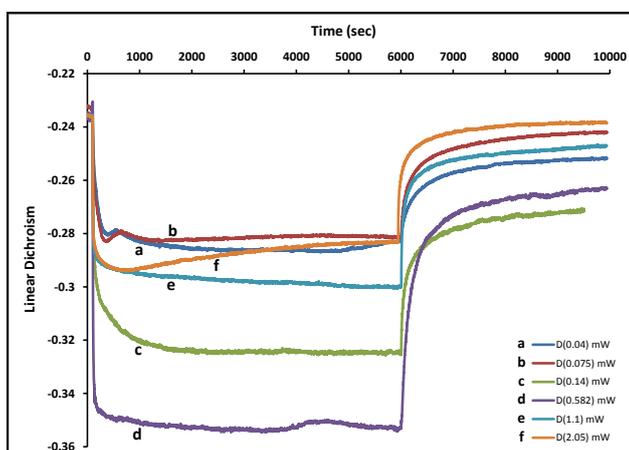


Fig. 5. Linear dichroism of Sudan II / PMMA thin films at different laser intensities ((a): 0.04, (b): 0.075, (c): 0.14, (d): 0.582, (e): 1.1 and (f): 2.05 mW).

Mechanism of photoinduced effect

When irradiated with polarized light, with wavelength inside the absorption band, the chromophore molecules undergo the well-known photoisomerization. The molecular geometrical change from a *trans* state to a metastable *cis* state; that occurs during this photoisomerization process at ambient temperature, quickly return to the more stable *trans* state¹, (Fig. 6 shows *trans* and *cis* isomers of Sudan II chromophore.) This reversible (*trans-cis-trans*) changes can lead to a random change of orientation of the photochromic molecules⁶.

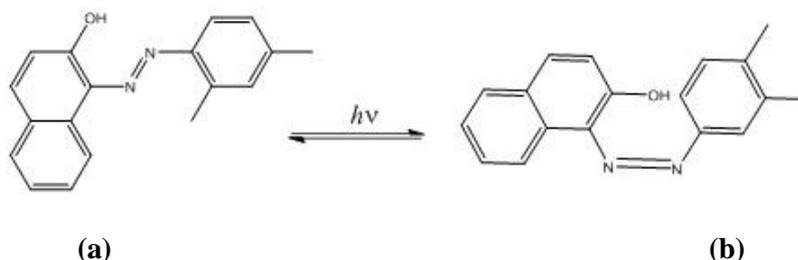


Fig. 6: Isomers of Sudan II molecules; *trans* (a) and *cis* (b)

The probability for a *trans* molecule to be pumped into the *cis* state upon irradiation is proportional to the angle between the long axis of the *cis* molecule and the beam polarization direction¹⁷. The orientation of the *trans* form is defined using polar coordination by the angles θ and φ (Fig.7). The probability, P , for a *trans* molecule to be pumped into the *cis* state is then given by

$$P \propto \cos^2 \theta \cdot \sin^2 \varphi \quad (4)$$

The absorption probability, proportional to $\cos^2 \theta$, leads to a selective depletion of the *trans* molecules parallel to the pump light polarization direction and resulting in having more *cis* molecules. This generates a "hole" in the angular distribution of the *trans* molecules along the pump beam polarization direction¹⁸. The photoisomerization process is more probable when the molecular axis is along the polarization direction of the incident light; this changes the local order of the system and generates anisotropy. This anisotropy is responsible for photoinduced effect such as dichroism¹. Angular hole burning (AHB) leads to a decrease in the absorption in all directions for wavelengths close to the absorption maximum of *cis* forms. Pump light intensity, and the lifetime of the *trans* form plays an important role in the extension and the effectiveness of the angular hole burning.

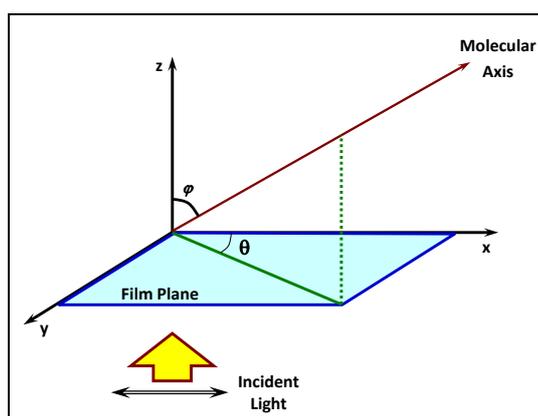


Fig. 7: Chromophore molecule orientation with respect to the polarization direction of the incident light

The relaxation time is very short so that there is no depletion in the population of *trans* molecules according to angular redistribution (AR) model. In other words, the *trans* molecules are selectively pumped into the *cis* state according to the $\cos^2 \theta$ angular dependence of Equation (4) and after a very short time they relax back to the *trans* state either thermally or through photoexcitation with a new orientation¹⁹. If the final *trans* molecule, after the photoisomerization cycle, still lies along the polarization direction of the pump light, it will go through a *trans-cis-trans* process again. As a result of this continuous angular selective interaction, more *trans* molecules are gradually aligned in a plane perpendicular to the polarization direction of the pump light. This causes the absorption parallel ($A_{//}$) to the polarization direction of the pump light to decrease due to

molecules being pumped away from this direction. On the other hand, the absorption perpendicular (A_{\perp}) to the polarization direction of the pump light increases as a consequence of more molecules being aligned in this direction. This is manifested in weaker intensity of the transmitted probe light in the case of orthogonal pump-probe beams scheme. Nevertheless, the depletion of the *trans* molecules away from the polarization direction of the pump beam does not go to completion because of the thermal energy of the *trans* molecules that causes random motion leading to oppose the alignment process¹⁷. Switching the pump beam off leads to have the anisotropy relaxing due to angular diffusion of the molecules²⁰. Figs. (3) and (4) can be explained according to the angular hole burning (AHB) model as the *trans* molecules are being depleted selectively and this process is dominant in the first part of the curves where the fast increase in the transmitted probe intensity is fast. In the second part, as the angular redistribution takes the advantage, the transmission of the transmitted probe intensity increases progressively. Reaching to a balance between *trans*→*cis* and *cis*→*trans* explains the saturation state which could persist until the pump is switched off. Switching the pump light off causes both transmissions (parallel and perpendicular probes) to decrease suddenly due to fast relaxation of the *cis* form; but the dichroism originating in the molecular orientation has much larger relaxation time.

Fig. 8 illustrates the variation of the calculated average extent of dichroism in the sample as a function of the irradiating intensity of the pump light. This figure shows that as the pump intensity increases up to 0.14 mW the average dichroism increase too, and reaches a maximum at 0.582 mW. However, further increase of the pump intensity leads to a decrease in the average dichroism. This phenomenon can be explained as follows: the first rapid increase in the average dichroism was mainly caused by a reorientation process. That is, when the pump beam became stronger, a higher population of chromophores were excited to undergo the repeated processes of the *trans-cis-trans* isomerization so that the reorientation effect of the azo-benzene groups became stronger, thus causing the higher dichroism.

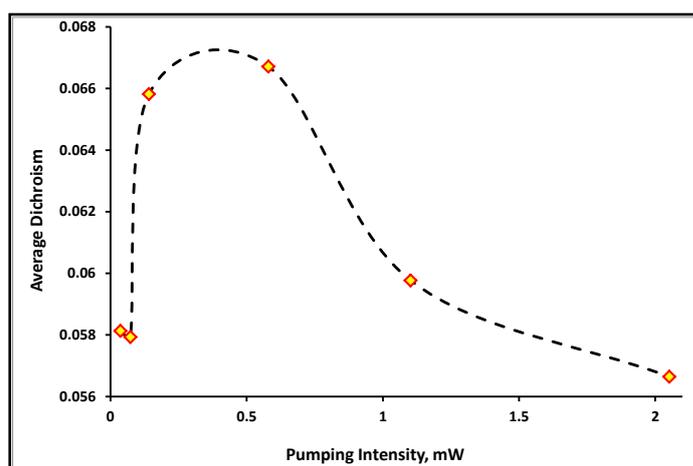


Fig. 8: Average linear dichroism as a function of the pump beam intensity at (0.04, 0.075, 0.14, 0.582, 1.1 and 2.05 mW) of Sudan II/ PMMA thin film.

Moreover, Fig. 8 shows that as the pump beam further increased to 1.1 mW and 2.05 mW, the dichroism dropped to a relatively low level. The possible mechanism is thought to be as follows: As a result of the further increase in the pump beam power, the reorientation would reach a saturated level. At this level, almost all the azo-benzene groups were excited to the *cis* states, and it was very difficult for them to return to the stable *trans* states due to the continuous strong irradiation, and the sample was abundant in *cis* isomers and lack of oriented *trans* ones. Consequently, the repeated processes of *trans-cis-trans* isomerizations were restrained, causing the reduction of the dichroism²¹.

Conclusion

In this research, we investigated photoinduced dichroism in Sudan II / PMMA thin films. The results showed that transmitted probe beam intensity in the case of parallel polarization state is greater than that of the perpendicular polarization one. When the pump beam is switched on the dynamic behavior of the dichroism showed that it increases rapidly, saturates and decreases when the pump beam is switched off.

The reorientation effect as a result of the *trans-cis-trans* isomerizations processes of the azo-benzene groups has controlled the dichroism behavior of the samples. This behavior showed that the dichroism increases, reaching a maximum and then decreases with increasing of the pump beam power.

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References

1. Marino I.-G., Raschellà R., Lottici P.P., Bersani D., Razzetti C., Lorenzi A., and Montenero A., Photoinduced effects in hybrid sol-gel materials, *J. Sol-Gel Sci Techn*, 2006, 37, 201–206.
2. King N. R., Whale E.A., Davis F.J., Gilbert A., and Mitchell G.R., Effect of media polarity on the photoisomerisation of substituted stilbene, azobenzene and imine chromophores, *J. Mater. Chem.*, 1997, 7(4), 625–630.
3. Chun C., Seo E.M., Kim M.J., Shin Y.D., Lee J.S., and Kim D.Y., Photoinduced behaviors of isocyanate-based azo molecular glass and polymer, *Optical Materials*, 2007, 29, 970–974.
4. Choi S., Chun C., Kim K.R., Kim M.-J., Yoo S.J., Kim D.Y., and Oh K., Interferometric inscription of surface relief gratings on optical fiber using azo polymer film, *Appl. Phys. Lett.*, 2003, 83, 1080–1082.
5. Yi D.K. and Kim D.Y., Polymer nanosphere lithography: fabrication of an ordered trigonal polymeric nanostructure, *Chem. Commun.*, 2003, 8, 982–983.
6. Sekkat Z., Prêtre P., Knoesen A., Volksen W., Lee V.Y., Miller R.D., Wood J., and Knoll W., Correlation between polymer architecture and sub-glass-transition-temperature light induced molecular movement in azo-polyimide polymers: influence on linear and second and third-order nonlinear optical processes, *J. Opt. Soc. Am. B*, 1998, 15(1), 401–413.
7. Watanabe T. and White J.L., Dichroic polyethylene terephthalate films based upon compounds containing chromophore stuffs, *Colloid Polym Sci*, 1992, 270, 519–526.
8. Abbas B. and Alshikh Khalil M., Investigation of dynamic dichroism properties of disperse orange 11 molecules and azo-molecules doped in poly(Methyl Methacrylate) thin films: A comparison, *Acta Physica Polonica A*, 2010, 117(6), 904–910.
9. Thulstrup E.W. and Thulstrup P.W., Polarization Spectroscopic Studies of Ordered Samples, *Acta Chim. Slov.*, 2005, 52, 371–383.
10. Choi D. Hand Kang S.H., Dynamic behavior of photoinduced birefringence of copolymers containing aminonitroazobenzene chromophore in the side chain, *Bull. Korean Chem. Soc.*, 1999, 20(10), 1186 – 1194.
11. Cojocariu C. and Rochon P., Light-induced motions in azobenzene containing Polymers, *Pure Appl. Chem.*, 2004, 76(7-8), 1479–1497.
12. Ghanadzadeh A., Zakerhamidi M.S., and Tajalli H., Electric linear dichroism study of some Sudan chromophores using electro-optic and spectroscopic methods, *Journal of Molecular Liquids*, 2004, 109, 143–148.
13. Lu W.Q., Chen G.Y., Hao Z.F., Xu J.J., Tian J.G., and Zhang C.P., Enhancement of modulation depth of an all-optical switch using an azochromophore-ethyl red film, *Chin. Phys. B*, 2010, 19(8), 084208-1 084208-8.
14. Mahimwalla Z., K Yager G., Mamiya J.I., Shishido A., Priimagi A., and Barrett C.J., Azobenzene photo mechanics: prospects and potential applications, *Polym. Bull.*, 2012, published online.
15. Ahmad F., Jamil M., Jeon Y.J., Woo L.J., Jung J.E., and Jang J.E., Investigation of nonionic diazochromophore-doped polymer dispersed liquid crystal film, *Bull. Mater. Sci.*, 2012, 35(2), 221–231.
16. Ivanov M., Nikolova L., Todorov T., Tomova N., and Dragostinova V., Photoinduced dichroism and birefringence in films of Modrant Pure Yellow/poly(vinyl alcohol): simultaneous real-time investigations at two wavelengths, *Optical and Quantum Electronics*, 1994, 26, 1013–1018.
17. Abbas B., Linear and nonlinear optical phenomena in thin sol-gel organic-inorganic films, Ph.D. Thesis, the University of Reading, Reading UK, 1999, 100.
18. Dumont M. and Sekkat Z., Dynamical study of photoinduced anisotropy and orientational relaxation of azochromophores in polymeric films: poling at room temperature, *SPIE Proc.*, 1992, 1774-24, 188–199.
19. Todorov T., Nikolova L., and Tomova N., Polarization holography. 1: A new high-efficiency organic material with reversible photoinduced birefringence, *Applied Optics*, 1984, 23(23), 4309–4312.
20. Sekkat Z. and Dumont M., Photoinduced orientation of azo dyes in polymeric films. Characterization of molecular angular mobility, *Synth. Met.*, 1993, 54, 373–381.

21. Li S., Chen J., Tang T., Zeng F., Wu S., and She W., Light-induced anisotropy in azobenzene-doped copolymer films, *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, 2009, 46, 268-273.
