

---

## Spectroscopic investigation of light induced response of a Cyano Azobenzene polymer

E. Bagherzadeh-Khajeh Marjan<sup>1\*</sup>, S. Ahmadi Kandjani<sup>1</sup>,  
M. S. Zakerhamidi<sup>1</sup> and Z. Rezvani<sup>2</sup>

<sup>1</sup>Research Institute for Applied Physics and Astronomy, University of Tabriz, Tabriz, Iran

<sup>2</sup>Department of Chemistry, Faculty of Science, Shahid Madani University of Azarbaijan, Tabriz, Iran

E-mail: [e.bagherzadeh@tabrizu.ac.ir](mailto:e.bagherzadeh@tabrizu.ac.ir)

---

### Abstract

In this paper, absorption spectra of both solution and films of cyano azobenzene polymer are investigated. The analysis of overlapped absorption spectra of polymer, related to trans and cis isomers, shows that the population of cis isomers is higher than trans isomers. It means that, cyano azobenzene molecules have a folded structure in polymer, in thermal equilibrium. Presence of cyano molecules causes this folded structure. Illumination of polymer films, prepared by THF solvent, with light of diode pumped solid state laser, results in increasing the population of isomers and their absorption peaks, due to trans-cis and cis-trans photoisomerization process. Then, Isopropanol is added to solution to enhance the freedom degree of molecules. So, the population of trans isomers in films and solutions, prepared by THF+Isopropanol are higher than trans isomers in films prepared only by THF. The illumination of polymer films prepared by THF+Isopropanol changes the concentrations of isomers due to photoisomerization process.

**Keywords:** Photoisomerization process; cyano azobenzene; trans isomer; cis isomer

---

### 1. Introduction

Azo dyes are industrial dyes with many applications, from wax and plastic (Long et al., 2011) to optical storage of data and dye sensitized solar cells (Dinçalp et al., 2010; Rais et al., 2005). These dyes' applications are due to their special photoisomerization process. Azobenzene chromophores contain two isomers: cis and trans. The trans isomer is about 50 kJ/mol more stable than cis isomer, thus in the absence of light, most azobenzene molecules are found in trans form (Iqbal et al., 2013). These molecules are highly light sensitive materials, meaning that by illumination of molecules with a light, with a wavelength in the absorption band of the trans isomers, they transform to cis isomers. Under illumination of linearly polarized light, the trans isomer absorbs the light, polarized along the transition dipole moment (long axis of azo molecule). The probability of absorption is proportional to  $\cos^2\phi$ , where  $\phi$  is the angle between the direction of the electric field of incident light and long molecular axis. For a primary angular distribution of chromophores, many chromophores absorb the light and become cis isomers, afterwards

they reorient and go back to trans isomer and redistribute in a random form, which can be affected by the polarization of light. This phenomenon is called the reorientation of azo molecules (Kaczmarek et al., 2012; Yager and Barrett, 2006; Sekkat, 2002).

According to Rau classification (Serwaczak et al., 2007), cyano azobenzene chromophores are push-pull derivatives of the pseudostilbene type, which have a strong overlap in the absorption spectra of trans and cis isomers. In fact, the addition of cyano group leads to the increment of orbital energy of N=N bonds, and decrement of the orbital energy of  $\pi^*$  antibonds. So, it results in reduction of the total energy of  $\pi$ - $\pi^*$  transition, which increases the photoisomerization rate in trans-cis and cis-trans directions. Furthermore, the addition of cyano group will result in a larger cis fraction (Yan et al., 2004; Serwaczak et al., 2006; Fukuda et al., 2006; Sekkat et al., 1995).

### 2. Experimental

#### 2.1. Material

The investigated polymer is methacrylate {{{4-[(E)-(4-cyanophenyl) diazenylo] phenyl} (methyl amino) ethoxy} ethyl, abbreviated as pCNOhomo. It belongs to pCNO family, in which the azo block

---

\*Corresponding author

Received: 27 July 2014 / Accepted: 1 December 2014

content is 100%. The cyano azobenzene chromophore is attached as a mesogenic side group to methacrylate main chain, which contains ethoxyethylene spacer and amino group that makes it a noncentrosymmetric structure and enhances its nonlinear optical properties. Ethoxyethylene spacer makes the molecule flexible and this flexibility will affect the response rate of material. pCNOhomo polymer shows features of side chain liquid crystalline polymers, so it has a smectic mesophase above  $T_g$ . It was synthesized by Stanislaw Kucharski and co-workers (2006). The chemical structure and the properties of the polymer are shown in Fig. 1 and Table 1.

## 2.2. Method

Thin films ( $1\mu\text{m}$ ) are prepared on a clean glass substrate, by spin coating method. The prepared polymer films differ from each other depending on the type of solvent used. In the first type of films, the solution contains 50mg of pCNOhomo polymer dissolved in 1mL THF, and in the second type, solvent contains 1mL THF and two drops of Isopropanol.

To investigate and compare the UV-Vis absorption spectra of polymer films, Shimadzu UV-2450 spectrophotometer is used. The absorption spectra of polymer films are recorded, before and

after illumination, via a linearly polarized beam of Diode Pumped Solid State (DPSS) laser, with wavelength of 532 nm and 100mW power.

Peak Fitting Origin.5 software is used to analyze absorption peaks.

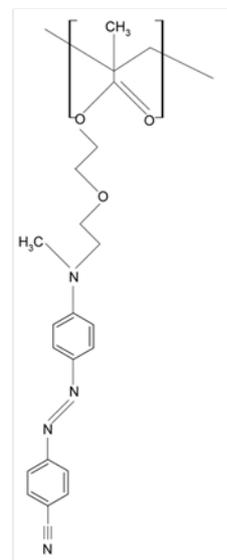


Fig. 1. Chemical structure of pCNOhomo polymer

Table 1. Properties of pCNOhomo polymer (Serwaczak et al., 2007)

| Sample    | Azo block Content (wg. %) | Mn(g/mol) | Mw(g/mol) | Mn /Mw | Phase transition |
|-----------|---------------------------|-----------|-----------|--------|------------------|
| pCNO homo | 100                       | 3190      | 7996      | 2.51   | G72S148I         |

G: Glass, S: Smectic, I: Isotrop

## 3. Results and discussion

For simplicity, the polymer films prepared by THF and those prepared by THF+Isopropanol are labeled sample1 and sample2, respectively.

Absorption spectra of sample 1, before and after illumination with DPSS laser, are shown in Fig. 2. As it can be seen from the absorption spectrum, upon illuminating the sample, the absorption peak rises. Considering that the cyano azobenzene polymer is in the pseudostilbene group, peaks of cis and trans isomers overlap. Therefore, the absorption peaks are in fact composed of two sub-peaks of cis and trans. To calculate the wavelength and sub-peak areas of spectra, the absorption spectra are fit through Gaussian function of Peak Fitting Origin. 5. Figure 3 depicts the sub-peaks of absorption spectra of Fig. 2.

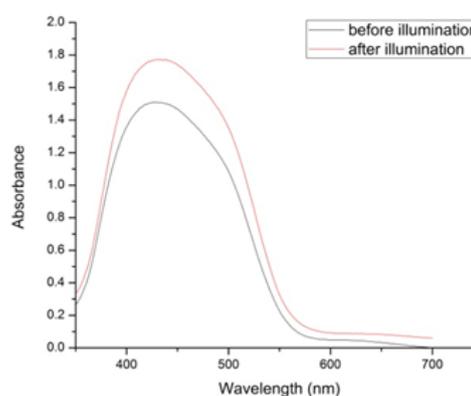
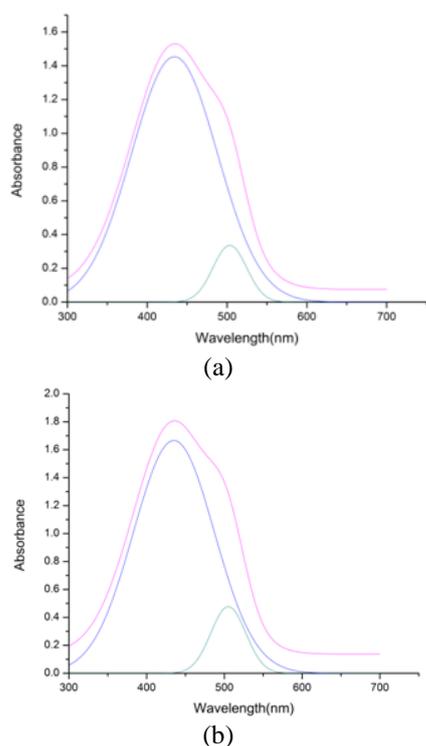


Fig. 2. Absorption spectra of sample1 before and after illuminating by DPSS laser with wavelength of 532 nm



**Fig. 3.** Sub-peaks of absorption spectra of Fig. 2. a) before and b) after illumination

Since cis isomers have higher energy than trans isomers, sub-peaks of cis isomers are located at shorter wavelength, and longer wavelength sub-peaks are related to trans isomers. As shown in the values of sub-peak areas in Table 2, before illuminating the polymer film, statistical populations of cis isomers are more than trans isomers. In fact, addition of cyano group will result in a larger cis fraction. Thus, the polymer has a folded structure.

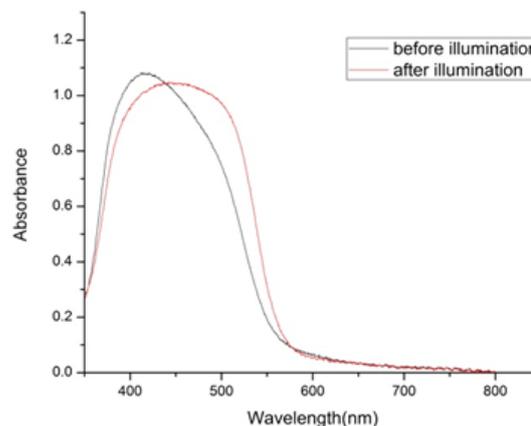
When we illuminate the sample 1, energy is introduced to the system. This energy increases the freedom degree of isomers, which leads to unfolding the polymer and transformation of cis isomers to trans forms. On the other hand, presence of cyano group enhances the photoisomerization process rate in trans-cis and cis-trans directions and increase the population of both forms. So, the absorption peak of sample 1 is increased after illumination.

**Table 2.** Calculations of sub-peak fitting of Fig. 3

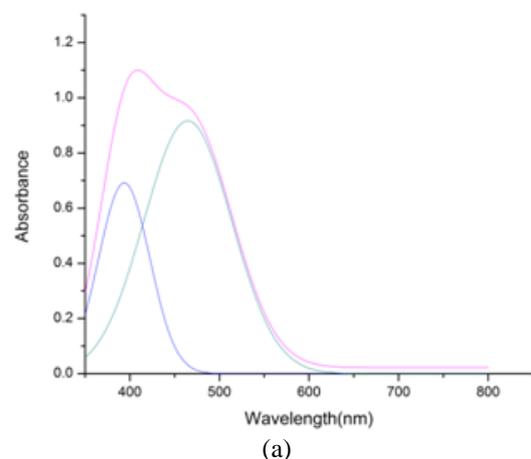
| Sample 1            | Function name      | Peak wave length(nm) | Peak area |
|---------------------|--------------------|----------------------|-----------|
| Before illumination | Subpeak1(cis)      | 434                  | 195.9     |
|                     | Sub-peak 2 (trans) | 503                  | 17.8      |
| After illumination  | Sub-peak1(cis)     | 435                  | 217.4     |
|                     | Sub-peak 2 (trans) | 505                  | 26.7      |

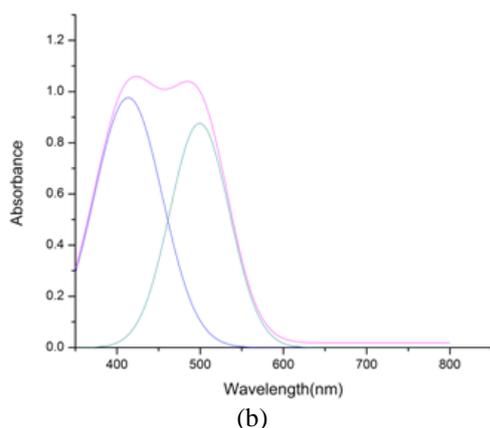
Now, we study the absorption spectra of sample 2. Absorption spectra of sample 2, before and after illumination, are shown in Fig. 4. Figure 5 demonstrates the sub-peaks of absorption spectra (Fig. 4) of sample 2. The values of absorption wavelength and sub-peak areas are given in Table 3.

Comparing the sub-peak areas of Table 2 and 3, it can be seen that, before illumination of samples, the population of trans isomers in sample 2 (112.3) is more than trans isomers in sample 1 (17.8). Since Isopropanol has a higher dielectric constant, compared to THF, it results in increasing the freedom degree of molecules and unfolds cis isomers and transforms them to trans. Therefore, the population of trans isomers, in thermal equilibrium in sample 2 is more than sample 1. By illuminating sample 2, the population of isomers will change, as a result of photoisomerization process.



**Fig. 4.** Absorption spectra of sample 2 before and after illuminating by DPSS laser with wavelength of 532 nm





**Fig. 5.** Sub-peaks of absorption spectra of Fig.4, a) before and b) after illumination

**Table 3.** Calculations of sub-peak fitting of Fig. 5

| Sample2                    | Function name     | Peak wave length(nm) | Peak area |
|----------------------------|-------------------|----------------------|-----------|
| Before illumination        | Sub-peak1 (cis)   | 393                  | 49.5      |
|                            | Sub-peak2 (trans) | 464                  | 112.3     |
| After illumination Sample2 | Sub-peak1 (cis)   | 413                  | 100.0     |
|                            | Sub-peak2 (trans) | 499                  | 78.5      |

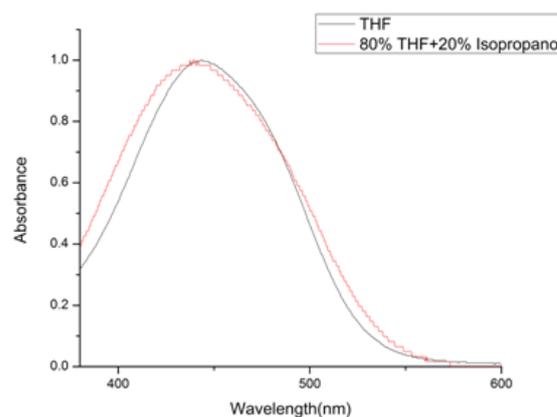
**Table 4.** Calculations of sub-peak fitting of Fig. 6

|  | Function name     | Peak wave length(nm) | 99.0 |
|--|-------------------|----------------------|------|
| <b>Solution of polymer and THF</b>                   | sub-peak1(cis)    | 444.0                | 4.3  |
|  | sub-peak 2(trans) | 488.0                | 93.8 |
|  | sub-peak1(cis)    | 432.9                | 21.5 |
| <b>Solution of polymer and 80%THF+20%Isopropanol</b> | sub-peak 2(trans) | 490.6                | 99.0 |

#### 4. Conclusion

Studying the absorption spectra of polymer films and solutions showed that, in thermal equilibrium, population of cis isomers was higher than trans isomers. It means that, the polymer had a folded structure. The population of trans isomers, in solution and polymer films prepared by THF+Isopropanol, was higher than samples prepared by THF. Since the polarity of Isopropanol was more than THF, it led to molecules being freer and thus increased the number of trans forms. Illuminating the polymer films in sample 1 resulted in photoisomerization process in trans-cis and cis-trans directions and increased both isomers. In sample 2, cis to trans isomerization augmented the cis forms. So, illuminating the samples changed the fraction of isomers.

Figure 6 presents the absorption spectra of the pCNOhomo polymer solution, in THF and 80% THF+20% Isopropanol. The spectra are normalized. Evaluating the sub-peak areas of Fig. 6 indicates that, the interactions of solvent-solute molecules in polymer and 80% THF+20% Isopropanol solution, increase the freedom degree of solute molecules and considering the sub-peak areas of solutions represented in Table 4, leads to increasing the population of trans isomers.



**Fig. 6.** Absorption spectra of cyano azobenzene polymer in THF and 80% THF+20% Isopropanol solvents

#### References

- Dinçalp, H., Yavuz, S., Haki, Ö., Zafer, C., Özsoyc, C., Durucasu, İ., & İçli, S. (2010). Optical and photovoltaic properties of salicylaldehyde-based azo ligands. *Journal of Photochemistry and Photobiology A: Chemistry*, 210(1), 8–16.
- Fukuda, T., Kim, J. Y., Barada, D., & Yase, K. (2006). Photoinduced cooperative molecular reorientation on azobenzene side-chain-type copolymers. *Journal of Photochemistry and Photobiology A: Chemistry*, 183(3), 273–279.
- Iqbal, D., & Samiullah, M. H. (2013). Photo-responsive shape-memory and shape-changing liquid-crystal polymer networks. *Materials (Basel)*, 6(1), 116–142.
- Kaczmarek, H., Borowska, M. Z., Chylińska, M., Kowalonek, J., & Wolnicka, M. (2012). Effect of azobenzene derivatives on the photochemical stability of poly (methyl methacrylate) films. *Polymer Degradation and Stability*, 97(8), 1305–1313.
- Long, C., Mai, Z., Yang, X., Zhu, B., Xu, X., Huang, X., & Zou, X. (2011). A new liquid-liquid extraction method for determination of 6 azo-dyes in chilli products by high-performance liquid chromatography.

- Food Chemistry*, 126(3), 1324–1329.
- Rais, D., Nešprek, S., Zakrevskyy, Y., Stumpe, Z., & Studenovský, M. (2005). Photo-orientation in azobenzene containing polybutadiene based polymer. *Journal of Optoelectronics and Advanced Materials*, 7(3), 1371–1375.
- Sekkat, A., (2002). *Photorefractive organic thin films*. The United States of America: Academic press.
- Sekkat, Z., Wood, J., & Knoll, W. (1995). Reorientation Mechanism of Azobenzenes within the Trans-Cis Photoisomerization. *Journal of Physical Chemistry*, 99(47), 17226–17234.
- Serwaczak, M., Wu`bbenhorst, M., & Kucharski, S. (2006). Photochromism and diffraction grating in cyano azobenzene polymer films. *Proceedings of SPIE*, 6335, doi:10.1117/12.680057
- Serwaczak, M., Wu`bbenhorst, M., & Kucharski, S. (2007). Optical and broadband dielectric investigations of photochromic polymethacrylates. *Journal of Non-Crystalline Solids*, 353(47–51), 4303–4312.
- Yager, K. G., & Barrett, C. J. (2006). Novel photo-switching using azobenzene functional materials. *Journal of Photochemistry and Photobiology A: Chemistry*, 182(3), 250–261.
- Yan, J., Liu, L., Ji, L., Ye, M., Xu, L., & Wang, W. (2004). Photo-isomerization induced rapid photo-degradation of optical nonlinearity in cyano substituted stilbene derivative doped poled polymer. *Journal of Physics D: Applied Physics*, 37(12), 1597–1602.