

Cyano azobenzene polymer films: Photo-induced reorientation and birefringence behaviors with linear and circular polarized light



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ABSTRACT

Photo-induced behavior of polymethacrylate polymer, with cyano azobenzene side group, was studied. The photoisomerization process occurs in cyano azo polymer, by illumination of a film with polarized and unpolarized light. The illumination of the polymer film with light results in color change, the color of film gets darker. This is in opposition to common azo polymers in which the result of illumination is a photo-bleaching. Study of spectrum changes of a dilute polymer solution shows that the color change under pump beam illumination is not due to interaction between dye molecules. Time evaluation of probe beam absorption induced by Ar⁺ laser pump beam shows the fast change in population of isomers at higher light powers. Light induced birefringence (LIB) experiments with high power pump beams shows uncommon new features. A high long-term stability of LIB is demonstrated when the polymer film is kept in the dark. Not only a circular polarized light cannot erase the birefringence but it also induces anisotropy in polymer film. It appears that this is relevant of a phase transition in the polymer film.

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1. Introduction

Azo dyes are a well-known class of dyes used abundantly for textile dyeing and paper printing [1]. They also have extensive applications in non-linear and photoelectronics [2], mainly in optical data storage, switching technologies and photo-refractive materials [3]. Due to their flat aromatic structure and their ability to undergo photoisomerization, optical properties of azobenzenes make them the active compounds in a variety of applications [4,5].

The photo responsive properties of azobenzenes lead to photoisomerization between prolate trans and bended cis isomers. This process results in remarkable changes in their molecular shape, dipole moments and color. Therefore, they are called photochromic materials [5,6]. When azobenzene chromophores are illuminated with linear polarized light, they orient in the direction perpendicular to the electric field of the incoming light [7,8]. In time, the competition between photoisomerization and thermal relaxation leads to a statistical redistribution of the trans form. According to Rau classification [9], the thermal cis to trans isomerization in pseudo-stilbenes shows a high rate. The steady-state composition is thus established fast. Cyanoazobenzene chromophores are

push–pull derivatives of the pseudo-stilbene type, which show a strong overlapping in the absorption spectra of the cis and trans isomers. Polymers containing azobenzene and its derivatives, with a fast thermal cis to trans isomerization, are required to create devices with high anisotropic molecular order and large macroscopic higher-order polarizabilities. The photoisomerization process known as photo-induced molecular reorientation of the polymer films can induce significant birefringence and dichroism. So, due to efficient photo-induced orientation, they are a suitable choice for photo-addressable devices [4,8–12].

Molecular reorientation is also induced with nonpolarized light, in films of polymers with side chain azobenzenes. When these materials are irradiated with unpolarized light, the azobenzene moieties become aligned in the propagation direction of the irradiation light, since only the propagation direction is perpendicular to the electric field vector of the light. Haitjema et al. suggested that the exposure of these films to visible light leads to orientational changes of the azobenzenes into preferentially perpendicular directions [13–15].

In the present work, we used a cyanoazobenzene polymethacrylate polymer films for the study of photoalignment and photo-induced birefringence behavior. The cyanoazobenzene chromophores attached as side chain on the polymethacrylate polymer control the optical properties of the polymer film and photo-induced reorientation.

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2. Experimental

2.1. Materials

The investigated polymer was methacrylate $\{[4-[(E)-(4-cyano-phenyl) diazenyl] phenyl] (methyl) amino] ethoxy\}$ ethyl. It was synthesized by Stanisław Kucharski and co-workers (Institute of Organic and Polymer Technology, Wrocław Technical University, Poland) [8]. The chemical structure of the polymer is shown in Fig. 1. It contains cyanoazobenzene chromophore as a mesogenic side group and methacrylate main chain as a linear backbone, abbreviated as pCNOhomo. Results of DSC and GPC analysis of pCNOhomo are summarized in Table 1. Thin films (1 μm), on glass substrates, were prepared via spin-coating of the polymer from THF solution, with a concentration of 50 mg/ml.

2.2. Absorption and transmission spectroscopy

Dual beam Shimadzu UV-2450 Scan UV-Visible spectrophotometer was used to record the absorption spectra, over the wavelength range of 350–700 nm. Green line of high-pressure mercury lamp and halogen lamp from Leybold were used as unpolarized light sources with wavelengths of 547 nm and 613 nm, respectively. Emission spectra of these lamps were measured with fiber spectrometer (Ocean Optics, USB 4000). 1 cm optical path length quartz cuvette was used for measurement in solution. The polymer concentration was chosen to be $\sim 9 \times 10^{-4}$ M. The solution of polymer was illuminated with an Argon ion laser beam (488 nm, 100 mW). Deuterium tungsten halogen light source (ocean-optics, DH-2000) was used as a probe, with spectral range of 215–2500 nm and the transmission change with time, were measured with fiber spectrometer.

To evaluate optically induced anisotropy of polymer film, different sources were used: (a) laser diode with wavelength of 532 nm and intensity of 150 mW/cm², (b) unpolarized light of mercury lamp and white light of halogen lamp.

2.3. Time evaluation of probe beam absorption

The time evaluation of probe beam absorption at various intensities of pump beam is performed as follows: The sample is irradiated with an Argon ion laser (488 nm), with the intensity of 100 mW/cm². The transmittance of a low power probe light

Table 1
Results of DSC and GPC analysis for pCNOhomo [8].

Sample	Mn (g/mol)	Mw (g/mol)	Mn /Mw	Phase transition
pCNOhomo	3190	7996	2.51	G 72 S 148 I

G: glass transition, S: smectic phase, I: isotropic phase.

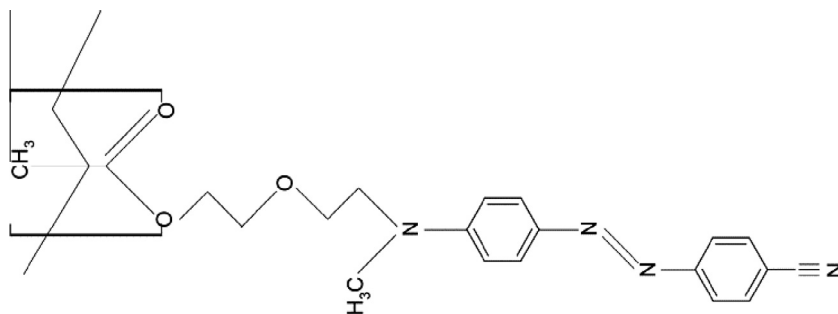


Fig. 1. Chemical structure of pCNOhomo.

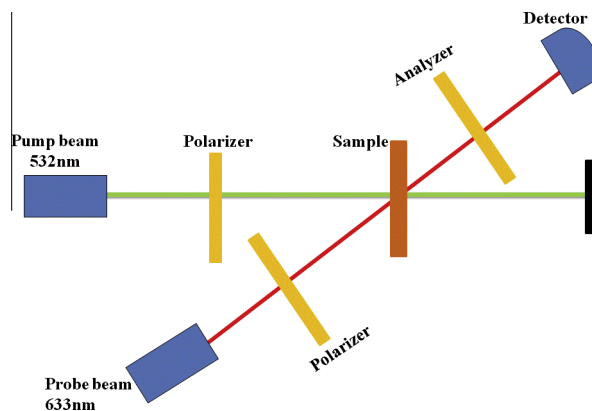


Fig. 2. Experimental set-up to measure photo-induced birefringence.

(532 nm) is measured with a photodiode, at various intensities of pump beam versus time. In order to investigate absorption changes of polymer film, the wavelength of probe light is selected in the absorption area of the polymer.

2.4. Photo-induced birefringence

The photo-induced orientation behavior of the pCNOhomo polymer film is studied through birefringence measurement. The experimental setup for photo-induced birefringence of the film is seen in Fig. 2. A line eds., ar polarized laser beam, obtained using a Glan prism from a diode laser with the intensity of 150 mW/cm², is used as a pump beam (532 nm). For birefringence measurements, a low power He-Ne laser, at 633 nm, is used as a probe beam. The sample is placed between a pair of crossed polarizers, which are set to 45° with respect to the polarization angle of the incident pump beam. The angle between incident laser beam and probe beam is fixed to 45°. The photo-induced birefringence of the polymer film is monitored by transmission of the probe beam. To investigate the recording speed of optical information on the film, the change of the birefringence is measured as a function of the power of pump beam. The photo-induced birefringence is also studied for circular polarized light.

3. Results and discussion

In the photochromic system, the long spacer improves the flexibility of the side chain dye moiety. Response rate of the material upon illumination is also affected by the flexibility of the molecule. Kucharski et al., showed that this homopolymer acquires a smectic mesophase above 72 °C, in which the side chain mesogens are tilted within the layers [6]. The molecular environment of the chromophores affects trans-cis-trans isomerization, mainly by rigidity

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