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SOME PHYSICAL FACTORS INFLUENCING THE AZOBENZENE POLYMERS PROPERTIES

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Abstract. Photonisotropic materials can be divided into two main groups: inorganic and organic materials. Polymers containing organic dyes are the subject of multiple studies in both areas of physics and medicine. Optical storage in azobenzene-containing polymers is based on the alignment of the polymer chains initiated by the reorientation and ordering of the azobenzene groups. This process requires considerably high recording energies but elevated temperature eases the mobility of the molecules thus making possible their reorientation by lower light intensities. On the other hand, an attractive approach is to use light, both to report on and control signaling proteins in cells, because light can probe cells in real time with minimal damage. Of particular interest is the development of chemically engineered proteins that are directly sensitive to light. The aim of this work is to present some physical factors influencing the azobenzene polymers properties used in various fields of science.

Keywords: azobenzene polymers; photoisomerization; photoinduced optical birefringence; carriers of drugs

Azobenzene polymers, in which azodyes are covalently attached usually in the side chains, are good candidates for holographic memories as they are highly efficient, stable in the dark, and reversible as well. It is known that linearly polarized light induces reorientation of the azobenzene groups through multiple *trans-cis-trans* isomerization cycles and induces large optical anisotropy into them. The value of the photoanisotropy achieved in different azopolymers depends on the concentration of the azochromophores and the polymer structure that influences the mobility of the azobenzenes, and the rate constants of the isomerization processes. It also depends on the intensity of the exciting light and the temperature. Shibaev et al. (1997) have observed that maximum birefringence is achieved at temperatures 30 – 40°C higher than the glass transition temperature (Tg) due to the increased mobility of the side chains and the azobenzenes linked to them. Wu et al. (1998) also found that the optimal temperature is much above Tg. A strong influence of the temperature and laser beam intensity on photoinduced anisotropy in azobenzene polyesters has been reported by Holme et al. (1996). In their polymer the optimal temperature is close to Tg and higher intensity induces higher birefringence. Zebger et al. (2002) made a detailed investigation of the photoanisotropy induced by an Ar$^+$ laser beam in an azopolymer with low Tg, varying the temperature and the beam intensity. The photoinduced birefringence in an azobenzene polymer is investigated at different temperatures between –20°C to +50°C. It is found that there is a peak value of photoinduced birefringence in the temperature dependence of the photoinduced birefringence under a certain pumping intensity. With the pump light in 90 mW/cm^2, the peak value of the photoinduced birefringence appeared at about 0°C (Hong-Tao et al., 2007). The effect of temperature on the photoinduced birefringence is discussed by authors using the competition mechanism between the photoinduced reorientation and the thermal random motion.

Ivanov et al. (2005) and Ilieva et al. (2006) investigated photoinduced birefringence in two types of acrylic cyan-azo polymers – one liquid-crystalline (LC) (T_g=35^{o}C) and one amorphous (T_g>100^{o}C) (Fig.1).

The thickness of the film is about 3 mm. The anisotropy was induced in the samples by a linearly polarized Ar$^+$ laser beam **l**=488 nm (in the absorption band of the polymer). The polarization of the pump beam was at 45° with respect to the vertical. The probe beam is vertically polarized with **l**=633 nm, far from the absorption band of the polymer. The samples were mounted on a variable – temperature holder. After the sample the output He – Ne beam is split by a Wollaston prism into two beams with orthogonal polarizations. The polarization of the first beam is parallel to the polarization of the input probe beam (vertical), its intensity is I_{par} and the second beam is polarized orthogonally, with an intensity I_{ort}. These two intensities are measured by two photodetectors. A personal computer (PC) controls the temperature of the holder, collects, and processes the data. The induced photoanisotropic phase shift Dj=2pDnd/l, where Dn is the birefringence and *d* is the thickness of the film, is calculated by:

$$\Delta\varphi = 2\arcsin\left(\sqrt{\frac{I_{ort}}{I_{par} + I_{ort}}}\right).$$

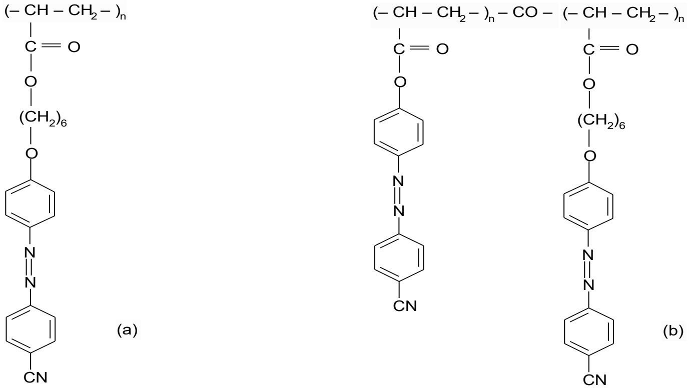

Figure 1. Structure of the polymers (a) liquid crystalline; (b) amorphous

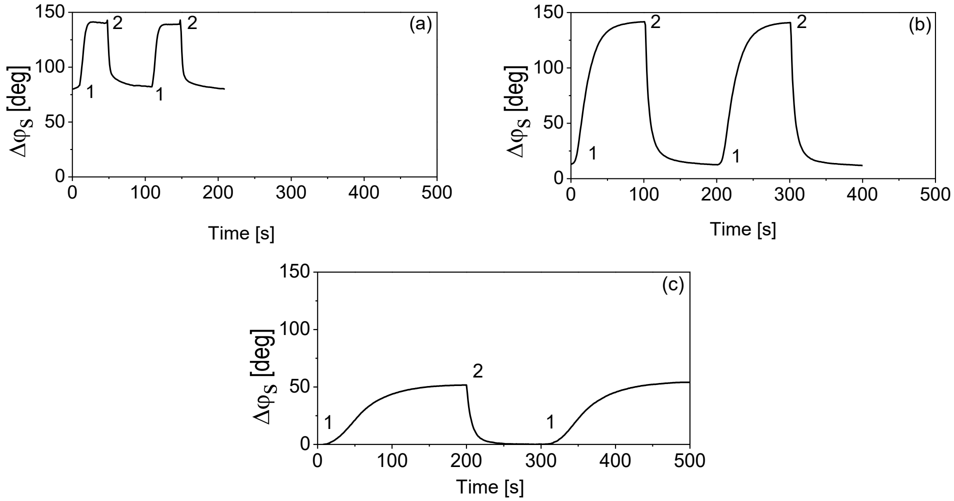

Figure 2. Changes in the value of Dj when the pump intensity alternates between 1 mW (point “1”) and 20 mW (point “2”) at constant temperatures: (a) 47°C, (b) 53°C, (c) 56°C

The curves in Figs. 2(a) –2 (c) are obtained at constant temperatures of the sample (47°C, 53°C, 56°C) by alternating the Ar^+ beam intensity between 1 and 20 mW. All these curves start in moments in which the intensity is changed from 20 to 1 mW (Ivanov et al., 2005). This causes an increase in the anisotropic phase to a new, higher stationary state. When the exciting beam intensity is increased again to 20 mW the value of Dj falls to the initial level. In such a way, by alternating the pump intensity the anisotropic phase shift can be switched repeatedly between two very different values. The difference between the two corresponding values of the birefringence in the 3 mm thick films is 0.07. The rate of the switching and the difference between the two values, $D(Dj)=Dj_{1mW}-Dj_{20mW}$ are very sensitive to the temperature in this range (44–56°C). The dependence of D(Dj) on the temperature is shown in Fig. 3.

Higher *cis* concentration causes a decrease in the photoinduced anisotropy. In our experiments, the exciting light (488 nm) is absorbed by both the *trans*- and *cis*-azobenzenes. On the other hand, the thermal *cis – trans* isomerization is very slow and we believe that even at elevated temperatures, the *cis – trans* transitions are initiated mainly optically.

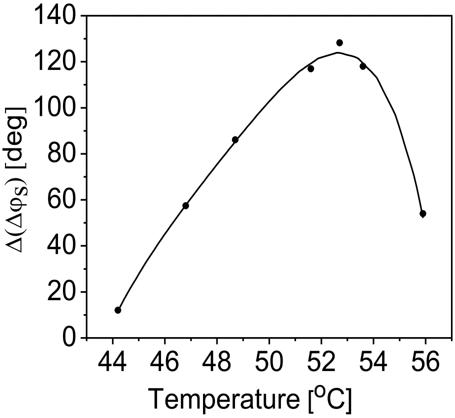

Figure 3. Dependence of $\Delta(\Delta\varphi) = \Delta\varphi_{1mW} - \Delta\varphi_{20mW}$ on the temperature.

In the publications by Ivanov et al. (2005), we are stated that the photoinduced optical birefringence in a low-molecular liquid-crystalline cyanazopolymer obtained by radical-type polymerization of 4-[4-(6-hydroxy–hexyloxyd) phenylazo] benzonitrile can be controlled by combined optical and thermal treatments. At elevated (44–56°C) temperatures, the value of the anisotropic phase difference can be switched between two values by alternating the pump beam intensity. The effect can be used for light-intensity controlled optical switching.

Ilieva et al. (2006) showed that for both types the light energy required for the recording can be reduced by an order of magnitude if the photoalignment is done at elevated temperatures. The optimal temperatures depend on the polymer. In our case they are 52 – 55°C for the liquid-crystalline polymer and 50 – 60°C for the amorphous polymer. At these temperatures birefringence as high as 0.07 can be obtained at light intensities 30 – 40 mW/cm^2 for about 100 s and these values are retained after cooling the polymer films. We think that lower photostationary values of the photoanisotropy for higher pumping intensities are due to the additional heating of the sample by high intensity light. But the mobility of the chromophores increases with the temperature and eventually leads to total isotropization. We found that the temperature of 53^{o}C is a good compromise between faster recording and thermal isotropization. We also investigated the stability of the birefringence induced at high temperatures. By using a low pump intensity of 40 mW/cm^2 we monitored the birefringence in the amorphous sample during the recording at 53°C and after lowering the temperature (marked as point 1), Fig. 4. One can see that the anisotropy is stable during cooling down to room temperature (RT). At point 2, we stopped the pumping Ar$^+$ laser, but this did not change the anisotropy. That value of Dj = 118 deg has been stable for months. The results for the LC sample are quite similar.

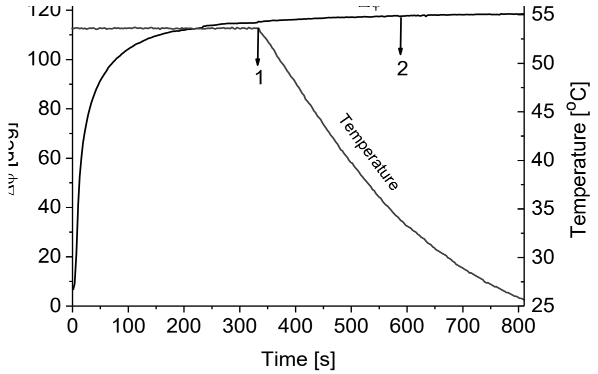

Figure 4. “Freezing” the anisotropy by cooling the sample from 53^{o}C to RT. At point (1) the cooling starts, at point (2) the Ar$^+$ laser is stopped

Ilieva et al. (2006) presented a method for achieving high values of the photobirefringence, typical for azo-dye polymers by using much lower laser powers (in the order of magnitude or even two). Elevated temperature eases the mobility of the molecules thus making possible their reorientation by lower light intensities. Depending on the polymer the range of optimal temperatures may vary. For our polymers we found that range to be 52 – 55°C. For higher temperatures isotropization takes place and the photoinduced anisotropy disappears. Beharry & Woolley (2011) made a detailed investigation that the photoisomerization of azobenzene has been known for almost 75 years but only recently has this process been widely applied to biological systems. The central challenge of how to productively couple the isomerization process to a large functional change in a biomolecule has been met in a number of instances and it appears that effective photocontrol of a large variety of biomolecules may be possible. This *critical review* summarizes key properties of azobenzene that enable its use as a photoswitch in biological systems and describes strategies for using azobenzene photoswitches to drive functional changes in peptides, proteins, nucleic acids, lipids, and carbohydrates.

Ten years ago interesting effect was observed in azobenzene, and has been reported by Gorostiza & Issacoff (2008). In biological research azobenzene has been attached to ligands (drug) in order to photo-modulate their affinity for proteins. Azobenzenes has been employed as a photoswitchable tether between a ligand and the protein: one end of the azobenzene is substituted with a reactive group that attaches to the target protein. The other end displays a ligand for the protein. Depending on where the azobenzene is attached to, either the *cis* or *trans* isomer will present the ligand to the ligand-binding site, while the other isomer prevents the drug from reaching the site. Again, photoswitching between isomers turns the protein on and off. When applied to ion channels in the nervous system, this approach affords optical control of electrical activity in neurons. Light-sensitive channels are particularly attractive because optical manipulation offers a high degree of spatial and temporal control protein activity with light and has been reported (Banghart et al., 2006).

From biophysical point of view, azo dyes can be used as carriers of drugs that facilitate the selective release of therapeutic agents in the colon and can thus improve their effects when administered orally. Due to the different structure of azo dyes, some azobonds degrade more slowly than others. For their more valuable application in medicine, the rate of release of azo dye-containing medicines is important. For example, if it is too low, the therapeutic concentrations of the drugs acting on the colon cannot be achieved. For oral administration, another important factor for easy drug absorption is the pH of the medium (Roldo et al., 2007). The selective delivery of drugs into the colon through the oral route may be particularly effective for the therapy of local conditions such as inflammatory bowel disease and colonic cancer. This selectivity may also improve the systemic bioavailability of drugs that are unstable at the low pH of the stomach, or those that interact with bile salts and hydrolytic enzymes. Once-a-day dosage forms may also benefit because, for some substances, the colon behaves like a homogeneous reservoir that releases the active agent into the bloodstream at a constant rate and in a regulated mode.

The pH sensitivity of the dynamic swelling behaviour was seen to increase with increasing proportions of ionisable functionalities in the polymer structure, whereas the equilibrium degree of swelling is reported to be dependent on the hydrophobic/hydrophilic ratio of the monomeric constituents (both features of some significance, as drug release involves diffusion through the matrix, which in turn is highly sensitive to the swelling behaviour and to the degradation characteristics of the polymeric network) (Roldo et al., 2007).

In conclusion, we can say that the photoinduced optical birefringence in azopolymer films can be controlled by combined optical and thermal treatments. Recent animal experiments have shown that azo polymers offer significant promise in the therapy of colon-related conditions by acting as a protective barrier for the colonic mucosa. The degradation of azo-polymeric carriers represents a most promising strategy for the delivery of active agents to the colon. Azobenzenes were screened for their antibacterial activity against Staphilococcus aureus, Streptococcus pyogenes, Escherichia coli, Pseudomonas aeruginosa, and Proteus vulgaris and for their antifungal activity against Candida albicans.

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