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Optical and Dielectric Properties of New Azobenzene Copolyethers Embedded in Polymer Matrices

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Summary: A new group of photochromic azobenzene copolyethers was synthesized. Their photochomic and dielectric properties were studied in poly(vinyl alcohol) and poly(methyl methacrylate) matrices.

Keywords: azobenzene; copolyether; dielectric properties; photochromism

Introduction

In a series of previous works, the synthesis of some polyethers by the phase transfer catalysis technique was presented [1-3]. These polymers were obtained by polycondensation of 3,3-bis(chloromethyl)oxetane (BCMO) and various bisphenols, some of them showing a liquid-crystalline (LC) behavior [4]. The presence of azobenzene units in the polymer structure confers on them important properties with practical applications in optics and optoelectronics. If anisotropic films are made of such a polymer, then the molecules of a nematic liquid crystal (which need not contain azobenzene units) that are in contact with the film can be aligned by photoisomerization of the azobenzene units by the action of the linearly polarized Ar^+ laser light [4]. It is assumed that the orientation of the liquid-crystal molecules by azobenzene units is mainly the result of specific molecular interactions between the photocromic units from the polymer layer and the liquid crystal molecules. These specific interactions depend on both the structure of the molecules and the area occupied by the azo units in the polymer surface layer.

In this work, copolyethers containing azobenzene groups in their main chains are studied. Because the copolymer is a thermotropic LC material with thermal transitions situated around 210 °C, it is impossible to study the photoisomerisomerism in the LC state (cis-trans transitions are thermally activated). As a consequence, the copolymer was incorporated in a matrix film.

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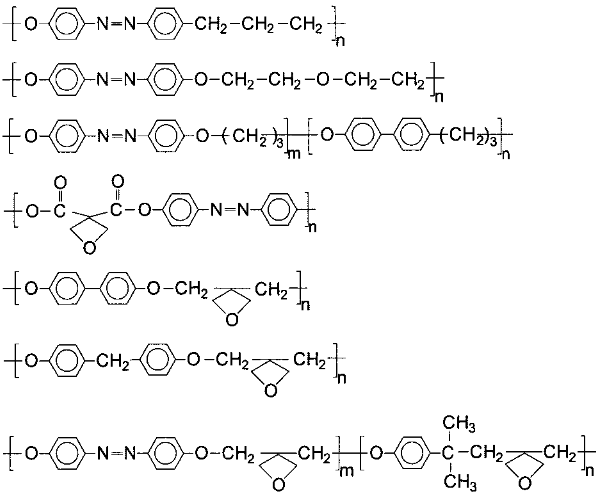
Thus the photochromic behavior can be studied at room temperature. Therefore, the obtaining of potential surface relief by modification of the polymer matrix and azobenzene concentration could be expected.

Copolymer synthesis

The molecular structure of the studied copolyethers are given in Scheme1.



Sample 1068

Sample 1069

Sample 1075

Sample 148

Sample 1064

Sample 1063

Sample 1075-a

Scheme 1

Preparation of PMMA-azo and PVA-azo Films

With the aim to produce homogeneous PVA-based films, the copolymers were dissolved in appropriate quantities of dimethyl sulfoxide and poly(vinyl alcohol) was dissolved in distilled water. In order to obtain homogeneous poly(methyl methacrylate) (PMMA)-based films, the copolymers and PMMA were disolved separately using chloroform as a solvent. The solutions were mixed and homogenized by magnetic stirring. The solutions thus obtained were poured on clean glass surfaces placed horizontally. A special device enables the rotation of the glass substrate at a speed small sufficient to obtain films with quite uniform structure and constant thickness. Chloroform was removed from the films by a special drying procedure. Drawing of the films was performed using a machine at a temperature of about 80 °C (the film was in thermal contact with a metallic cylinder during the stretching process). Films with stretching ratios ranging between 2 and 6 were obtained.

Absorption electronic spectra in natural and polarized light

The behaviour of copolyethers embedded in the PVA matrix was studied using the electronic absorption band at $\tilde{\nu}_{max} \approx 27400$ cm^{-1}, a band assigned to benzene rings in azobenzene moieties in trans positions with respect to azo groups.

The spectra in polarized light and the channeled spectrum were recorded with a Specord UV-VIS spectrophotometer (Carl Zeiss Jena). The thickness of the films ranged between 20 and 70 μm. This fact enabled us to use a device, constructed by V. Pop and M. Strat that allowed to obtain polarization and channeled spectra [5,6].

The equipment used consists of a spectrophotometer with two beams and an attachment formed by two optical systems: S_1, placed in the path of the measured beam, and S_2, placed in the path of the reference beam.

The system S_1 is made up of two polarization filters P_1 and P_2 that can be used with their transmission directions perpendicular or parallel. An anisotropic transparent polymer film L (with thickness ≥ 60 μm), for which the birefringence dispersion has to be determined is introduced between P_1 and P_2. In the case of thin polymer films with thickness ranging between ~20 and 60 μm, the attachment also contains an anisotropic transparent plate (stretched polymer or anisotropic crystal), which is placed between P_1 and L [6]. The system S_2 is made up of two polarization filters P_3 and P_4, which compensate the transmission modification introduced by polarizers P_1 and P_2 when they have parallel transmission direction. The parts of the device (Fig. 1) are fixed in settings, which can be rotated around the radiation direction, having the capacity to measure the rotation angle.

The components of the system must be oriented as follows: the polarizers P_1 and P_2 parallel (or crossed) and the film L with its stretching direction at 45° versus the transmission directions of the polarizers. Under these conditions, a channeled spectrum of transmission is obtained. The numbers of maxima and minima in this spectrum are determined by the path length difference between the ordinary and the extraordinary waves introduced by the film L. For obtaining absorption electronic spectra of the film L in polarized light, only polarization filters P_1 and P_3 are needed.

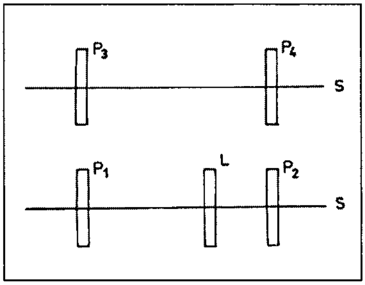


Fig. 1. Scheme of the device for polarization and channeled spectra.

Experimental and Results

i) Photochromic properties

Under the influence of the 27400 cm^{-1} UV radiation, the benzene rings in the azobenzene moieties switched from trans to cis positions. This transition can be rendered evident by spectral methods since the cis photoisomer absorbs at lower wavenumbers ($\tilde{\nu}_{max} \approx$ 21700-21300 cm^{-1}). The assignment and interpretation of the absorption electronic bands has been carried out using existing theories which explain and classify the transitions between molecular electronic states. The absorption bands at around 27400 and 21500 cm^{-1} are associated with the π-π* and n-π* transitions of the azo aromatic rings, respectively. The results are shown in Figs. 2 and 3.

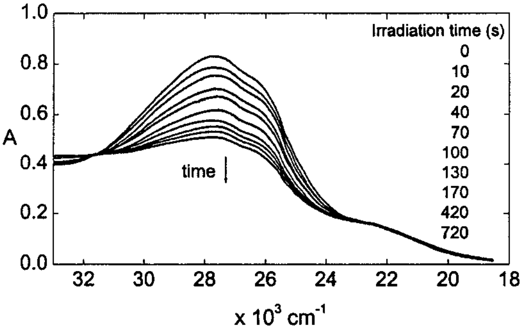


Fig. 2. Electronic absorption spectra of sample 3 in PVA film for different irradiation times.

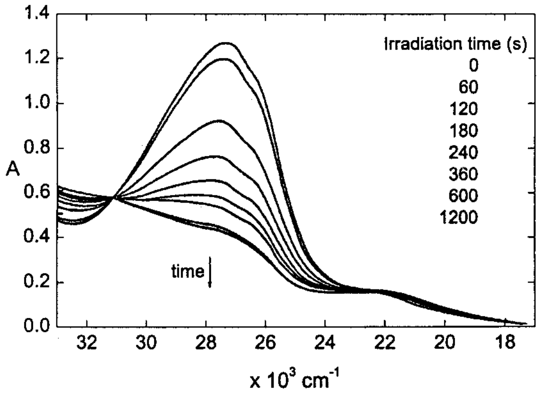


Fig. 3. Electronic absorption spectra of sample 1 in PMMA foil for different irradiation times.

The photochromic effect of these copolyethers embedded in the polymer matrices is reversible. The benzene rings of the azo groups convert from the cis to trans positions under the influence of laser radiation with $\lambda = 514$ nm, produced by an argon laser operating in the continuous regime. The photochromic effect appears as the result of molecular deformation of azobenzene moieties. A general feature of the compounds studied in this work is that the azobenzene moieties are parts of the polymer chain. Under these circumstances, it is more difficult to produce molecular deformation, as compared to other polymer structures in which the azo group is in the side chain.

ii) Polarization spectra

In order to record the spectra in polarized light, an optical device was designed and produced as an auxiliary to a Specord UV-VIS spectrophotometer (Fig. 1). The electronic absorption spectra were recorded by orienting the transmission direction of the polarizer placed in the measured beam both parallel and perpendicular to the sample stretching direction ($P_{||}$, $P_{\perp}$). In the path of the reference beam was placed a polarization filter, identical with the one placed in the measured beam, which compensated the transmission modification introduced by the polarizer.

The degrees of polarization were calculated every 50 cm^{-1} all along the existence range of the electronic band, using the relation: $P\,(\%) = \frac{A_{||} - A_{\perp}}{A_{||} + A_{\perp}} 100$,

where $A_{||}$ is the absorbance for $P_{||}$ and $A_{\perp}$ - the absorbance for $P_{\perp}$. By using the values of the polarization degrees, the polarization spectra (P (%), ν) were drawn for all the studied samples.

The birefringence values, Δn, for the stretched samples were determined using a Babinet compensator and the channeled spectra were obtained with the auxiliary device attached to the spectrophotometer (Fig. 1).

Table 1. Characteristic temperatures, order parameter S and birefringence Δn.

Sample	$T_{\mathrm{k\text{-}m}}$ (°C)	T_{i} (°C)	S	Δn
1	210-230	260	0.21	0.015
2	240-250	270	0.15	0.017
3	180	200	0.14	0.016
4	150-190	230	0.22	0.014
5	190-200	212	0.16	0.018

The order parameters, S, of the studied copolyethers were also calculated by using the relation: $S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}$. The orientation degrees, S, correspond to the substances incorporated in the PVA matrices. The anisotropy, Δn, results primarily from stretching the matrix. The temperature values (T) at which the mesophase appears in these copolymers are quite high (Table 1), which implies that special attention must be paid to crosslinking, which might occur as the result of breaking oxetane rings at high temperatures (260 – 280 °C) [2].

iii) Dielectric properties. Thermally stimulated polarization current measurements.

The samples investigated from the polarization and depolarization viewpoints were shaped as tablets. The samples were heated at the rate $v = 3 \times 10^{-2}$ K/s in the presence of electrostatic field, $E = 25 \times 10^{5}$ V/m.

The temperature dependence of the polarization current was recorded with a Philips XY recorder. The device also contained a thermostatted furnace, electronic voltmeter, picoampermeter and Al electrodes.

The total current (conductivity and polarization) during the thermal and electric treatment of the sample has one peak at about 330 K for all the studied polymers. The obtained experimental data show that the conductivity current is very low compared with the polarization current. The accuracy of measurements of polarization currents was 10^{-13}A.

The temperature dependence of the polarization current density $J(T)$ is given in Fig. 4. For all the compounds, the dependences are of the same type.

Processing the experimental data using the Gauss function (Eq. 1) has led to a good agreement between the obtained results and the dipolar polarization model using the Langevin function, $L(\beta)$ (Eq. 2) (Fig. 5).

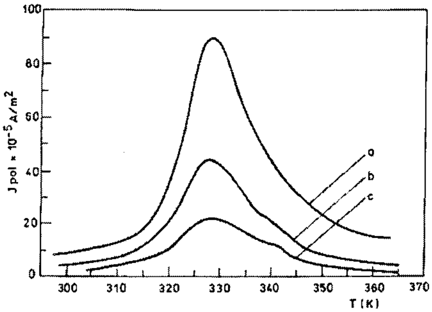


Fig. 4. Thermally stimulated polarization current density for: a 1075 sample, b 1068 sample, c 148 sample.

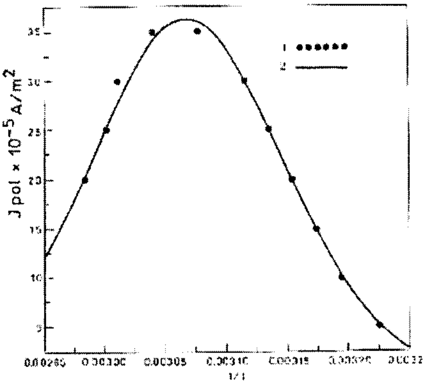


Fig. 5. Thermally stimulated polarization current density for the 1075 sample (1 experiment, 2 theory).

$$J(1/T) = \frac{A\sqrt{\frac{\pi}{2}}}{w} \exp\left(\frac{-2(x-x_c)^2}{w^2}\right) + y_0 \qquad (1)$$

$$L(\beta) = \text{ctgh}\,\beta - \frac{1}{\beta} \qquad (2)$$

where $\beta = \frac{pE}{kT}$, p is dipole moment, E is electric field. The physical values of the quantities from formula (1) is: $x \sim 1/T$, $x_c = 3 \times 10^{-3}\,\text{K}^{-1}$, $w = 1.568 \times 10^{-4}\,\text{K}^{-1}$; $\text{A} = 7 \times 10^{-3}\,\frac{\text{A}}{\text{K}\cdot\text{m}^2}$.

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