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PHOTOCROMIC PROPERTIES OF SOME DIAZOBENZENE COPOLYMERS IN SOLUTIONS

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New copolyethers and polyesters based on chloromethyl oxetane and phenol mixtures presenting properties of a liquid crystal (LC) have been studied. Their thermotropic properties are favored by the presence of diazobenzene and phenol groups within the polymer structure. The diazobenzene groups in the polymer structure confer them characteristics with important application in optics and optoelectronics.The presence of diazobenzene groups in the molecular structure of the polymeric chain confers it photochromic properties. Due to this property, the anisotropic foils obtained from such a polymer are able to bias the nematic crystal liquid molecules if they come in touch with the foil, when the obtained physical system is UV irradiated. The liquid crystal characteristics of the studied polymers have not been dealt with, since the mesophase occurs at temperatures ranging between 170-200 °C, yet certain preliminary research has shown that the oxetane ring from the polymeric chain presumably favours a reticulation process too, occurring around 195 °C.

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1. Introduction

New copolyethers based on phenol mixtures presenting properties of a liquid crystal (LC) have been studied [1,2]. The diazobenzene groups in the polymer structure confer them characteristics with important applications in optics and optoelectronics.

The presence of diazobenzene groups in the molecular structure of the polymeric chain confers it photochromic properties. Due to this property, the anisotropic foils obtained from such a polymer are able to bias the nematic crystal liquid molecules if they come in touch with the foil while the obtained physical system is UV irradiated [3,4]. These polymers have been studied in solution [5-8].

This paper reports the results obtained during the investigation of photochromic properties of some diazobenzene copolymers.

2. Photochromic characteristics. Results

The chemical structures of the investigated compounds are given in Scheme I.

The photochromic effects in polyethers have been studied by means of electronic absorption spectra in visible range.

Under the influence of the Hg radiation with the wave number at the emission maximum of about 27.400 cm^{-1}, the nitrogen nuclei from the diazobenzene group pass from trans- to cis- position (E/Z-isomerization). This transition can be rendered evident by spectral methods since the Z photoisomers absorb at low wave numbers ($\upsilon_{max}^{abs} \approx 22000 - 21500$ cm^{-1}). Some characteristics of the synthesised polymers are presented in Table 1.

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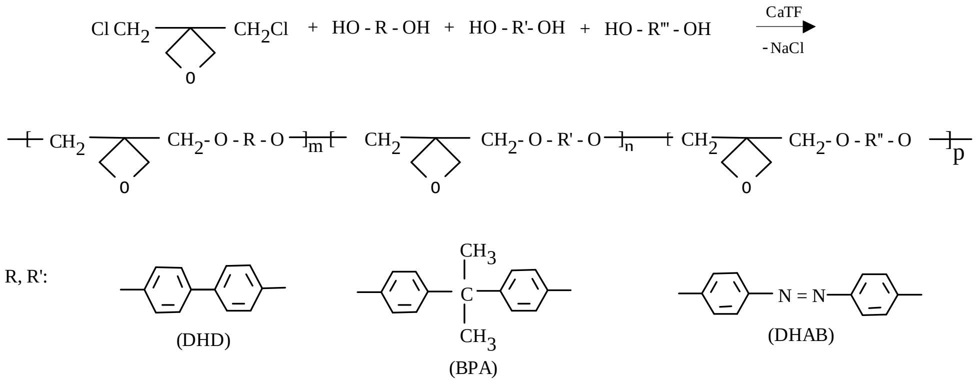

Scheme I

Table 1. Some characteristic of the synthesised copolyethers.

Sample number		Copolymer composition	$(CH_2)_n$	M_n
1	1202	DHAB/BPA/DHD = 3.8/2/1	3	1,900
2	1205	DHAB/BPA = 3.2/1	4	2,000
3	1206	DHAB/BPA = 1.1/1	5	2,200
4	1287	DHAB/DHD = 3.7/1	8	1,800
5	1297	DHAB/BPA = 2.8/1	9	1,400

The electronic absorption bands assigning and interpretation in the case of the compounds investigated in this work have been done by means of existing theories that explain and classify the transition between molecular electronic states [7]. The absorption bands with maxima at about 27.800 cm^{-1} and 21.800 cm^{-1} and belonging to azobenzene groups have been assigned to the π-π^* and n-π^* transitions, respectively. The obtained results are shown in Figs. 1-4. The photochromic effect in these copolyethers is reversible. The nitrogen nuclei from the units convert from the cis to trans positions (Z/E isomerization) under the influence of laser radiation with λ=514 nm, produced by an ion argon laser working in the continuous regime. The reversibility has been noticed either with polymers dissolved in different solvents, embedded in PMMA and PVA– based polymer matrices or as thin films deposited on quartz disks.

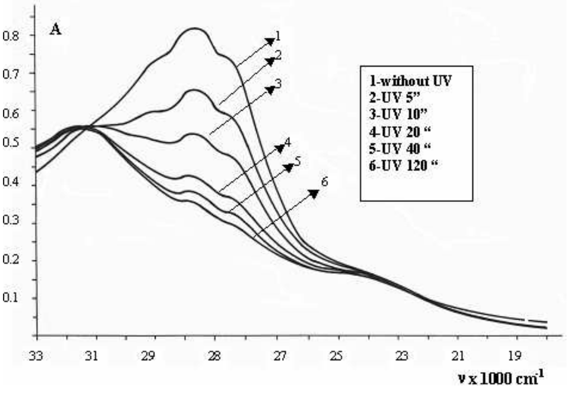

Fig. 1. Electronic absorption spectra of sample 1202+THF.

As already specified, a general characteristic of the compounds studied in this work is that the azobenzene groups belonging to the polymer chain are aligned along the polymer chain structure. The photochromic effect appears as the result of molecular strain in diazobenzene units.

Considering all these, it is more difficult to induce a deformation in the polymer chain as compared to other polymer structures, where the azobenzene units also belonging to the polymer structure, yet being perpendicular to it. The analysis of the electronic absorption spectra presented in Figs.1, for example, leads to the following conclusion: when increasing the irradiation time, more and more trans isomers of the diazobenzene groups go to the cis-pozition, and as the result, the intensity of the electronic band assigned to the trans photoisomers (π-π^*) ($\upsilon_{\max}^{\text{abs}} \approx 27.800$ cm^{-1}) progressively decreases and in the final stage, the photoequilibrium has been reached. The presence of the isobestic points at 31.000 and 20.500 cm^{-1} in the electronic absorption spectra of the investigated polyethers shows that within the system there are only two absorbing species present.

The E/Z photochromic isomerization process has been evaluated by means of a first order kinetic reaction of the form:

$$\ln \frac{A_0 - A_\infty}{A_t - A_\infty} = Kt\,, \tag{1}$$

where A_0, A_t and A_∞ are the sample extinctions ($\upsilon_{\max}^{\text{abs}} \approx 27.800$ cm^{-1}) at the times 0, t and ∞, respectively, and K is the rate constant. The dependences of $\ln\left[\frac{A_0 - A_\infty}{A_t - A_\infty}\right]$ on the irradiation time t for the studied polymers in the hydrofurane (THP) is linear for small irradiation times (Fig. 5). As shown, for small irradiation times, the phtoizomerization process of azo units is faster in solutions when the polymers have a shorter polymer chain, but the molar fraction of trans isomer in the photo-stationary state is approximately the same for all cases.

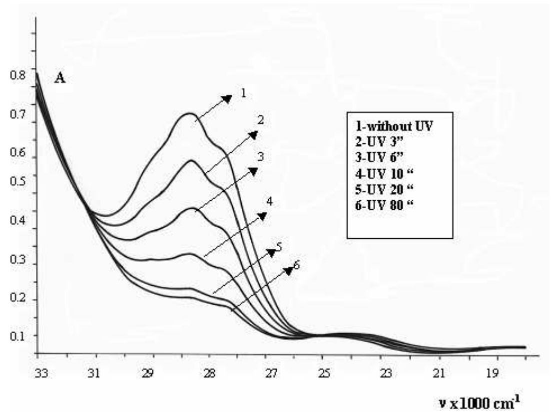

Fig. 2. Electronic absorption spectra of sample 1205+THF.

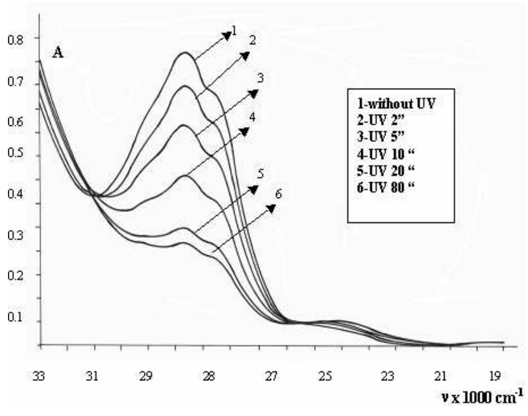

Fig. 3. Electronic absorption spectra of sample 1206+THF.

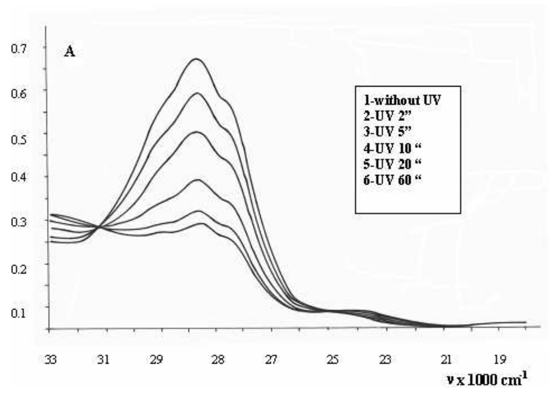

Fig. 4. Electronic absorption spectra of irradiated sample 1287+THF.

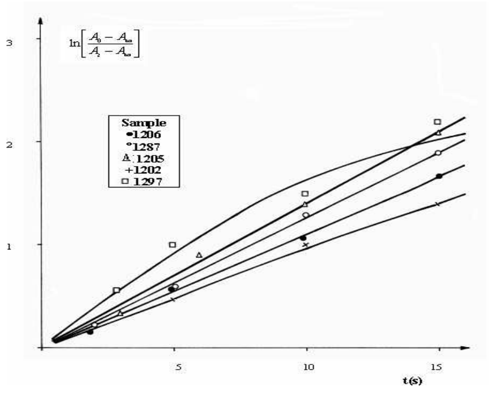

Fig. 5. Kinetic of trans-cis photoizomerization of azobenzene units in polymer matrices.

In another paper [2] we have found that the rigidity of the matrix influences the transition rate. For the same polymer in two different polymer matrices we have been obtained different transition rates. At the same time, one can not exclude the influence of the intermolecular interactions in the local system.

This photochromic effect can be explained as follows: since the polycondensation reaction was conducted with an excess of dihydroxyazobenzene relative to the other biphenols, an excess of azo units in copolymer composition is expected, statistically. It is thus probable that a number of chain ends will be of the azo type. This conclusion is also favoured by the molecular mass law action applied to the studied polymers [2].

3. Conclusion

The photochromic effect of the studied compounds can be explained as follows: since the polycondensation reaction was conducted with an excess of dihydroxyazobenzene relative to the other biphenols, an excess of azo units in copolymer composition is expected, statistically.

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