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Photochromic Liquid Crystalline Structures Containing Azobenzene Moieties

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Summary: Novel liquid crystalline photochromic materials of the type 4–R–C_6H_4–N=N–C_6H_4–$O(CH_2)_n$–$N(CH_2CH_2OH)_2$, where R is NO_2, H, CN, O–*n*-C_8H_{17}, phenyl, 4–$O_2NC_6H_4$, were prepared. Some of them are photoconductive. These materials were used for the preparation of light-sensitive polymers in which the photoactive moieties were attached to polyurethane chain. Photochromism of these compounds is based on trans-cis isomerization of azobenzene group. An example of the photochromic activity is presented on solid solution of one material (R = O–*n*-C_8H_{17}, $n = 5$) in poly(methyl methacrylate) matrix.

Keywords: azobenzene; liquid crystal; photochromism; photoconductivity

Introduction

With the increasing demand for novel devices with optical applications, the search for new materials for data storage becomes a priority. There is a strong interest in this field to find new polymer materials containing photochromic molecules[1], which occupy a prominent position, or functional chromospheres[2]. The azobenzene chromospheres have been widely studied for novel technological applications because their molecules have the ability to photoisomerize[3,4] and the azobenzene moieties can easily undergo photoinduced anisotropy. When exposed to a specific wavelength of polarized light, a reversible anisotropic trans-cis isomerization occurs, which is associated with orientational redistribution of the chromosphere[5]. By irradiating an interference pattern with an appropriate laser light, a surface relief grating can be formed [6] on an azobenzene-

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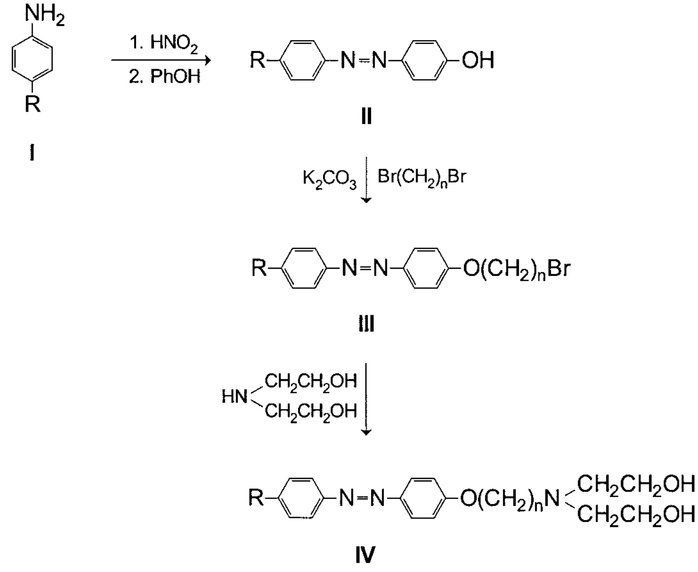
containing thin film. The existence of these effects has stimulated the synthesis of azobenzene copolymers, comonomers of styrene, methyl methacrylate and methyl acrylate, and the preparation of homopolymer blends with azobenzene derivatives[7-9]. Among them, liquid-crystalline structures are expected to show interesting properties.

Experimental

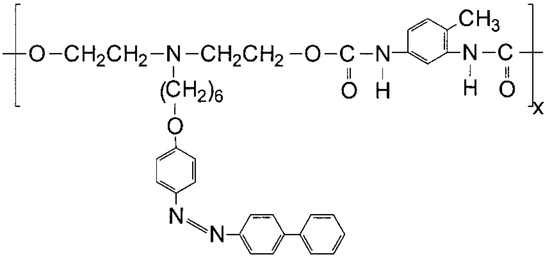
Starting hydroxyazobenzenes **II** (see Scheme 1) were obtained by diazotation and azo coupling of corresponding anilines **I** with phenol. Diols **IV** were obtained by heating corresponding phenols **II** to 60 °C with five-fold excess of 1,5-dibromopentane or 1,6-dibromohexane in an excess of anhydrous potassium carbonate in acetone. The products were crystallized from acetone and then heated with excess of diethanolamine in isopropyl alcohol at 85 °C. For R = H (L32, L33; Table 1), mesophases do not occur. If R = CN (L46), the nitrile group increases the longitudinal dipole moment of the molecule, which causes higher intermolecular interactions, and a smectic mesophase appears. This mesophase changes to an undefined glassy phase which



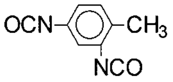
Scheme 1. Synthesis of diols

crystallizes during heating due to a lower viscosity. A longer alkoxy substituent (L41) leads to the expected decrease in the melting point due to a lower dipole moment of the molecule. Introduction of an unsubstituted benzene ring stabilizes the mesophases and a nematic phase appears. The basic characteristics of the synthesized diols **IV** are summarized in Table 1.

The above mentioned diols were used for the preparation of photochromic polymers of the type (e.g., L21 and toluenediisocyanate, TDI).



They were prepared by the reaction of the respective diol **IV** with TDI.



The (L21 – TDI) polymer behaves as an isotropic liquid at 117 °C (during heating) and as an ordered liquid at 120 °C (during cooling). It is photoconductive, the sensitivity parameter S (the ratio of the electrical current of the cell under irradiation (j_{irr}) and in the dark (j_{dark}), $S = j_{irr}/j_{dark}$ was found to be $S = 3.7$.

Absorption spectra of ethanolic solutions of **IV** were measured with a Shimadzu 2401 PC UV-VIS spectrophotometer. Photochromism was studied on thin films of solid solutions of diol IV in poly(methyl methacrylate) (PMMA, M_w 500 000, sample thickness ca. 9 μm) matrix. Samples were irradiated with a xenon discharge lamp 450 W with appropriate filters.

Photoelectrical sensitivity was measured using a Keithley 617 electrometer as a change of the electrical current of the surface photocells with meander-like electrodes (distance 1 mm) at room temperature. The voltage applied to the cell was 200 V, electrode distance 1 mm. The cell was irradiated with a 250-W iodine lamp placed at a distance of 20 cm from the sample.

Results and discussion

The positions of the long-wavelength maxima optical absorption of ethanolic solutions of diols **IV** are given in Table 1 (column 1). All materials absorb light in the region 200 ~ 500 nm. Interestingly, some of the materials show photoconductivity as it follows from column 2. The highest photoconductivity was observed with material L41.

Table 1. Basic characteristics of synthesized diols **IV**

Diol	R	n	1	2		Melting point	Isotropic melt	Nematic phase	Smectic phase
			UV absorption λ (nm)	dark current j_{dark}(A)	sensitivity S	(°C)	T (°C)	T (°C)	T (°C)
L11	O_2N	6	373	5.1×10^{-6}	–	102	* 130	* 123	* 68
L21	Ph	6	361	7.6×10^{-5}	–	137	* 146	* 138	* 133
L22	O_2N	5	372	8.1×10^{-8}	1.2	90	* 128	* 125	* 69
L32	H	5	345	4.5×10^{-7}	1.1	77	*	–	–
L33	H	6	345	2.5×10^{-8}	1.2	92	*	–	–
L41	n-$C_8H_{17}O$	5	358	1.7×10^{-7}	1.8	117	* 114	* 52	* -18
L46	NC	5	360	2.5×10^{-6}	–	103	* 106	–	* 99

Sensitivity S is the ratio of j_{photo}/j_{dark}, where j_{photo} is the current under irradiation.

When the material was irradiated with the light of an appropriate wavelength, cis-trans isomerization was observed. The characteristic spectral changes for diol L41 in PMMA matrix are given in Figure 1. The "dark" spectrum (curve 1) shows a characteristic band with a maximum at 360 nm and a shoulder at 460 nm. Irradiation of the sample with the 360 nm light stimulates the isomerization; the peak at 360 nm decreases and new peaks at 310 and 460 nm appear. The process can be reversed by heat or by irradiation with light of λ = 460 nm (cf. curves 6 - 9 in Figure 1). Full reversibility was obtained by heating to 60 °C (curve 9).

As it follows from Figure 2 the thermal bleaching kinetics taken at different temperatures are not purely exponential. It could be described by a stretched exponential function[10]

$$[M(t)] = [M(0)]\exp\left[-(\nu t)^{\alpha}\right], \tag{1}$$

where $[M(t)]$ and $[M(0)]$ is the concentration of colored species at time t and 0, respectively, ν is the decay rate constant, and parameter α ($0 < \alpha < 1$) measures the deviation from the pure exponential behavior. The reason for the dependence (Eq. 1) is that the photochromic reaction is space-demanding process; thus, the kinetics of the photochemical reaction should depend not only on the nature of reacting species but also on their environment. One may, therefore, expect a distribution of the reaction rates.

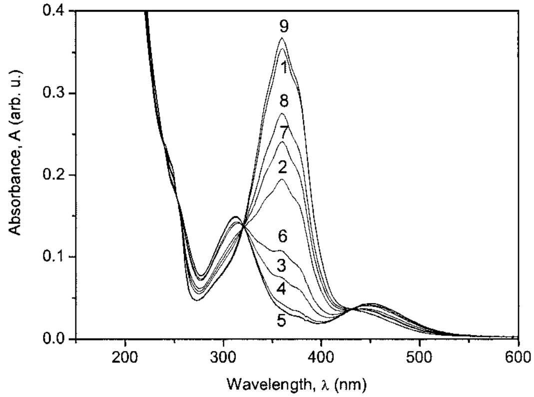


Figure 1. Spectra of L41 in solid PMMA matrix in the dark and after irradiation. Curve 1 – in the dark, curves 2 - 5 – irradiated with light of λ = 360 nm for 11, 35, 65, and 95 min, respectively; curves 6 - 8 – irradiated with the light of λ = 460 nm for 10, 40, and 130 min, respectively; curve 9 – after heating to 60 °C.

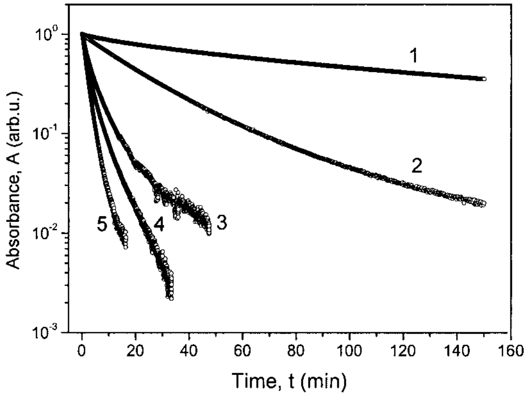


Figure 2. Thermal bleaching kinetics at temperatures 40, 60, 80, 85, and 90 °C (curves 1-5, respectively).

It is not simple to put forward a method allowing to extract information about the rate constant and parameters of its energetic distribution from the shape of the decay curves. A possible method[11], which can be directly employed for measured decays, consists in examining the time dependence of the absorbance × time product: the maximum of the resulting function is directly related to the time constant of the kinetic process, its width to the distribution of the activation energies. The curves replotted from the photochromic decays in Figure 2 are given in Figure 3. The dependences show well-developed maxima. The time constant at 40 °C was $\tau = 2 \times 10^4$ s.

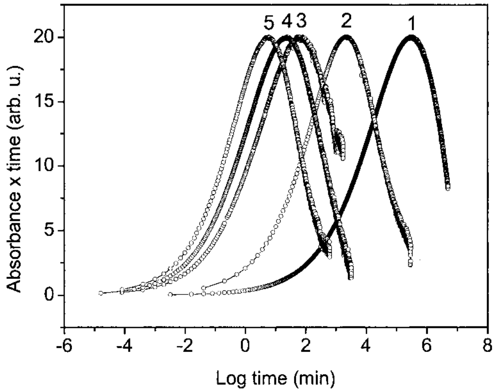


Figure 3. Dependence of the normalized absorbance × time product on logarithm of time.

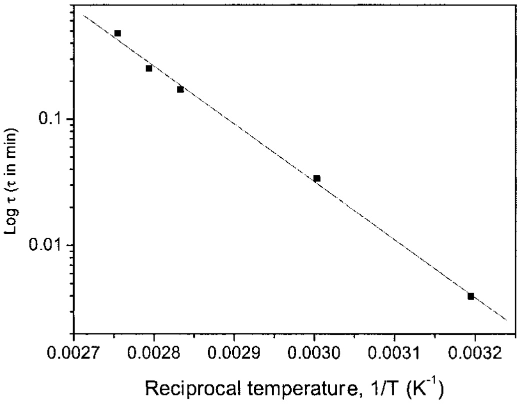


Figure 4. The plot of τ on reciprocal temperature.

The plot of τ vs. reciprocal temperature is linear (cf. Figure 4). The found activation energy of the thermal bleaching process was 87 kJ/mol, the frequency factor $\nu = 2 \times 10^{11}$ s^{-1}.

Conclusion

Novel liquid crystalline photochromic diols of the type 4-R–C_6H_4–N=N–C_6H_4–$O(CH_2)_n$–$N(CH_2CH_2OH)_2$, where R is NO_2, H, CN, O–*n*-C_8H_{17}, phenyl, 4-$O_2NC_6H_4$, were prepared. Their photochromism is based on trans-cis isomerization of the azobenzene group. Typical photochromic parameters for solid solution of the above mentioned material (R = O–*n*-C_8H_{17}, n = 5) in poly(methyl methacrylate) were: bleaching time constant at 40 °C, $\tau = 2 \times 10^4$ s, activation energy of the thermal bleaching process, E_a = 87 kJ/mol, frequency factor, $\nu = 2 \times 10^4\ s^{-1}$, maximum of UV absorption in the dark, λ = 360 nm, characteristic absorption bands in the metastable form, λ = 310 nm and 460 nm. The photochromic process is fully reversible. The above mentioned diols can be used for the preparation of liquid-crystalline, photochromic, and photoconductive polymers by reaction with diisocyanates.

Acknowledgements

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