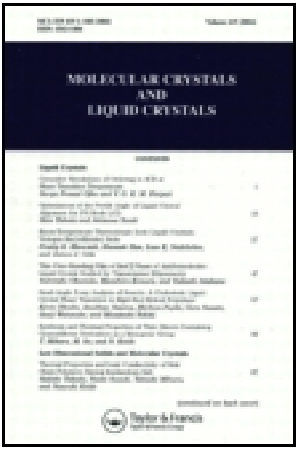

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Photoorientation of Polymer Fragments in a System Azo-Polymer-Microporous Glass

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Anisotropy induction in the azo-polymer introduced into microporous glass under irradiation with polarised UV light is investigated. Practically pure "angular hole burning" mechanism is realised. Influence of the porous matrix on the life-time of cis-isomers, dipol-dipol interaction of polymer side chains, main-chain ordering was established.

Keywords: azo-polymer; porous glass; light induced anisotropy

INTRODUCTION

Photoinduced anisotropy in azo - dyes containing polymers is extensively studying during the last years [1-7]. These polymers are promising from the application point of view, for example, for storage of optical information [1-5] and for orientation of liquid crystals [6-7]. It is also interesting from the fundamental point of view to study the mechanisms of light induced orientational ordering of molecular fragments. First of all it concerns the

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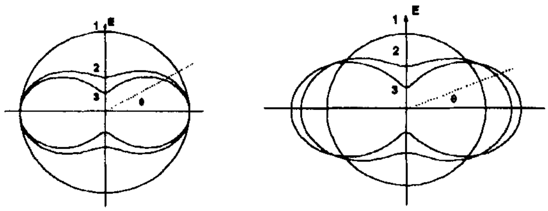
light sensitive fragments [1-3]. There are some studies on the orientational ordering of the polymer molecular fragments that do not absorb the light [4,8]. Many results indicate that light induced ordering depends significantly on the rigidity of the matrix, which contains the absorbing centres [3]. In this paper we studied the mechanisms of azo-polymer photo-orientation in porous glass (rigid matrix).

MECHANISMS OF PHOTO-ORDERING OF LIGHT SENSITIVE FRAGMENTS.

Probability to absorb light by photosensitive fragment depends on its orientation with respect to the polarisation of exciting light. For the fragments oriented in such a way that their dipole moment is parallel to the light polarisation the probability to absorb the light is bigger, and therefore photochemical reaction is more effective for them. In the case of azo-polymers this photochemical reaction is trans - cis isomerisation. The process of photo induced ordering depends on the orientational mobility of photosensitive fragments in the matrix. Recent detailed analysis of possible mechanisms of orientational ordering of the photosensitive fragments depending on their mobility and life-time of the photo-isomers was done by M.Dumont [2]. He considers two mechanisms. The first one realises in the "soft" and "rigid" matrices when rotational diffusion of photo-fragments is fairly high or very low. In this case initially isotropic orientational distribution of photosensitive fragments in trans-state transforms to anisotropic one due to only trans - cis isomerization (Fig.1a). This mechanism of induced anisotropy is usually called "angular hole burning" (AHB) mechanism [2] or photoselection [3]. There are intermediate states between "soft" and "rigid" matrices when orientational mobility of chromophores is not very high. Then in the result of many acts of light absorption the fragments will accumulate in the direction with their dipole moment being perpendicular to the light polarisation to minimise the absorption. It leads to the transformation of the initially isotropic distribution function of trans-isomers as it is shown in Fig 1b. This mechanism of orientational ordering is usually called "angular redistribution" (AR) [2].



a) b)

FIGURE 1 Dynamics of distribution function for trans-isomers under the illumination for AHB (a) and AR (b) mechanisms; $t_1=0<t_2<t_3$.

AHB and AR mechanisms are characterised by different kinetics of anisotropy recording and relaxation. In Fig.2. we show the typical kinetic dependencies of $D_\parallel$ and $D_\perp$ ($D_\parallel$ and $D_\perp$ are optical density components of the film at the light wave length corresponding to maximal absorption measured in the direction of azo-fragments' orientational ordering and perpendicular to this direction respectively) [2,9]. At AHB ordering mechanism the light causes decreasing of both $D_\parallel$ and $D_\perp$, while increasing of $D_\parallel$ and decreasing of $D_\perp$ corresponds to AR mechanism. In the first case the relaxation of light induced anisotropy is characterised by monotonic increasing of both components $D_\parallel$ and $D_\perp$ and by their return to the initial state. Relaxation in the case of AR mechanism is characterised by increasing of the component $D_{\perp}$ and decreasing of $D_{\parallel}$. Light induced anisotropy may be reversible or irreversible depending on the viscosity of polymer matrix.

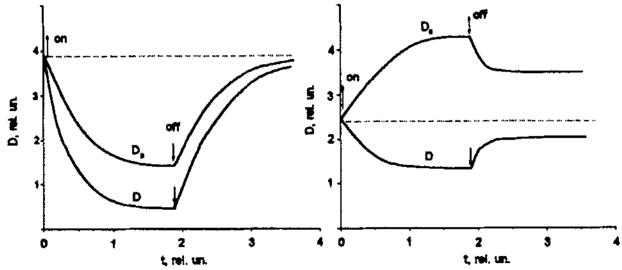


FIGURE 2 Schematic picture of kinetics of $D_{\parallel}$ и $D_{\perp}$ for recording and erasing processes for AHB (a) and AR (b).

In real systems these mechanisms are observed simultaneously. Which one is dominant depends on the properties of matrix and illumination conditions. In the films of azo-polymers the angular redistribution mechanism is usually realised[1] [1,2,4,5]. The angular hole burning mechanism takes place in the solid polymer solutions of azo-dyes because of high rate of orientational mobility of azo-fragments. Up to now, pure AHB mechanism for azo-fragments was not realised in rigid matrices. One of the ways of doing this is deep cooling of the film. Another possibility is to confine the azo-polymer to porous matrix. To realise this idea Dumont et al. Embedded azo-polymer into sol – gel film [9]. They observed the evolution from the behaviour close to AR to behaviour close to AHB upon film solidification. At the same time, even in the rigid film they did not observe pure AHB mechanism. We think that this is because the size of pores

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[1] "Angular hole burning" mechanism could be realized under the short-pump irradiation. This case is considered theoretically in [9].

containing polymer is quite big (in the case of sol – gel – process pore diameter reaches 300 – 1000 A [10]. At the same time, crossover to surface behaviour is at more small pore size. The evidence of it is that nematic to isotropic transition becomes gradual at pore diameter about 100 A [11].

EXPERIMENTAL PART

Sample

Azo polymer. We used the polymer synthesised by us previously [12]. Structure formula of polymer is $[-O-CO-CH(Sp-M)-CO-O-(CH2)8-]_{16}$, where Sp-M is a side chain consisting of alkyl spacer $Sp=(CH_2)_6$ and azobenzene fragment $M=-O-Ar-N=N-Ar-NO_2$. Flexible alkyl spacer Sp provides effective orientational mobility of azobenzene unites. Due to the polar group NO_2 side fragment possesses significant dipole moment. Polymer has two mesophases in the following range of temperatures $Cr(34^0C)\ Sm_A(45^0C)\ N(52^0C)I$. The mechanisms of light induced anisotropy in the films of this polymer were studied by us in [5,8].

Porous glass. Microporous matrices with strongly interconnected and randomly oriented pores with average pore diameter of 80 A (volume fraction of pores was 27%) were prepared from the original sodium borosilicate glasses. Like Vycor glass [13] the porous glasses used in our experiments are characterised by narrow distribution of pore sizes. The samples with a thickness of 0.5 mm in our experiments were used.

Filling method. Porous glass slabs were annealed at temperature of 450^0C during 3 hours. After that they were cooled till near room temperature, and then dipped for 30 minutes into solution of azo-polymer in dichloroethane (concentration $c_{azo} = 10g/l$). Finally slabs were aired in heater at 60^0 C during 12 hours to remove the solvent completely.

Experimental methods

Absorption spectra of microporous glass filled with azo polymer were measured in UV and visible diapasons by means of modified spectrometer KSVU (LOMO, Snt. Petersburg, Russia). Same equipment was used for measurements of the kinetic dependencies of both optical density at wave length corresponding to the maximum of azo-polymer absorption. Kinetic of anisotropy induction and relaxation was also measured by light induced birefringence method [8]. High pressure mercury lamp was used as the source of irradiation. Glan - Thomson's prism was applied to polarise the radiation. Influence of porous matrix on the phase states of azo-polymer was studied by DSC method.

Results and discussion

DSC measurements shown that peaks corresponding to S_A-N and N-I transitions of polymer in porous matrix are strongly suppressed. This result is common for LCs in microporous matrix [10,13]. It means that bulk properties of the polymer are good enough suppressed and polymer-matrix interaction plays important role.

An absorption spectrum of azo polymer in porous glass is shown in Fig. 3 (curve 1). Curve 2 corresponds to polymer spectrum measured just after irradiation during 15 min by non-polarised light of mercury lamp. Curve 3 was measured in 120 min after termination of excitation process. Irradiation decreases the intensity of main absorption band, corresponding to absorption by trans-isomers, and increases the absorption by cis-isomers. In the frame of the mistake of measurements one can say about isobestical point at λ=318 nm that makes picture of spectral changes similar to the picture observed for this polymer in solutions. Isobestical point is absent for photo-induced spectral changes in films of this polymer.

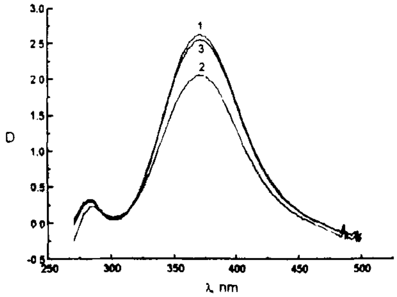

FIGURE 3 Absorption spectra of the polymer in porous glass; 1 - spectrum before irradiation; 2 - spectrum measured just after irradiation during 15 min; 3 - 120 min later after termination of irradiation.

Another difference between spectra in films and porous glass is lack of shift of absorption maximum for polymer in porous glass in comparison with polymer films. In the last case this shift was 5-7 nm [5]. "Blue" shift in the absorption by azo-polymer film was associated with the strengthening of dipole–dipole interaction of chromophores upon their orientational ordering, this strengthening changed the positions of energy levels. Absence of such a shift in the case of azo-polymer confined in porous glass may be connected with the absence of orientational ordering of chromophores. Another reason may be high dispersion of polymer in pores, when almost each polymer molecule is isolated in a pore, and therefore dipole – dipole interaction between polymer molecules does not play significant role.

In fig.4a and Fig.4b we plot the kinetic dependencies of optical density components, $D_{\parallel}$ and $D_{\perp}$, and birefringence, Δn, for both processes of anisotropy recording and relaxation. Comparing Fig.4a and Fig.2 it is seen that qualitatively behaviour of $D_{\parallel}$ and $D_{\perp}$ corresponds to the AHB mechanism. Therefore we can expect that chromophores in our system are quite well "frozen" in matrix and they do not change their orientation during the trans - cis isomerisation.

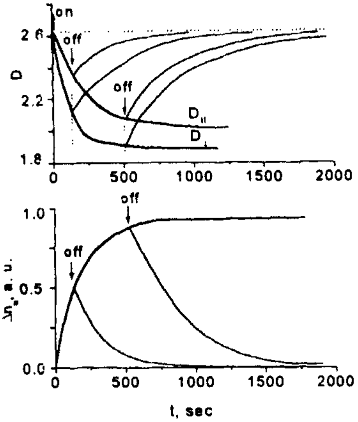

FIGURE 4 Kinetic dependencies of $D_{\parallel}$ и $D_{\perp}$ (λ=370 nm) and birefringence Δn for recording and erasing processes. Arrows ↑ and ↓ correspond to switching on and off of the exiting irradiation respectively.

Dependencies $D_{\parallel}(t)$, $D_{\perp}(t)$ and $\Delta n(t)$ have exponential law with approximately only one and the same characteristic time for all of them. In the case of angular hole burning mechanism it is the life – time of cis-form. In our experiment this time was about 9 minutes. This value is almost twice bigger than life–time of cis-form in a bulk [8]. It means that porous glass influences not only the freedom of chromophores to rotate, but increases the barrier of cis– trans - transition. There is no suppression of the process of cis–trans-isomerisation as it was observed in [14].

From the fact that all $D_{\parallel}(t)$, $D_{\perp}(t)$ and $\Delta n(t)$ have the same characteristic time it follows that they reflect the same process of ordering. It is process of ordering of chromophores. In contrast to the bulk case [11] the dependence $\Delta n(t)$ which indicates orientation of all fragments of polymer molecule does not "feel" orientation of macro chains. It is reasonable to suppose significant decrease of mobility of polymer chains due to their interaction with pore's walls. The mechanism of this interaction we are currently studying.

CONCLUSION

To conclude we can state that light induced anisotropy in azo polymer confined to microporous glass reflects the angular hole burning mechanism practically in its pure form. Microporous glass is an ideal matrix where rotation of chromophores is almost "frozen", but at the same time they can undergo trans – cis isomerisation. Life-time of cis-isomers increases in microporous matrix. Orientational ordering of azo-fragment practically does not influence the orientational ordering of polymer main-chain due to their strong interaction with pores' walls.

Acknowledgements

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