Influence of acid-base modifiers on photoinduced mass transport in amorphous azobenzene amino acid

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The effect of acid-base modification of 4-((4-(bis(5,5,5-Triphenylpentyl) amino) phenyl) diazenyl) benzoic acid in context of the sensitivity to the polarization holographic recording was studied. Diethylamine and acetic acid as the modifiers were added to the amino acid solution immediately prior to application by spin-coating method. The relief formation by photoindused mass-transport in the films under the action of lasers with wavelengths of 405 and 532 nm was examined.

(Received December 1, 2016; accepted February 12, 2018)

Keywords: Photoinduced mass transport, Azobenzene compounds

1. Introduction

Since the discovery of surface relief grating (SRG) formation by illumination of the amorphous films with two coherent laser beams, the phenomena of photoinduced mass transport have been attracting a great deal of attention. Photoinduced SRG formation has been reported not only for amorphous azobenzene containing polymers [1-3], but also for amorphous films of chalcogenide semiconductors (As-S, As-S-Se) [4-7].

In previous work [8], we have presented the results showing the possibility of low molecular weight organic glass application as a medium for direct holographic recording (surface grating formation) without chemical etching operation. We made the comparison of the sensitivity of different materials in this aspect. The concept of sensitivity interpreted as the exposure required to form regular surface relief height of 200 - 300 nm: this height is necessary to obtain the maximum diffraction efficiency of holographic image at the replication. The compound 4 - ((4- (bis (5,5,5-Triphenylpentyl) amino) phenyl) diazenyl) benzoic acid (KRJ-8), whose structure is shown in Fig.1 shows the best results.

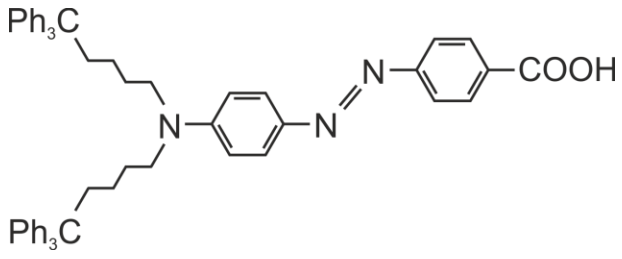

Fig. 1. Chemical structure of KRJ-8

As seen from the picture, the compound KRJ-8 structurally is azobenzene amino acid. As is known [9], the amino acid can form different ions depending on the acidity of the environment in which they are located. The possibility of ionic pair formation in chloroform solutions in similar system in the process of acid-base interaction was showed Barrow and Yerger in [10,11] and Smith in [12]. Proceeding from the fact that films of KRJ-8 were obtained from the same solvent, it seemed interesting to us to research how the acid-base modification can affect to the system recording sensitivity. Especially as it was shown [13] that the activity of formation of photo-induced relief in diazocompound directly is related with the dipole moment of the molecules.

Since the relief formation occurs in the dry film, it is obvious that modifications can be made in the compound solution prior to application. In the first stage of the research presented in this article, we decided to choose a modifier that would have left the film in the drying process. Based on these considerations, diethylamine and acetic acid were selected as modifiers.

2. Experimental

2.1. Preparation of the solutions

The solutions of KRJ-8 in chloroform (Table 1) were prepared by following ingredients:

- KRJ-8 was synthesized by method, described in [8];
- Chloroform (Chempur, CAS# 67-66-3, pure p.a.);
- Anhydrous acetic acid was synthesized from acetic anhydride (Chempur, CAS# 108-24-7, pure p.a.) by method, described in [14];
- Diethylamine (Aldrich, CAS# 109-89-7, pure p.a.).

Table 1. Parameters of KRJ-8 solutions and ratio with the modifiers.

	KRJ-8, mg	Chloroform, mg	Modifiers		Molar ratio KRJ-8 : Modifier
			Acetic acid, mg	Diethylamine, mg	
Solution #1	30	580			1:0
Solution #2	30	580	2,15		1:1
Solution #3	30	580	4,30		1:2
Solution #4	30	580	6,45		1:3
Solution #5	30	580		2,70	1:1

2.2. Films formation on the glass and quartz substrates

The solutions were applied to a glass and quartz substrates by spin-coating. The films were dried during 48 h in dark place at room temperature. The thickness of dry films was 350-400 nm, determined by the Veeco Dektak 150 surface profiler. The transmission spectra were measured by the Ocean Optic HR4000CG spectrometer.

2.3. Holographic recording and surface relief measurement

Holographic recording was performed by the lasers with a wavelength of 405 nm and 532 nm. In the first case, the recording was made with the setup described in [15, 16], with p-p polarization of the recording beams (electric field vector lies in the coincidence plane of the interference beams). Period of recorded gratings (frames with size 155x116 μm) was 1000 nm by the appropriate software. Exposure of the recording beams was in the range of 0 - 100 J/cm^2 at an intensity of 7.8 W/cm^2.

Recording by laser at 532 nm was carried out using the setup described in [17]. In the experiments the recording beams with p-p and +45°/-45° polarization was used. Recording was performed with the exposure in the range of 0-100 J/cm^2 at an intensity of 0.165-0.220 W/cm^2 with the grating period 1 micron.

Measurement of the diffraction efficiency was carried out in the reflectance mode by laser with a wavelength of 532 nm. Diffraction efficiency is calculated by the formula $DE_t = 100\% * (I_{+1} / I_0)$.

Surface topography was determined by AFM.

3. Results

Fig. 2 shows the transmission spectra of the modified KRJ-8 films in comparison with the film of the unmodified compound. The graph shows that the spectrum of the pure KRJ-8 film and the acetic acid modified compound is practically the same. This is true for all samples containing acetic acid. However, in the case of the diethylamine modified compound a shift of the absorption peak in the blue region is observed.

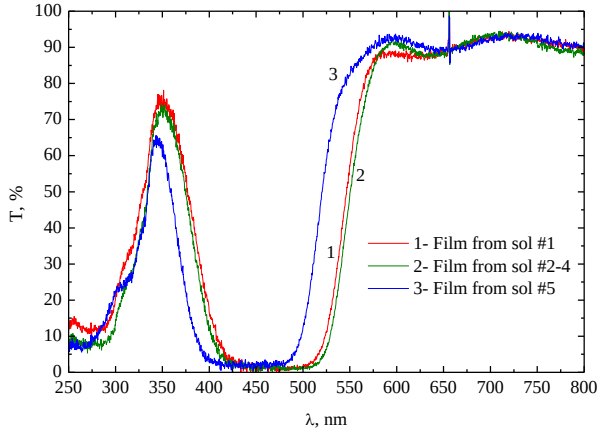

Fig. 2. Transmission spectra of samples films

Fig. 3 demonstrates the difference in recording speed of the base film comparison with the modified samples. It is seen that the recording speed in the acetic acid modified samples is close to the recording speed of the base material. While the film modified by diethylamine shows significant decreasing of the sensitivity to surface relief grating formation.

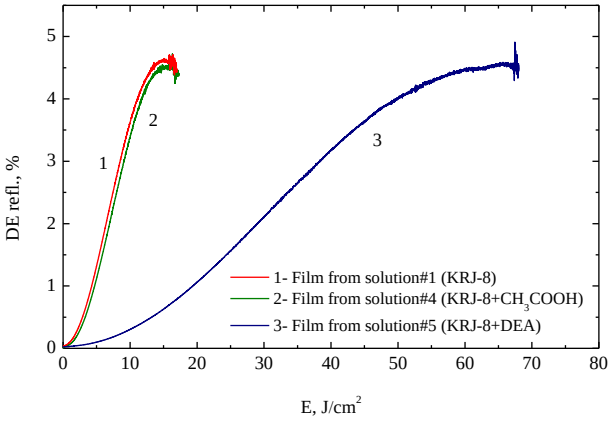

Fig. 3. The dependence of the reflection diffraction efficiency on exposure records for KRJ-8 modified and unmodified samples. Recording laser wavelength is 532 nm, beam polarization are ± 45°, intensity 0.22 W/cm^2 the grating period is 1 micron.

General information about the recording materials sensitivity to wavelength 532 nm is shown in Table 2. The sensitivity of the films was determined as the tangent of the angle of the diffraction efficiency curve inclination to the y-axis. The table presents the data obtained with the polarization of the recording beams of ± 45°.

Results obtained in standard commercial pixel-recording installation [14,16] with a laser wavelength of 405 nm and a p-p polarization of beams, shown in Fig. 4. Unlike the chart 3, there is shown the dependence of the surface relief height on the exposure. It can be seen that the curve showing the relief formation at the surface of the unmodified KRJ-8 film is almost identical with those for acetic acid modified material.

Table 2. The sensitivity of the KRJ-8 films to wavelength 532 nm determining as the tangent of the angle of the reflection diffraction efficiency curve inclination to the y-axis.

Sample	tg α,%*cm^2/J
KRJ – 8	0,48
KRJ – 8 + DEA	0,11
KRJ – 8 + acetic acid (2.15 mg)	0.43
KRJ – 8 + acetic acid (4.30 mg)	0,41
KRJ – 8 + acetic acid (6.45 mg)	0,47

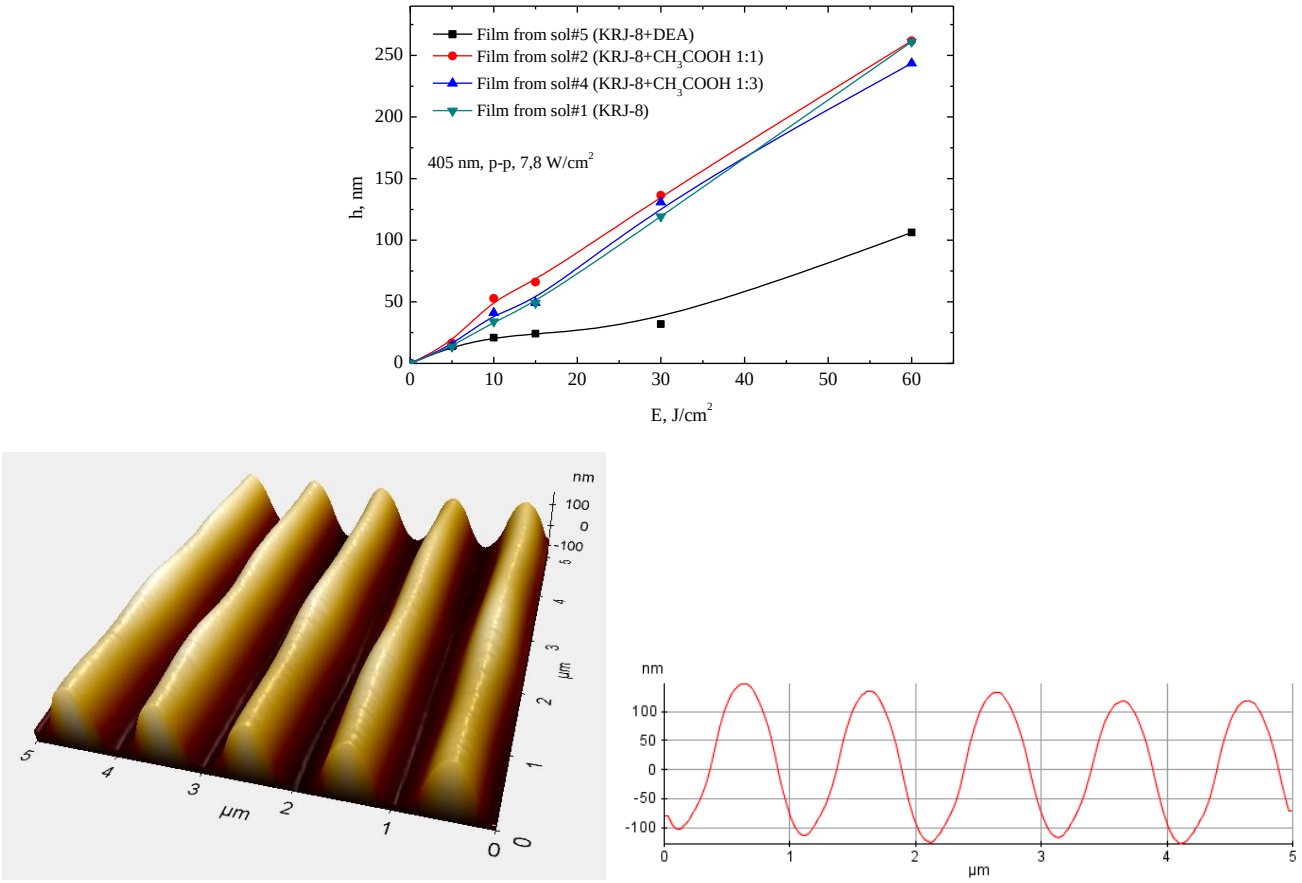

Fig. 4. The dependence of the surface relief modulation depth on exposure records for KRJ-8 modified and unmodified samples and AFM-image of typical grating (KRJ-8 + CH_3COOH 1:1). Recording laser wavelength is 405 nm, the grating period is 1 micron.

4. Discussion

Coincidence of spectra of KRJ-8 film and the films modified with different amounts of acetic acid suggests that KRJ-8 without modification has in the "acidic" form, i.e. free electron pairs of all three nitrogen atoms are in the hydrogenated state. Probably, this configuration is laid on the stage of the synthesis and purification of the compound. This conclusion is confirmed by the fact that the attempt to increase the amount of acetic acid during the modification did not produce significant changes in the spectra and compound sensitivity.

Results of the holographic records, as by laser with a wavelength of 532 nm, as by the pixel installation with wavelength 405 nm indicate that the compound in acidic state has the greatest sensitivity for non-etching relief formation. It can be assumed that the presence of protons on the free electron pairs of the nitrogen atoms transforms the compound to the trans-modification. This assumption suggests itself if we take into account the theory of the valence shell electron pair repulsion [18], and the results

of some research on protein materials enabled azobenzene molecule fragment [19, 20].

It is noteworthy that the change of the wavelength and polarization of recording beams is not influenced by the relative activity of the modified compounds. As in the case of record by the rays with wavelength of 532 nm (with polarization ± 45 °), as in the case of the laser of 405 nm (p-p with polarized beams), acidic form of the compound gives the highest activity. And, if in case of record by wavelength of 532 nm it can be explained by the greatest absorption, in the case of 405 nm, the situation is just opposite - the diethylamine modified film absorbs this wavelength more.

5. Conclusions

The compound KRJ-8 has the highest sensitivity to photo-induced mass transport at the polarization holographic recording wavelengths of 532 nm (with the polarization of ± 45 °) and 405 nm (with a p-p polarized beams) without modification. Addition of acetic acid did not significantly affect this parameter. Modification by diethylamine reduces the sensitivity of the original compound to 20-25%.

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