

The synthesis of different variants of azo-polyurethane polymers for optical recording

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The method of synthesis of photosensitive polyurethanes polymers on glycerine, toluenediisocyanate and Disperse Red 1 base was described. Two types of polymers with different amount of Disperse Red 1 fragments in macromolecules were compared. Films of the polymers were obtained from solutions in organic solvents on glass substrate. The dry film thickness was in the range of 3,5 – 4.5 μm . The transmission spectrums of the films were studied. Possibility of formation of side product in the process of synthesis was observed. The photobirefringence measurements of polymers films were performed. Surface relief grating (SRG) formation was observed during polarization holographic recording process. A profile of SRG was studied by AFM.

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1. Introduction

The last time many photosensitive polymers (PP) for different optical devices were synthesized and described [1-6]. The advantage of photosensitive polymer films (PPF) in comparison with another composition (for example, inorganic) based on two features: relative simplicity of coating on the substrate and wide possibilities for chemical modification of materials. The simplicity of coating of PP on the substrate reached by using of spin-coating or applicator methods, but the possibilities for chemical modification – by adding of different chemical groups in macromolecules. Also formation of composite films is possible on PP base.

However, the price of such polymers on the market is relatively high. The reasons of that are multiphase synthesis, subsequent cleaning and separation of products.

One of the perspective directions of PP evolution we consider synthesis of polyurethanes (PUR) photosensitive materials. The interaction between $-\text{OH}$ and $-\text{NCO}$ groups take place at low temperature (lower $100\text{ }^\circ\text{C}$), this reactions are good investigated [7] and there are many catalysts for PUR synthesis.

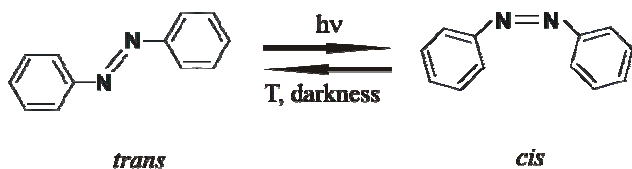


Fig. 1. Isomerization mechanism of azochromophores.

Synthesis and studies of optical properties of some photosensitive polyurethanes were described in the publications [6, 8, 9, 10]. The photosensitivity of this polymers based on presence of azochromophores parts in macromolecules. Photoisomerisation mechanism of

azochromophores is showed in Fig. 1. Described polymers by structure can divide on two types:

1. Group $\text{N}=\text{N}$ is the part of main macromolecule chain (Fig. 2a).

2. Group $\text{N}=\text{N}$ is the part of side chain (fig. 2b).

For polymer synthesis in the first case azocompounds with two or more $-\text{OH}$ groups in different sides rather $\text{N}=\text{N}$ bond were used [8,9]. In the second case, the photosensitive PUR formation from diazodiols with two $-\text{OH}$ groups in the one side rather $\text{N}=\text{N}$ was described [6, 10].

In this publication we describing another mechanism: for main chain formation we use glycerol as polyol, but $\text{N}=\text{N}$ groups incorporated in macromolecule through diisocyanate. Such scheme gives th possibility to use azocompound with only $-\text{OH}$ group in molecule, for example – Disperse Red 1 (DR1).

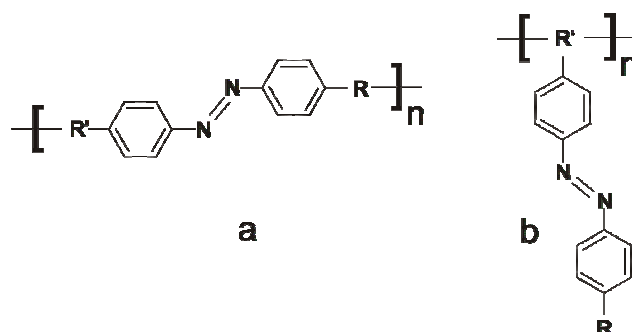


Fig. 2. Two types of azo-polymers structures.

2. Experimental

Disperse Red 1 (DR1) delivered by Fluka (CAS 2872-52-8); N,N -dimethylformamide pure (DMF) (CAS 68-12-

2); 2,4- and 2,6-toluene diisocyanate (TDI) in the ratio 67 : 33, purity $\geq 99,5\%$ and glycerol pure (CAS 56-81-5) were used as raw materials. N,N-dimethylformamide and glycerol were dried directly before synthesis.

2.1 The polymer G-DR266 synthesis

- TDI-DR semiproduct preparation.

116 g 1,3 % (wt) filtered solution of DR1 in DMF through dropping funnel was added in flask with magnetic stirrer, where preliminarily was loaded 2,2 g of TDI. The DR-1 solution was added not fast 5 hours at temperature

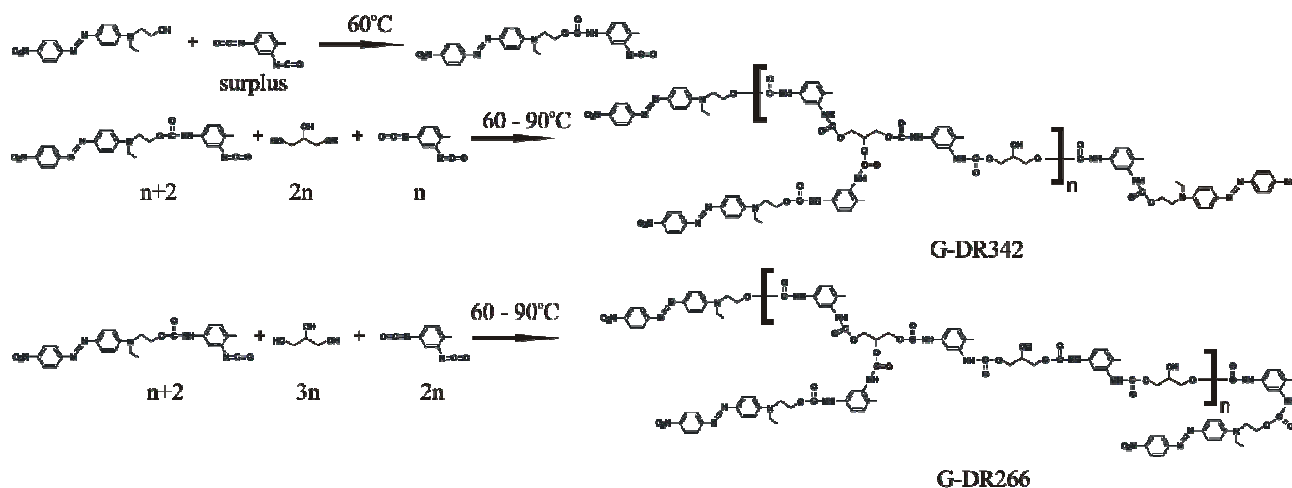


Fig. 3. Reactions of polymers G-DR342 and G-DR266 synthesis.

2.2 The polymer G-DR342 synthesis

- TDI-DR semiproduct preparation.

131.5 g 1,3 % (wt) filtered solution of DR1 in DMF through dropping funnel was added in flask with magnetic stirrer, where preliminarily was loaded 2.45 g of TDI. The DR-1 solution was added not fast 5 hours at temperature 333 K. After adding, the mixture was exposed at 363 K during 2 h.

- The polymer G-DR342 solution preparation.

0,84 g of glycerol was loaded in flask with magnetic stirrer and was dissolved in 5,00 g of DMF. 133.9 g of the TDI-DR solution during 3 h through dropping funnel was added in reaction flask with the glycerol solution at 333 K. After that, the reacting mixture was heated up to 363 K, and the vacuum evaporation of DMF was performed while the non-volatile components of polymer solution were $50\pm 5\%$ (wt).

2.3 Polyurethane and DR1-TDI-DR1 composite solution preparation

- The polymer G-TDI solution preparation.

10 g of glycerol was loaded in flask with magnetic stirrer and was dissolved in 23 g of DMF. 20 g of the 62 %

333 K. After adding, the mixture was exposed at 363 K during 2 h.

- The polymer G-DR266 solution preparation.

0,55 g of glycerol was loaded in flask with magnetic stirrer and was dissolved in 5,00 g of DMF. 58 g of the TDI-DR solution and 0.3 g of TDI during 3 h through dropping funnel was added in reaction flask with the glycerol solution at 333 K. After that, the reacting mixture was heated up to 363 K, and the vacuum evaporation of DMF was performed while the non-volatile components of polymer solution were $50\pm 5\%$ (wt).

(wt) TDI solution in DMF during 3 h through dropping funnel was added in reaction flask with the glycerol solution at 333 K. After that, the reacting mixture was heated up to 363 K during 5 h. The content of non-volatile components of polymer solution was 70,7 % (wt).

- DR1-TDI-DR1 synthesis and composite solution preparation.

9.8 g 1,4 % (wt) filtered solution of DR1 in DMF and 0.15 g TDI were loaded in a flask with magnetic stirrer, the mixture heated up to 363 K during 5 h. After that the vacuum evaporation of DMF was performed while the non-volatile components of solution were $50\pm 5\%$.

- 0.16570,7 % (wt) filtered solution of G-TDI was added in the flask and mixed during 1 h.

2.4 Fabrication of the polymer films

Fabrication of films from the polymer solutions were performed by company BYK Gardner GmbH applicator, the thickness of liquid layer was 30 μm . A glass plates were used as substrate. The films were dried in oven at temperature 423 K during 10 min and after that 8 h in dark place at room temperature. The thickness of dry films was $3.75\pm 0.25\ \mu\text{m}$, determined by the Veeco Dektak 150 surface profiler.

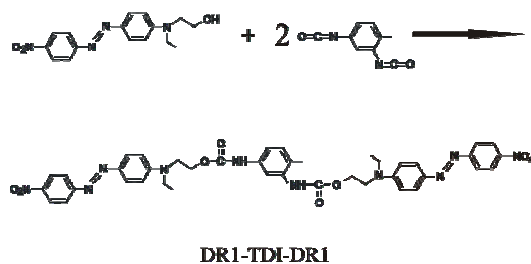


Fig. 4. Reaction of DR1-TDI-DR1 formation.

2.5 Photobirefringence measurements and holographic record

Photobirefringence measurements have been performed in both G-DR266 and G-DR342 polymers and composite films. Detailed procedure and scheme were described in [11]. As pump laser Verdi-6 with 532 nm wavelength was used. As probe laser was used 634 nm diode laser with intensity $I=0.4 \text{ mJ/cm}^2$. Refraction index changes Δn were calculated by formula:

$$\Delta n(t) = \frac{\lambda}{\pi d} \arcsin \left(\sqrt{\frac{I(t)}{I_0}} \right) \quad (1)$$

For holographic recording Verdi-6 laser with wavelength $\lambda_1=532\text{nm}$ was used. Experimental set-up was shown in [11]. Holographic recording was performed with orthogonally circularly polarized two beams – L-R/R-L (left-right/right-left). An angle between recording beam and normal was $15,4^\circ$, thus, grating with period $\Lambda=1.0 \mu\text{m}$ was recorded according to interference maxima condition.

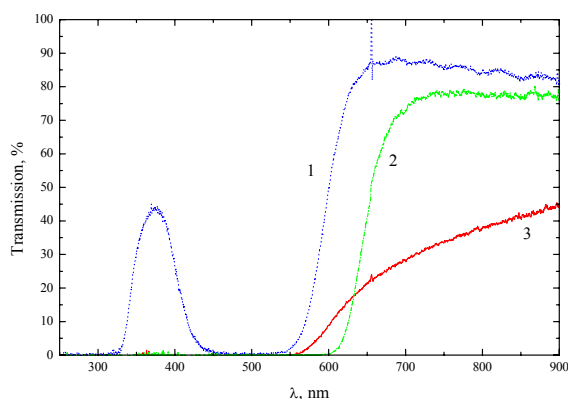


Fig. 5. Transmission spectra of the films: (1) G-DR266; (2) G-DR342; (3) Composite, containing DR1-TDI-DR1.

Diode laser with $\lambda=632.8 \text{ nm}$ and $\lambda=650 \text{ nm}$ was used as reading beam. ± 1 diffraction maximums were measured in transmission mode with photodiodes which were connected to PC. After recording, the surface relief of the samples was analyzed by Atomic Force Microscope (AFM).

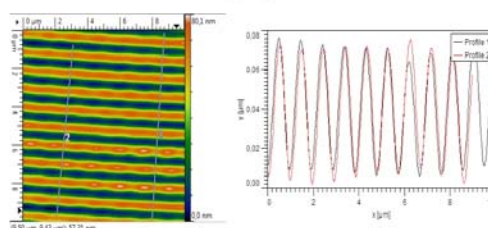
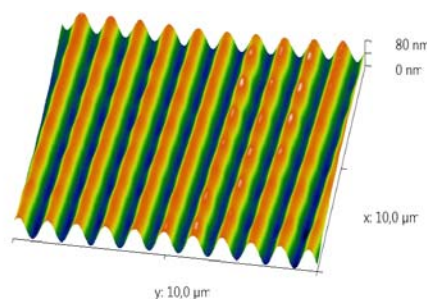
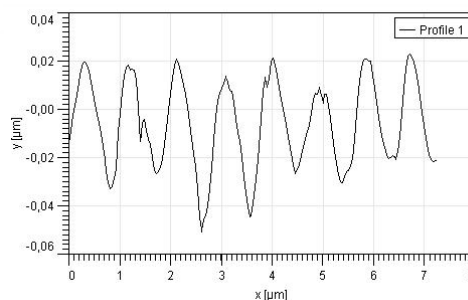
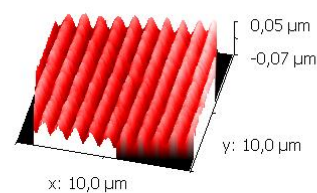


Fig. 6. Surface relief of polymers films after holographic record. Polymer G-DR342 (each recording beam $P=0.7 \text{ W/cm}^2$, left picture) and G-DR266 (each recording beam $P=0.5 \text{ W/cm}^2$, right picture).

3. Results and discussion

The additional complication for polymer synthesis on DR1 base gives the fact of low solubility the azocompound in anhydrous DMF. We could reach only 1.5 % (wt) in our experiments. So the first part of polymer synthesis is gone in low concentration environment. The macromolecules form very slowly, that is why solvent vacuum evaporation was used. Besides, DMF has high value of surface energy and the low-viscosity solutions on it base very bad wet the glass surface.

The reactions and prospective structures the synthesized polymers are showed in figure 3. Theoretically it is possible formation of dendroid structure of the macromolecules, but because of low activity of secondary $-\text{OH}$ group of glycerol we assumed that is improbable. As can see, the difference between the

polymers is amount of DR1 fragments in macromolecules, i.e. conditionally – quantity N=N bonds in polymers.

In the first phase of synthesis it is possible formation of collateral product as showed in figure 4. We tried to estimate how the compound DR1-TDI-DR1 can influence in optical properties of the polymer films. For this task we specially synthesised glycerol – TDI polymer and mixed it with DR1-TDI-DR1 as described in paragraph 2.3. The amount DR1 fragments amount in the composite is the same it amount in the polymer G-DR342 – 34.2 %.

Fig. 5 shows the transmission spectra of the polymers G-DR266 and G-DR342 films and the spectra of the composite G-TDI + DR1-TDI-DR1 film. It is visible that the presence of DR1-TDI-DR1 in polyurethane polymer increase optical scattering of the film. The reason of the scattering probable is thermodynamic incompatibility of composite components. As the spectra of the polymer G-DR266 and G-DR342 films have low value of scattering, we assumed that the amount of DR1-TDI-DR1 in the polymers is insignificant.

We measured the photobirefringence of polymer G-DR266 and G-DR342 films. The curves and more detailed description presented in [11] but here we show only dn values under 532 nm laser-light illumination: for polymer G-DR266 film dn is 0.083, but for G-DR342 dn=0.066. The dependence dn of the polymers on concentration of N=N bonds probable will be the theme of further studies. The dn value of composite film (DR1-TDI-DR1 in polyurethane polymer) is 0.035.

The holographic record by method of polarization holography [12] was performed in the polymer films by laser 532 nm. Fig. 6 shows AFM images of grating surface. The intensity of each recording beam were 0.5 W/cm² for G-DR266 polymer film and 0.7 W/cm² for G-DR342. The grating relief depth in the first case (G-DR266) was 40-50 nm, and in the second case (G-DR342) was approximately 70 nm. More detailed data about diffraction efficiency presented in [11].

4. Conclusions

The synthesised polymers G-DR266 and G-DR342 can be used as media for holographic record. The photobirefringence of the polymers give possibility to record relief diffraction grating by polarization holographic method. The depth of the gratings relief reached 70 nm in the G-DR266 and 40-50 nm in the G-DR342 film.

Presented in the work the two-stage synthesis method can be used for producing the same polymers with different amount of DR1 fragment in the macromolecules below 35 %. The possibility to obtain the polymers with more high concentration of DR1 fragment in molecules can be the next studies theme.

Theoretically, another polyol or oligomers with free –OH groups can be used except of glycerin. However, in this case the reactivity of the –OH groups must be note for gel formation avoiding.

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