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Photoinduced mass transport in low molecular organic glasses and its practical application in holography

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ABSTRACT

In this paper we present the synthesis and optical properties of amorphous low molecular compound 4-((4-(bis(5,5,5-Triphenylpentyl)amino)phenyl)diazenyl)benzoic acid. The surface relief gratings formation by polarization holography method on these thin films (thicknesses are 200–1700 nm) was shown. The dependence of the surface relief modulation on various parameters: recording exposure dose, the polarization state of the recording beams, the grating period and the film thickness of the material was demonstrated. Values of surface tension at the air-film before and after irradiation of the substance by polarized radiation were measured.
The efficiency of surface relief formation in different medium was compared. The possibility of practical application of 4-((4-(bis(5,5,5-Triphenylpentyl)amino)phenyl)diazenyl)benzoic acid in the holography as a non-etching photoresist was showed.

1. Introduction

The formation of direct micro and nano-relief on the photosensitive material surface under polarized coherent radiation is a phenomenon that has both applied and academic importance. From the application point of view, the phenomena is useful for the production of a variety of optical and electro-optical devices, and academic — opens up new feature action of light to the substance. Over the past two decades the behavior of different classes of light-sensitive compounds in different conditions has been studied. That allowed to propose some models of the processes describing this phenomenon [1–10], as well as to understand the boundaries within the phenomena that can be used in practice.

The main method of the direct relief formation, which is used for the study of this phenomenon, is the polarization holography [1]. The method consists of illumination of photosensitive surface by coherent polarized radiation. As a result, the movement of matter which forms a surface relief grating (SRG) takes place due to the gradient of the electric field tension on the surface and in the photoresist layer.

Despite of the large amount of the studied materials — organic [11–18], inorganic [19–21], composites [22–24] and polymers of different chemical compositions [25–29], the direct relief formation phenomenon used in practice is limited. One of the most critical issues is the amount of energy required for the formation of the SRG. Non-etching photoresists (NEP) do not reach necessary levels of exposure required for the formation of relief to values that are comparable with those used for classical photoresist where relief is formed by chemical etching after illumination (for example AZ15xx, AZ18xx series from MicroChemicals GmbH). NEP with the necessary parameters can significantly increase the attractiveness in industrial processes of micro/nano-structure production, due to exclusion of the etching operation.

If we consider the problem from this point of view, materials based on azobenzene groups in which cis–trans isomerization occurs relative to N=N bond are the most promising. Firstly, there are the composites of low molecular compounds included in the neutral polymeric matrix [15,30] and their complexes [31]. Secondly, there are different types of polymers in which the diazo group is chemically incorporated into the polymer chain [27,32], or attached as side groups [25,26,29,33,34]. And thirdly, there are low molecular weight organic glasses (LMOG) capable of forming an optically uniform film of thickness up to several microns [11–14,43–45].

As noted earlier [12], an important issue is to study the effect of chemical composition and structure of the light-sensitive media on the peculiarities of the SRG formation. It is obvious that the chemical structure of photochromes defines factors such as the energy of the intermolecular bonds, the quantum yield of cis–trans isomerization and differences in dipole moment between the cis- and trans-isomers. Searching of the chemical structure, in which a combination of these factors leads to a reduction of exposures required for the SRG formation is one of the goals of this work.

In this study, we present the low molecular weight organic amorphous compound 4-((4-(bis(5,5,5-Triphenylpentyl)amino)phenyl)diazenyl)benzoic acid (hereinafter KRJ-8). We have studied the optical

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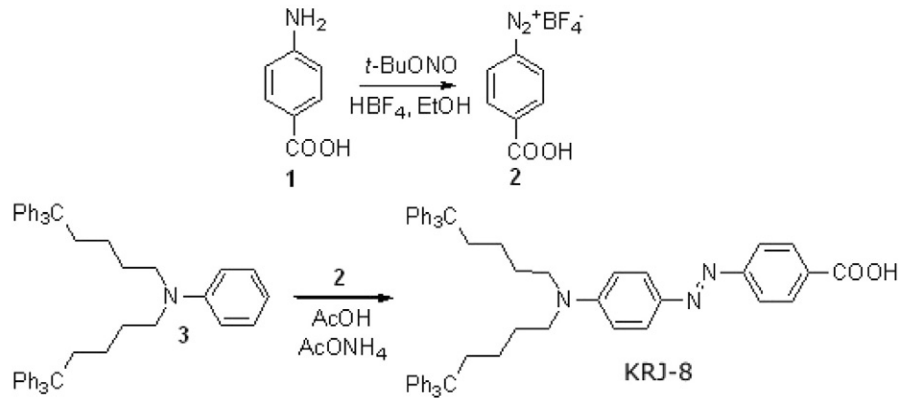

Fig. 1. Synthesis scheme of the KRJ-8.

properties of the material, examined various modes of formation of the surface relief and compared the energy parameters of the SRG formation with published data for other materials. We also tested the possibility of KRJ-8 used in the application of holography.

2. Experimental

2.1. The synthesis of KRJ-8

N,N-bis(5,5,5-Triphenylpentyl)aniline (3) [35] (3.00 g, 4.3 mmol) was dissolved in acetic acid (5 mL) and 4-carboxybenzenediazonium tetrafluoroborate (2) [36] (1.54 g, 6.5 mmol) was added to the solution at room temperature, followed by the addition of sodium acetate (0.46 g, 6.0 mmol). After stirring for 2 h water (50 mL) was added and a red precipitate formed which was collected by filtration, washed with water and air dried. The crude product was purified by column chromatography over silica gel using toluene/ethyl acetate (2/1) as eluent. After the evaporation of solvent from the clean fractions, the obtained red glass was dissolved in DCM and ethanol was added. DCM was fractionally removed under reduced pressure and the red precipitate was filtered to yield KRJ-8 as orange powder (2.50 g, 69%). ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 1.02 (^{4}H, m), 1.49 (^{4}H, m), 2.50 (^{4}H, m), 3.06 (^{4}H, t, $^3J = 7.3$ Hz), 6.47 (^{2}H, d, $^3J = 9.4$ Hz), 7.07–7.29 (^{30}H, m), 7.78 (^{2}H, d, $^3J = 9.0$ Hz), 7.82 (^{2}H, d, $^3J = 8.7$ Hz), 8.16 (^{2}H, d, $^3J = 8.5$ Hz) (Fig. 1).

2.2. Glass transition temperature definition

Differential scanning calorimetry (DSC) measurements were carried out by using Mettler Toledo DSC 1/200W equipment under nitrogen atmosphere and Simultaneous Thermal Analyzer STA 6000.

2.3. KRJ-8 films formation on the glass substrate

For different thickness film preparations, 5–50 mg of KRJ-8 was dissolved in 560 mg of $CHCl_3$ (Chempur, CAS# 67-66-3, pure p.a.). The solutions were applied to glass substrates by spin-coating. The films were dried during 24 h in dark place at room temperature. The thickness of dry films was 200–1700 nm, determined by the Veeco Dektak 150 surface profiler. The transmission spectra were measured by the Ocean Optic HR4000CG spectrometer.

2.4. Measurement of the contact angle and the calculation of surface tension on the film-air border

Definition of surface tension was carried out by measuring of the contact angle θ of water droplets (bidistillate) and ethylene glycol (Aldrich, CAS # 107-21-1, 99.8%, anhydrous) on the surface of non-irradiated and irradiated film KRJ-8, a layer thickness was 500 nm. Irradiation was carried out immediately before the measurement on an area of 2.5 cm^2 by a laser beam with a wavelength of 532 nm, pre-expanded through the lens. Beam intensity was 53 mW/cm^2. Irradiation was carried out for 30 min, which corresponds to the exposure 95.4 J/cm^2. Measurement of the contact angle was performed by photographing the droplets and digital processing of photo. Calculation of the surface tension was performed by the method described in [37].

The equilibrium contact angle θ is determined from three interfacial energies by Joung's equation:

$$0 = \sigma_{SG} - \sigma_{SL} - \sigma_{LG} \cos\theta, \quad (1)$$

where SG stands for surface between solid/gas, SL — solid/liquid, and LG — liquid/gas. Calculation of thin film surface tension means finding the value of σ_{SG}. There is one unknown parameter σ_{SL}. The value of

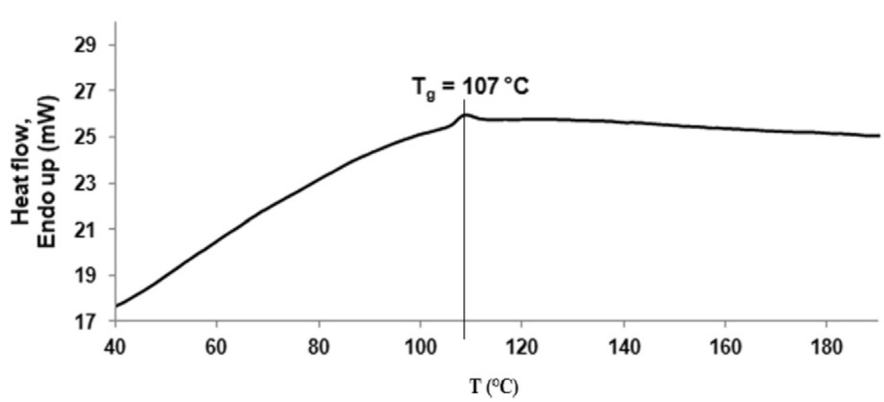

Fig. 2. DSC curve of KRJ-8. $T_g = 107$ °C.