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Photoorientation of azobenzene side groups in a liquid-crystalline polybutadiene-based polymer

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Abstract

The light-induced orientation of azobenzene side groups of a polybutadiene based liquid crystalline polymer was studied. The polymer is based on HO-terminated telechelic polybutadiene Krasol LBH 3000 grafted with 5-(4-{[4-(octyloxy)phenyl]azo}phenoxy)pentane-1-thiol units. Linearly polarized light of wavelengths 325, 365 and 488 nm influenced the photoorientation process. While irradiation with the 325 and 488 nm light generated optical anisotropy, UV light of 365 nm resulted in isotropic films. Pre-irradiation with the 365 nm light and subsequent irradiation with 325 nm led to dichroic ratio of about $R_D = 11$. Further irradiation with 365 nm erased the anisotropy again.

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1. Introduction

The photogeneration of anisotropy in organic photochromic materials is a promising approach for reversible optical data storage, photoalignment of liquid crystals (LC) or for fabrication of optical components. It was observed in glassy state of amorphous [1] and liquid crystalline polymers [2–4], in LB multilayers [5], in low molecular glasses and in liquid crystals [6,7]. A system formed by combining polymer with liquid crystal inherits characteristics, which are typical for the components. Liquid crystalline polymers show increased viscosity with respect to the low molecular liquid crystals, which allows them to form a glassy state – a property typical for polymers. It was demonstrated that polymer chain structure strongly influences film-forming properties, photochemical and optical properties, spatial organization of chromophores and temperature stability of induced anisotropy. A self-organization ability of liquid crystalline polymer and the photoorientation ability influence each other mutually [8]. It was shown that under irradiation with linearly polarized light the azobenzene moieties change their spatial orientation [9–12]. In this way anisotropy – dichroism and birefringence – is generated. This process was used for optical switching [13], digital and holographic data storage [14] and optical modulators [15].

In this article we present a new class of azobenzene-containing LC polymers with promising properties. The material is based on a prepolymer from which linear copolymers or polymer networks can be prepared by reactions of its terminal hydroxy groups with isocyanate groups of diisocyanates or triisocyanates. In this way, some properties of the

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polymer, such as stability of orientation at higher temperatures, could be fine-tuned for needs of particular application. Detailed investigations of phase transitions and induction of optical anisotropy are presented.

2. Experimental

The structure of the investigated polymer is shown in Fig. 1. Films of the polymer were spin-coated (at 1000 rpm) from chloroform solution (25 mg per 1 ml of the solvent) on quartz glass substrates. The prepared films were dried at room temperature for at least 24 h. Photoreactions in solutions were studied at the concentration 0.03 mg of the polymer per 1 ml of tetrahydrofuran.

Optical anisotropy in films (thickness ca. 150–200 nm) was induced by linearly polarized light of three wavelengths: visible light of an Ar^+ laser ($\lambda = 488$ nm, 500 mW cm^{-2}) and UV irradiation with a He–Cd laser ($\lambda = 325$ nm, 10 mW cm^{-2}) and mercury discharge lamp with an interference filter ($\lambda = 365$ nm, 10 mW cm^{-2} after the filter). The irradiation was carried out at normal incidence (propagation direction in the film normal). Thermal Z–E isomerization kinetics in both films and solutions were measured after UV exposure (365 nm) using a mercury discharge lamp with a band filter. Information about optical anisotropy in the oriented samples was obtained by transmission null-ellipsometry [10]. Using this technique one can estimate in-plane $(n_x - n_y)d$ and out-of-plane $(n_x - n_z)d$ retardation in the film.

UV–vis polarized spectra were measured with a Lambda 19 spectrometer (Perkin Elmer) equipped with Glan–Thompson polarizer driven by computer-controlled stepping motor. The phase behavior of the polymer was investigated by differential scanning calorimetry (DSC) using a Netzsch DSC 200. The samples were examined at a scanning rate of 10 K min^{-1} by applying several heating and cooling cycles.

Small-angle X-ray scattering measurements were carried out with a Nonius rotating anode ($U = 40$ kV, $I = 100$ mA, $\lambda = 0.154$ nm) using image plates. With the image plates placed at the distance 40 cm from the sample, a scattering vector range of $q = 0.07$–1.0 nm^{-1} was available. 2D diffraction patterns were transformed into 1D radial averages. Wide-angle X-ray scattering (WAXS) measurements were performed using a Nonius PDS120 powder diffractometer in transmission geometry. A FR 590 generator was used as the source of Cu Kα radiation. The primary beam was monochromatized with a curved Ge crystal. Scattered radiation was measured with a Nonius CPS120 position-sensitive detector of resolution 0.018° in 2θ.

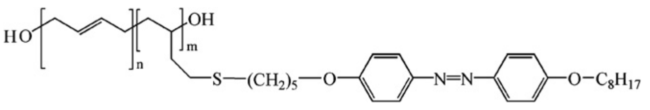

Fig. 1. Chemical structure of the polymer under investigation.

3. Results and discussion

3.1. Polymer synthesis

The polymer was prepared by the radical addition of a mesogenic thiol to double bonds of HO-terminated telechelic polybutadiene at 80 °C in the presence of 2,2-azobisisobutyronitrile as initiator. The thiol, 5-(4-{[4-(octyloxy)phenyl]azo}phenoxy)pentane-1-thiol, containing both the mesogenic azobenzene group and pentane-1,5-diyl spacer group, was prepared by a five-step synthesis (see Fig. 2). Molecular weights of the polymer were $M_n = 12{,}000$ and $M_w = 14{,}000$. The molar ratio of the photochromic thiol to butadiene unit of Krasol polymer was 36%.

Materials: 4-acetamidophenol (Fluka), 1,5-dibromopentane (Fluka), thiourea (Fluka), octyl bromide (Fluka) and solvents were used as received. Phenol was purified by distillation (b.p. 70 °C/1.56 kPa). Telechelic polybutadiene Krasol LBH 3000 (Kaucuk Kralupy, Czech Republic, $M_n = 3000$).

3.1.1. Synthesis of 5-(4-{[4-(octyloxy)phenyl]azo}-phenoxy)pentane-1-thiol (4)

Synthesis of 4-(octyloxy)aniline (1): 37.56 g (0.284 mol) of 4-acetamidophenol was dissolved in a solution of 13.5 g KOH in 375 ml of aqueous ethanol (1:1), 51.18 g (0.265 mol) of octyl bromide was added and temperature was raised to 75 °C. Stirring was continued for 48 h. Then the reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The precipitate was filtered off and washed with 5 wt.% aqueous NaOH and water. The crude *N*-[(4-(octyloxy)phenyl]acetamide was heated with 200 ml of 30 wt.% sulfuric acid at 95 °C for 2 h. Then the reaction mixture was cooled to room temperature, the amine salt was filtered off and repeatedly washed with water. The salt was suspended in 375 ml of water at 80 °C, a solution of 7.5 g of NaOH in 15 ml of water and 150 ml of toluene were added and the reaction mixture was heated under reflux for 8 h. After cooling to room temperature, the toluene layer was separated and water layer was extracted three times with 25 ml of toluene. The toluene solution was dried over anhydrous Na_2SO_4 and molecular sieves. The filtrate was concentrated in a rotavapor and the residual oil was purified by distillation; b.p. 140 °C/6.7 Pa. After cooling the product crystallized; m.p. 33 °C. Yield 38.0 g (69.1%).

Synthesis of 4-hydroxy-4′-(octyloxy)azobenzene (2): a mixture of 22.1 g of 4-(octyloxy)aniline and 45 ml of 18 wt.% HCl was heated until the amine completely dissolved. The solution was cooled and kept at 0–5 °C (solution A).

$NaNO_2$ (10.1 g) was dissolved in 58 ml of water, the solution was cooled to 0–5 °C and added dropwise to solution A. The clear solution of diazonium salt was kept at 0–5 °C and added dropwise to a solution of 20.5 g of phenol and 17.4 g of NaOH in 215 ml of water. The reaction temperature was maintained below 5 °C. Finally the reaction

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