



Thermal, optical and photoinduced properties of a series of homo and co-polyimides with two kinds of covalently bonded azo-dyes and their supramolecular counterparts



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ABSTRACT

The paper describes the synthesis and characterization of new aromatic polyimides with one or two different moieties of the azo-dyes covalently attached to the polymer backbone and their supramolecular analogues. Azo-functionalized polyimides were prepared using *post*-polymerization method including the introduction of Disperse Red 13 and/or 4-[4-(6-hydroxyhexyloxy)phenylazo]pyridine to homo and co-polyimides containing hydroxyl groups *via* Mitsunobu reaction. The degree of functionalization of polymers with chromophores was estimated by UV–Vis spectroscopy. Polyimides containing hydroxyl groups were applied as matrixes to create supramolecular systems based on hydrogen bonds. Hydrogen-bond interactions in azosystems were studied by FTIR spectroscopy. The polymers were characterized by ¹H NMR, FTIR, X-ray, UV–Vis, DSC and TGA methods. The photoisomerization process was investigated in supramolecular systems. The light-induced anisotropy was studied in a holographic gratings recording experiment and by photoinduced birefringence measurements. The polymer films were investigated by atomic force microscopy (AFM) after the diffraction grating recording to confirm formation of surface relief gratings (SRGs). To the best of our knowledge, that the first time photoinduced anisotropy has been studied by birefringence measurements in polyimides containing two different azo-dyes.

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1. Introduction

Azo-polymers are one of the most interesting groups of polymers for potential application in the fields of photonics and optoelectronics, *e.g.* optical information storage, diffractive optical elements, optical switching and liquid crystal display technology [1–3]. The possibility for such applications of the azo-polymers is based on the reversible photoisomerisation of the azobenzene groups placed in the polymer chain. Upon irradiation by linearly polarized light of appropriate wavelength, they undergo reversible cycles between a thermodynamically stable *trans*-form and a meta stable *cis*-form [4,5]. Perpendicular alignment of the azobenzene molecules to the electric field vector generates a photoinduced optical anisotropy, which is observed as changes in the absorption

coefficient (ΔA) and the refractive index (Δn) [5–7]. Moreover, the cyclic photoisomerisation of azobenzene-based groups can lead to large-scale mass transport of the polymer chain, which is observed as a sinusoidal modulation of the polymer film referred to a surface relief grating (SRG) [8–11].

Three kinds of azo-polymers are commonly described in the literature *i.e.* functionalized polymers containing covalently attached azo-dyes, polymers doped with azo-dyes and supramolecular systems based on hydrogen bonds, cooperative, ionic or π – π interactions between the polymer and the dye [5,12–14]. The supramolecular systems possess many advantages over the functionalized and doped polymers. First of all, they are prepared simply by mixing the polymer matrix and the chromophore, which avoids costly and time-consuming organic synthesis in comparison to the covalent azo-polymers and expands the possibility of using various kinds of chromophores [2,12]. Unlike to polymers with dispersed azo dyes, the formation of intermolecular interactions

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allows for increasing the concentration of the chromophores in the polymer matrix, and prevents disadvantageous evaporation and aggregation of the chromophores, thus improves the optical and thermal stability of the resulting materials [1,2,12]. Moreover, non-covalent interactions make a selective removal of the chromophore from the material possible, which leads to a precise control of the molecular weight of the host polymer [2,12,15]. In the past few years, a lot of studies reported the formation of SRGs in supramolecular systems containing azobenzene derivatives based on H-bonds [16–18]. The most popular matrixes used to prepare azopolymers are poly(4-vinylpyridine) (PV4P) [2,16,19,20], poly(4-vinylphenol) (PVPh) [4,8,21] and co-poly(4-vinylpyridine) with polystyrene (PV4P-PS) [22–24]. As far as we are aware, the idea of the preparation of supramolecular system based on polyimides and azochromophores attached via H-bonds was only applied in our previous works [13,14]. Despite the fact that azopolymers were extensively studied in the past years, the idea of synthesizing the azopolymers containing two different azo-chromophore in a polymer repeating unit is quite new. The photoinduced anisotropy in polyimides containing two different azochromophores covalently bonded to the backbone has only been reported only by our research group [25–28].

This work is the part of our continuing effort in developing new functionalized azo-polyimides and azo-supramolecular systems based on the hydrogen bonds [13,14]. Here we report the synthesis and characterization of the series of new azo-polyimides with one or two different dyes covalently attached to the polymer backbone and their supramolecular analogues based on the hydrogen bonds. By utilizing different chromophores in a macrochain the possibility of exciting the *trans*–*cis* isomerization with the wavelengths from a wide spectral range is offered. Azo-polymers with covalently attached chromophores were prepared using the *post*-polymerization functionalization *via* Mitsunobu reaction. Thus, in the first step of this study, homo- and co-polyimides containing phenolic hydroxyl functional groups were synthesized and characterized as the matrix for the preparation of both functionalized azo-polymers and hydrogen-bonded azo-polyimide complexes. Two types of chromophores, that is, commercially available Disperse Red 13 and 4-[4-(6-hydroxyhexyloxy)phenylazo]pyridine, which was reported in the literature, were applied [13,14]. The study involves the structural (X-ray), thermal (DSC, TGA) and optical (UV–Vis) properties of the synthesized polymers. The photoisomerization process (the photochromic reaction) was investigated for the supramolecular self-assemblies. Moreover, for the polymers containing covalently bonded azo-chromophores their ability for both holographic diffraction gratings recording, including the SRGs formation, and photoinduced birefringence generation was explored.

In this paper, to the best of our knowledge, for the first time (i) the photoinduced birefringence was investigated in the polyimides containing two azo-chromophores differ in their absorption spectra, (ii) the values of the photoinduced birefringence of polymers with covalently bonded azo-chromophores were compared to their supramolecular analogues and studies of photoisomerization were carried out for supramolecular polymers films.

2. Experimental section

2.1. Materials

Disperse Red 13 (DR13), triphenylphosphine, 6-chlorohexanol, *N*-methyl-2-pyrrolidone (NMP), *o*-dichlorobenzene, 4,4'-(hexafluoroisopropylidene)bis(phthalic anhydride) (6FDA), 3,3'-dihydroxybenzidine, bicycle-[2,2,2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride were purchased from Sigma–Aldrich

Chemical Co. *N,N*-dimethylformamide (DMF), phenol, chloride acid, methanol were purchased from POCH. 4-aminopyridine was purchased from Acros. Diethylazodicarboxylate (DEAD) was purchased from Fluka.

2.2. Measurements

¹H NMR spectra were recorded on an Avance II 600 MHz Ultra Shield Plus (Bruker) Spectrometer in DMSO-*d*₆ as solvents and TMS as the internal standard. The infrared (IR) spectra of the polymers were recorded with a Nicolet 6700 FTIR apparatus (Thermo Scientific) by using KBr pellets. FTIR spectra of the supramolecular systems were acquired on a Bio-Rad FTS 40 A Spectrometer in the transmission mode using KBr pellets. UV–Vis spectra were recorded in NMP solution of polymers and as films on glass substrates using a V-570 UV–Vis–NIR Spectrophotometer (Jasco Inc.). The photoisomerization process was induced by irradiation of the azopolymers films independently, by two different single light beams at a wavelength of 405 nm and 532 nm and measuring the changes in the absorption spectrum at appropriate time of exposure. The intensities of light beams were 17 mW/cm² and 150 mW/cm², respectively. The measurements were performed at room temperature. The X-ray diffraction pattern of solid samples were recorded using Cu K α radiation on a wide-angle HZG-4 diffractometer (Carl Zeiss Jena) working in the typical Bragg geometry. Differential scanning calorimetry (DSC) was performed with a TA-DSC 2010 apparatus (TA Instruments) under nitrogen using a heating/cooling cycles of 20 °C min⁻¹. Thermogravimetric analysis was performed on derivatograph type Q-1500 Hungarian production under nitrogen flow of 7 l/h in the temperature range from 20 to 800 °C at a heating rate of 10 °C/min. The molar mass and dispersity (M_w/M_n) of the polymers were determined using gel permeation chromatography (GPC) measurements conducted at 80 °C with DMF as an eluent at a flow rate of 1 ml min⁻¹. A Knauer apparatus with MIXED-DPL gel columns (Knauer) and polystyrene standards were used. The measurements of the light-induced optical anisotropy were performed using a holographic recording setup described elsewhere [29,30] employing an Ar⁺ laser at 514.5 nm. The recording beams intensities were the same and equal to ca. 140 mW/cm². The angle between writing beams was fixed at $\theta = 8.25^\circ$, resulting in a pattern periodicity of $\Lambda = 3.6 \mu\text{m}$ (according to $\Lambda = \lambda/2 \sin(\theta/2)$). Diffraction gratings were recorded for *p*–*p* polarization configuration and the exposure time lasted 60 min. After the grating recording, the topography of the polymer surface at the illuminated area was examined by an atomic force microscopy (AFM, Dimension V Scanning Probe Microscopy, Veeco) working in a tapping mode.

The polymer in-plane birefringence was induced by continuous-wave linearly polarized beams at either 405 or 445 nm. The generated birefringence changes were probed using a second weaker and smaller in diameter 690-nm beam. The transmission of the probing beam through the sample placed between two crossed polarizers was detected by a silicon photodetector and measured using a lock-in amplifier. For a maximum resulting change in the transmission signal the polarization of the writing beam was set at 45° with respect to the horizontal polarization of the probing beam.

2.3. Synthesis of azo-chromophore

Chromophore Disperse Red 13 (denoted as **DR13**) was purchased from Sigma–Aldrich Chemical Co, while chromophores 4-(4-hydroxyphenylazo)pyridine (denoted as **AzPy-1**) and 4-[4-(6-hydroxyhexyloxy)phenylazo]pyridine (denoted as **AzPy-2**) were described in our previous publications [13,14].

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