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Influence of supramolecular interactions on photoresponsive behavior of azobenzene poly(amide imide)s

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This study presents the comparison between the photoresponsive behavior of a series of six poly(amide imide)s bearing azobenzene-derivative chromophores as side groups. The solubility, molecular weight, glass transition temperature and thermal stability of the polymers are reported. The chosen azopolymers contain one or two azochromophores in the repeating units attached to the main chain at different locations, i.e., one of the aromatic cores of azobenzene is a part of backbone connected in the 2 and 4 position with either the amide or/and imide groups. UV–vis spectroscopy shows that the chromophore position affects the polymer absorption band. The photoinduced birefringence measurements reveal large differences in the photoresponsive behavior of the materials. The birefringence of order of 0.02 and 0.05 is achieved for the polymers of moderate molecular weight containing one azo-dye per structural unit attached between the amide groups or for the polymers with two chromophores per structural unit placed between both the amide and imide groups, respectively. The lack of optical anisotropy is observed for the polymers of a low molecular weight containing the azochromophores located between the imide groups, indicating a very low efficiency of the *trans–cis* isomerization process in these materials. The explanation of the observed relationship based on H-bond formation is confirmed by FTIR and ^{1}H NMR analysis.

1. Introduction

Azopolymers, that is, macromolecules with the azobenzene-dye derivatives incorporated into the polymer host exhibit unique photoinduced phenomena, such as generation of optical anisotropy and stable surface patterns, or mechanical bending [1–3]. The phenomena result from light-driven molecular motions, which are accompanied by clean and reversible *trans–cis* isomerization reactions of azobenzene. Being investigated for 20 years the azopolymers are still an important class of materials, fascinating not only from the fundamental point of view but also because of the exceptional applicational potential in optical data storage and processing, nanofabrication, nanoscale machines or photoalignment of liquid crystals [4–8].

A linearly polarized light may generate the orientational order in the alignment of azo-dye moieties. It results from the angular selectivity of absorption events by highly anisotropic *trans* azo molecules and from the *trans*–cis isomerizations. During the photochemical reaction (*trans*–cis or *cis*–trans) or during the lifetime of the *cis* isomer the rotation of the photochromic molecules may take place [9]. As a consequence of many isomerization cycles the azochromophores align in one of the directions perpendicular to the laser polarization i.e., in the position, for which the light is no longer absorbed by the molecules. An initially isotropic material becomes an anisotropic one, showing photoinduced optical anisotropy, i.e., dichroism and birefringence appearing as an increased absorbance and refractive index in directions perpendicular to the polarization of the excitation light, respectively [10,11].

As light-induced preferable alignment of azochromophores involves the molecular motions the photoresponsive behavior of the azopolymer (in particular a rate of birefringence growth, a maximum birefringence value and its stability after ceasing the excitation beam) depends strongly on the chrompohore and the

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polymer chain architecture [12]. The polarity, bulkiness and content of the azo-dye substituent, the type of binding between the azo group and the macrochain, liquid crystallinity, and the nature of polymer matrix are among crucial factors that may enable or restrict the chromophore motions.

The photoresponsive properties of azopolymers have been investigated in a wide range of polymer matrices: poly(methyl methacrylate)s and its copolymers, polycarbonates, poly(vinyl pyridine)s, polystyrenes, polyurethanes or polyimides [12–17]. For a given polymer the azochromophores can be either dispersed or covalently/non-covalently attached to the backbone as side-chain via different spacers. In general, the influence of polymer matrix on light-induced anisotropy has been related to the available free volume for *trans*–cis photoisomerization and to a glass transition temperature (T_g) of the polymer [18–20].

Our recent scientific investigations are focused on the development of photoresponsive polyimides, which may retain the photoinduced azochromophore order for larger periods of time. Polymers belonging to the polyimide family exhibit good mechanical properties, high stability against temperature, solvents and liquid crystals and thus they are considered as very attractive candidates for applications in optical storage or liquid crystal alignment [21]. From that point of view gaining a new knowledge on correlation of the azopolyimide chemical structure and arising photoresponsive behavior is an important area of research. Recently, we have shown that the characteristics of light generated birefringence of certain groups of azopolyimides may be tailored by a proper modification of the main chain structure, a proper type of a linkage between the main chain and the azo-dye or by the chromophore concentration [22–24].

In this work a series of six side-chain poly(amide imide)s (**PAI**) containing the azochromophores with a —CH_3 or —OH substituent in para position is presented. Three of them are the newly synthesized materials. The key difference in the structures of the studied polymers is the location of the azochromophores in the macromolecules, that is, one of the aromatic cores of azobenzene is a part of backbone attached in the 2 and 4 position either between the amide or imide groups, or between both of the groups in the case of the materials possessing two azochromophores per a repeating unit. Moreover, the poly(amide imide)s differ in their molecular weights. In this work we investigate the photoresponsive behavior of the polymers by means of the photoinduced birefringence measurements at 405-nm excitation wavelength. We show that the studied poly(amide imide)s exhibit a very different photoresponsive properties, i.e, either efficient or non-detectable photoorientation of azochromophores, and relate it with the formation of intermolecular hydrogen bonds.

2. Materials and methods

2.1. Materials

4-Aminophenol, *m*-phenylenediamine, trimetilic anhydride chloride, *N*-methyl-2-pyrolidone (NMP), 4,4′-methylenebis(2,6-dimethylaniline), 1,2-dichlorobenzene were purchased from Sigma–Aldrich Chemical Co. Chloride acid, acetone, *p*-toluidine, pyridine were purchased from POCH.

2.2. Characterization

^{1}H NMR spectra have been carried out on an Avance II 600 MHz Ultra Shield Plus (Bruker) spectrometer in DMSO-d_6 using TMS as the internal standard. The infrared (IR) spectra of the chosen polymer films were acquired with a Nicolet 6700 FTIR apparatus (Thermo Scientific) using KBr pallets. UV–vis spectra were measured with a V-570 UV–vis-NIR spectrophotometer (Jasco Inc). The X-ray diffraction patterns of solid samples were recorded using CuKα radiation on a wide-angle HZG-4 diffractometer (Carl Zeiss Jena) working in the typical Bragg geometry. The molecular weights and dispersity were determined by size exclusion chromatography (SEC) using a multiangle light scattering detector (k = 658 nm) DAWN HELEOS of Wyatt Technology and a refractive index detector Dn-1000 RI from WGE Dr. Bures. Measurements were performed in DMF at 45 °C at a nominal flow rate of 1 ml min^{-1} with a set of columns: 100 Å, 1000 Å, 3000 Å (Polymer Standard Service). The results were evaluated based on polystyrene calibration using WinGPC Unity(Polymer Standard Service). Thermogravimetric analysis (TGA) was performed using pre-calibrated TA Instruments SDT Q600 analyzer operating under high-purity (99.999%) argon purge-flow of 100 ml/min. Samples (5–10 mg) were placed inside open alumina pans and the measurements were carried out in 10 °C min^{-1} constant heating rate conditions. Prior to the TGA measurements the poly(amide imide)s have been dried at 120 °C for 1 h in argon to remove water. Thermal analysis was performed under nitrogen by differential scanning calorimetry (DSC) (TA-DSC 2010 apparatus, TA Instruments) with a heating rate of 20 °C min^{-1}.

2.3. Synthesis of diamines

Detailed synthesis and characterization of the chromophores 2,4-diamino-4′-methylazobenzene (**AK–CH_3**) and 4-diamino-4′-hydroxyazobenzene (**AK–OH**) have been reported previously [23,25].

2.4. Synthesis of dianhydrides (DA)

Detailed synthesis and characterization of the azo-dianhydrides containing —CH_3 (denoted as **DA–CH_3**) or —OH (denoted as **DA–OH**) groups have been reported previously [24]. Trimellitic anhydride acid chloride (24 mmol) was dissolved in 25 ml dry acetone in a round-bottomed flask equipped with a magnetic stirrer and dropping funnel, and the solution was stirred at 60 °C under argon atmosphere. Then, the prepared mixture of *m*-phenylenediamine (16 mmol) and pyridine (2.2 ml) in 25 ml of acetone was added dropwise to the flask. The solution was stirred and heated under reflux for 1 h. After cooling down to room temperature the pyridine hydrochloride was precipitated. The product was washed several times with dry acetone and dried in a vacuum oven at 80 °C for 6 h. The crude product was crystallized from acetic anhydride and dried in a vacuum oven at 80 °C for 24 h.

^{1}H NMR (DMSO-d_6, ppm): 7.34 (t, ArH, 1H); 7.53 (d, ArH, 2H); 7.78 (d, ArH, 1H); 8.01 (t, ArH, 2H); 8.16 (d, ArH, 2H); 8.53 (t, ArH, 2H). FTIR (KBr, cm^{-1}): 3076 (—NH); 1706, 1699 (—C=O in anhydride); 1647 (—C=O in amide). Anal. Calcd. for: C, 63.16%; N, 6.14%; H, 2.65%. Found: C, 64.68%; N, 6.02%; H, 2.48%. Yield: UV–vis (NMP): λ_{max} = 282 nm (ε_{262} = 1.3 × 106 l mol^{-1} cm^{-1}), Mp = 101 °C.

2.5. Synthesis of poly(amide imide)s

The synthesis of three poly(amide imide)s, i.e., the ones with the azo-dyes between the imide groups with either the hydroxyl (**PAI-3**) or methyl (**PAI-4**) substituent as well as the poly(amide imide) containing the —OH substituted azo-dyes located between the amide groups (**PAI-1**) was carried out according to the procedure described in our previous publication [25]. A solution of equimolar amounts of dianhydride and diamine in a mixture of solvents of NMP and 1,2-dichlorobenzene [80/20 (v/v), 20% of the total monomer concentration] was stirred at 175 °C for 3.5 h. The