



Functionalized polymers with strong push-pull azo chromophores in side chain for optical application

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ABSTRACT

In this paper, we show that the optical properties such as extinction coefficient, refractive index, optical conductivity and optical energy band gap of aminoazobenzene and pseudostilbene-type azobenzene polymers can be effectively manipulated by changing or adding various substituents in their polymeric system.

We found that the absorption spectrum of aminoazobenzene polymer thin film is shifted to blue compared to pseudostilbene-type azobenzene polymer thin films. Therefore, the optical energy band gap for aminoazobenzene polymer thin film is higher than for pseudostilbene-type azobenzene polymers. We also noticed that the studied azo dyes polymer thin films exhibit high photoresponse proper for use in the optoelectronic applications.

1. Introduction

Azo compounds are a very important class of chemical compounds receiving attention in scientific research. They are used in many practical applications such as coloring fiber, printing systems, liquid crystal displays, optical storage technology, and photoelectronic applications [1–4]. They have also attracted attention due to their interesting electronic features in connection with their application for molecular memory storage, nonlinear optical elements and organic photoconductors [5–8].

Azobenzenes are the π -conjugated compounds, where two or more phenyl rings are bridged by the azo ($N=N$) linkage. This π -conjugation gives rise to strong absorption at ultraviolet and visible (UV-VIS) wavelengths, as well as is greatly sensitive to substitutions influence [1,9,10]. Their most attractive properties are that the azobenzene units can exist in two isomeric forms: *trans* and *cis*. Their photo-physical properties can be modified by proper irradiation. Under the influence of irradiation with the appropriate wavelength, the stable form of *trans*-azobenzene transforms into a less stable *cis* form [2]. Since the azo group has a free pair of electrons on both nitrogen atoms, it can be isomerized according to two possible mechanisms: to pass $n-\pi^*$ electrons with the inversion of the atom and to pass $\pi-\pi^*$ that follow the rotational mechanism [11]. It has been intensively investigated by different computational and experimental methods that the *trans* and *cis*

isomers have different physical and chemical properties, because their molecules have different interatomic distances [12–14]. It is well known that the *trans* azobenzene absorption spectrum is characterized by an intense, symmetrical $\pi-\pi^*$ ultraviolet transition band and low-intensity, low-energy $n-\pi^*$ pass band in the visible region. In contrast, in the absorption spectrum of *cis* azobenzene, there is a more intense $n-\pi^*$ electron transition band.

The studied functionalized polymers can be attributed to the aminoazobenzene-type and pseudostilbene-type by Rau classification [15]. The pseudostilbene-type molecules are push-pull molecules, which contain an electron-acceptor (A) group and an electron-donor (D) unit. These groups are connected with each other by a π -conjugated organic backbone. Such structure (D- π -A) provides a good transport of charge between electron-donor and electron-acceptor groups D \rightarrow A charge transfer (CT), which gives a high value of dipole moment [16]. Aromatic azo derivatives containing intramolecular D- π -A CT show excellent photo-physical properties since they have extensive π -systems delocalized between the acceptor and donor units across the azo linkage. With appropriate electron-donor/acceptor ring substitution, the π -electron delocalization of the extended aromatic structure can yield high optical nonlinearity [17–20].

Among the pseudostilbene-type molecule, a very commonly used is Disperse Red 1 (DR1). In this azo-compound, the $n-\pi^*$ and $\pi-\pi^*$ transitions overlap, and it has been indicated that the latter is the lowest-

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excited singlet state with the strongest absorption because of its push-pull archetype. DR1 molecular motifs lead to a structureless absorption band in the *trans* isomer. The presence of the *trans* form of DR1 is characterized by the absorption band centred at about 490 nm. Excitation of a molecule to the first excited state by a photon of suitable energy leads to its subsequent decay to one of two possible ground states: the stable (*trans*) form or metastable (*cis*) form. The latter, at room temperature, relaxes spontaneously to the *trans* form with an environment-dependent rate. In the *trans* form, molecules are strongly anisotropic (rod-like), while in the *cis* form they are bent and their anisotropy is less pronounced [21].

In respect to photoreactive units molecular systems containing two or more azobenzene units are interesting for the fields of dyes, pigments and advanced materials due to their multiphotochromic nature. The main advantage that such compounds can exist in many different states (up to 2ⁿ, where n is the number of photochromic units). This kind of behavior may be useful for storage and information processing at molecular level. In such bis-azo compounds, the cooperation of the different photoisomerisable units can produce an overall amplification of the geometrical changes related to the *trans-cis* transformation, leading to new light-induced functions [22]. The compounds containing two azobenzene units have been studied by other research groups [23,24]. In most cases, the two azobenzenes were found to be basically non-interacting, giving rise to a behavior determined by the simple superimposition of the properties of the two isolated units [25,26]. In a recent paper, we had quantified both the second- and the third-order nonlinearity for push-pull side chain bis azobenzene polymers [27].

In this paper, the refractive index, the extinction coefficient, the optical conductivity and the optical energy band gap of selected bis-azo dye attached polymer thin films are presented in comparison with a mono-azo dye based polymers. The goal of this work was to present the influence of various substituents of azo dyes on their optical properties. These optical properties were measured using spectroscopic ellipsometry (SE) combined with transmittance measurements (T). Additionally, atomic force microscopy (AFM) was used to examine the surface topography of the studied thin films.

It should be mentioned that the studied functionalized polymers are promising candidates for applications in optical data storage, information storage, surface relief gratings, photoswitching, optical elements and nonlinear optics [2,4,27].

2. Experimental

2.1. Materials

2.1.1. Characterization methods

¹H NMR (500 MHz) spectra were measured on a Bruker Avance DRX-500 spectrometer (Bruker Corp., Karlsruhe, Germany). Chemical shifts are given in ppm from the internal standard tetramethylsilane (TMS). The glass transition temperatures (T_g) of all polymers are determined by Differential Scanning Calorimetry with Q20 Differential Scanning Calorimetry model (TA Instruments, New Castle, PA, USA) with a continuous N₂ purge. The sample was initially stabilized and after the first scan was made at a heating rate of 10 °C/min up to 200 °C then cooled to 20 °C, a second scan was performed with the same parameters to obtain the values of T_g.

2.1.2. Materials synthesis

Standard distillation procedures were performed for triethylamine and THF just prior to use. 2,2'-Azobis (isobutyronitrile) (AIBN) was recrystallized twice from absolute methanol. Methacrylic chloride was vacuum-distilled, immediately before use. Methylmethacrylate (MMA) was washed with aq NaOH to remove inhibitors, dried with CaCl₂ under nitrogen at reduced pressure.

The azobenzenes 4-(*N*-ethyl-*N*-(2-hydroxyethyl)amino)-4-(4-nitrophenylazo)-azobenzene and *N*-ethyl-*N*-(2-hydroxyethyl)-4-(4-

cyanophenylazo)aniline are obtained by azo coupling reaction which includes initial diazotization of an aromatic amine at low temperature and then diazonium salt (weak electrophiles) reacts with an electron rich aromatic nucleophile having electron donor groups. The substitution reaction takes place at the para position to the electron donor group [27]. The initial azo chromophores *N*-ethyl-*N*-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline, 4-[4-(phenylazo)-1-naphthylazo]phenol, 2-[4-(2-chloro-4-nitrophenylazo)-*N*-ethylphenylamino]ethanol were commercially available (Aldrich).

The monomers of azobenzene chromophores were prepared as previously reported [27,28].

4-((2-Methacryloyloxyethyl)ethylamino)-4-(4-nitrophenylazo)-azobenzene: Dark purple crystals yield 60%, mp 160 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.40 (d, 2H, Ar-H), 8.12–7.92 (m, 8H, Ar-H), 6.85 (d, 2H, Ar-H), 6.12 (s, 1H, CH₂), 5.61 (s, 1H, CH₂), 4.38 (t, 2H, OCH₂), 3.75 (t, 2H, NCH₂), 3.55 (q, 2H, NCH₂CH₃), 1.97 (s, 3H, CH₃), 1.28 (s, 3H, CH₃). UV-vis (THF): λ = 340, 502 nm.

4-((2-Methacryloyloxy)-1-azonaphthalene: Red solid residue yield 75%, mp 90 °C. ¹H NMR (500 MHz, DMSO-*d*₆): δ 9.01–8.98 (m, 2H, naphthalene), 8.14 (d, 2H, Ar-H), 8.05 (d, 2H, Ar-H), 7.92 (s, 2H, naphthalene), 7.85 (d, 2H, Ar-H), 7.78–7.81 (m, 2H, naphthalene), 7.63–7.58 (m, 3H, Ar-H), 6.35 (s, 1H, CH₂), 5.9 (s, 1H, CH₂), 2.07 (s, 3H, CH₃). UV-vis (THF): λ = 325, 428 nm.

4-(N-ethyl-N-2-methacryloyloxyethylamino)-2-chloro-4-nitroazobenzene: Red solid residue yield 72%, mp 85 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.31 (s, 1H, Ar-H), 8.07 (d, 1H, Ar-H), 7.87 (d, 2H, Ar-H), 7.70 (d, 2H, Ar-H), 6.76 (d, 2H, Ar-H), 6.03 (s, 1H, CH₂), 5.52 (s, 1H, CH₂), 4.34 (m, 2H, OCH₂), 3.67 (m, 2H, NCH₂), 3.49 (m, 2H, NCH₂), 1.87 (s, 3H, CH₃), 1.2 (m, 3H, CH₃). UV-vis (CHCl₃): λ = 475 nm.

4-[(2-Methacryloyloxyethyl)ethylamino]-4-cyanoazobenzene: Red solid residue, yield 87%. ¹H NMR (500 MHz, CDCl₃): δ 7.89, 7.87 (d, 4H, Ar), 7.75, 7.73 (d, 2H, Ar), 6.82, 6.8 (d, 2H, Ar), 6.1 (s, 1H, CH₂), 5.6 (s, 1H, CH₂), 4.36 (m, 2H, OCH₂), 3.7 (m, 2H, NCH₂), 3.55 (m, 2H, NCH₂), 1.94 (s, 3H, CH₃), 1.25 (m, 3H, NCH₂CH₃).

4-((2-Methacryloyloxyethyl)ethylamino)-4-nitroazobenzene: Dark red crystals, yield 80%, mp 83 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.35 (d, 2H, Ar-H), 7.92 (t, 4H, Ar-H), 6.85 (d, 2H, Ar-H), 6.1 (s, 1H, CH₂), 5.6 (s, 1H, CH₂), 4.38 (m, 2H, OCH₂), 3.75 (m, 2H, NCH₂), 3.56 (m, 2H, NCH₂), 1.94 (s, 3H, CH₃), 1.24 (m, 3H, CH₃). UV-vis (THF): λ = 475 nm.

The copolymers B1-B5 were synthesized by free radical polymerization using azobenzene methacrylic monomers and MMA in 10% DMF solution with AIBN as radical initiator at 80 °C (argon atmosphere) as previously reported [27,28].

The glass-transition temperatures were measured by differential scanning calorimetry to be 140 °C, 110 °C, 125 °C, 120 °C, 128 °C for the copolymers B1, B2, B3, B4 and B5, respectively.

The structures of the B1-B5 copolymers (see Fig. 1) were confirmed by ¹H NMR spectroscopy and a reasonable accord was found between the observed n/m values in the polymers and the respective amounts of both monomers which were introduced 1:3.

2.2. Thin film preparation

BK7 glass slides were cleaned in a solution of 3:1 H₂SO₄:H₂O₂, then thoroughly rinsed in deionized water. Finally, the solutions of the polymers B1-B5 in 1,1,2 trichloroethane were spin coat on the substrates at 1000 rpm for 60 s. The same polymer concentration of 83 mM was used. Immediately after the deposition, the films were cured in an oven at 50 °C and for 120 min in order to eliminate any remaining solvent.

2.3. Measurements

Transmission measurements (T) were performed using spectrophotometer Cary 5000 (Agilent). While, the absorption spectra

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