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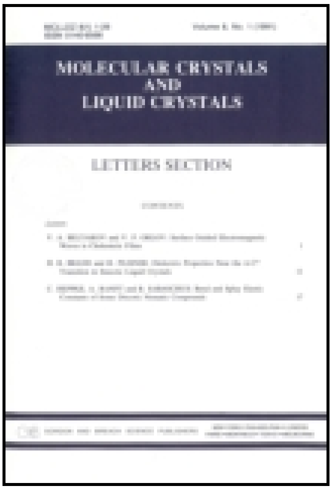

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Synthesis, Characterization, and Study of Novel Push-Pull Azobenzene Polymers

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Synthesis, Characterization, and Study of Novel Push-Pull Azobenzene Polymers

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In this paper, novel polymers with azobenzene moiety with alkyl spacer and different substituents units are presented. Azopolymers were obtained by a two-step synthetic approach. This includes the preparation of a methacrylic monomers and their polymerization. Their photophysical and photochemical properties have been investigated. Polymers were characterized and evaluated by ^{1}HNMR, IR, UV spectroscopy. Thermal stability was characterized by DSC method. The synthesized polymers exhibited glass transition temperatures in the range of 110–140°C.

Keywords chromophore; methacrylic monomers; azo polymers; free radical polymerization

1. Introduction

Within the last decade various types of optical polymers were synthesized with different active chromophores in the side chain: polyalkylmethacrylates, polyalkylvinylethers, polystyrenes, polyimides, polyacrylamides and many more [1–3].

Some of the advantages of polymer-based molecular systems are their low cost, the high laser damage threshold and the fact that they can be easily tailored to match specific experimental needs [4]. Moreover, in the case of side-chain polymers stability is higher than in other types of polymer systems (i.e. guest-host systems) [4], while the spatial organization of the active side chain residues along the polymeric backbone is of critical importance regarding mechanical and structural properties of the material.

Azobenzenes are frequently used as NLO [5–7] moieties in such systems as they exhibit high nonlinear optical response, which emanates from the strong intrinsic charge transfer taking place within these units. In addition, the spatial organization of the active side chain residues along the polymeric backbone is of critical importance regarding mechanical and structural properties of the material. Moreover, due to the photoinduced cis-trans isomerization they can be used in several applications including optical data storage, surface relief gratings etc [8]. Among them the azo dye Disperse Red 1 is one of the most widely investigated and many studies can be found in the literature [9,10].

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2. Experimental

Apparatus

^{1}H NMR (500 MHz) spectra were recorded by a "Bruker Advance DRX-500" spectrometer. Chemical shifts are in ppm from the internal standard tetramethylsilane.

UV-VIS measurements were performed at room temperature either in solutions in a quartz liquid cell, or as thin films deposited on glass substrates, with a Perkin-Elmer UV/VIS/NIR Lambda 19 spectrometer. *Differential Scanning Calorimetry*: A Q20 model DSC (TA Instruments), with a continuous N_2 purge was used to determine the glass and phase transition temperatures (T_g) of all polymers. Two scans were run at a heating rate of 10°C/min up to 200°C, followed by a cooling to 20°C, giving the values of T_g.

Materials

Standard distillation procedures were performed for triethylamine and THF just prior to use. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from methanol. Methacryloyl chloride was in vacuo distilled, immediately before use. Methylmethacrylate (MMA) was washed with aq NaOH to remove inhibitors, dried with $CaCl_2$ under nitrogen at reduced pressure. The chromophores 4-(4-Nitrophenylazo)aniline, *N*-Ethyl-*N*-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline DR1, 4-[4-(Phenylazo)-1-naphthylazo]phenol DO13 purchased from Aldrich and were purified by the double recrystallization from methanol solution. All other reagents and solvents were commercially available and used as received.

4-(N-Ethyl-N-(2-hydroxyethyl)amino)-4′-(4-nitrophenylazo)azobenzene 4-(4-Nitropheny. lazo)aniline (5 g, 20.6 mmol) was dissolved in a solution of concentrated hydrochloric acid 10 ml and DMF 80 ml. The reaction mixture cooled down in an ice-water bath to 0°C and stirred for 15 min. Then a solution of sodium nitrite (1.45 g, 21 mmol) in 5 ml of water was added dropwise. The reaction mixture was stirred for 2 h at 0°C and then the N-ethyl-N-(2-hydroxyethyl)aniline (3.5 g, 21 mmol) in 15 ml of acetic acid was added dropwise. After stirring at 0–5°C for 5 h and 12 h at room temperature large amount of a dark precipitate formed. The precipitate was collected by filtration and then washed with saturated sodium bicarbonate solution and dried. The crude product was purified by column chromatography on silica gel (toluene: acetone, 1:1.5), followed by recrystallization from THF:hexane obtained as dark purple crystals m.p. 225°C, 62%.

^{1}H NMR (500 MHz, DMSO-d6): δ 8.46(d, 2H, Ar-**H**), 8.00 (d, 2H, Ar-**H**), 8.12 (d, 4H, Ar-**H**), 7.85 (d, 2H, Ar-**H**), 6.90 (d, 2H, Ar-**H**), 4.85 (t, 1H, O**H**), 3.55-3.65 (m, 6H, $-C\mathbf{H}_2-$), 1.18 (s, 3H, $-C\mathbf{H}_3$). UV-VIS (THF): $\lambda = 346, 520$ nm.

4-((2-Methacryloyloxyethyl)ethylamino)-4-nitroazobenzene (M1). Azomonomer was synthesized in the same way as reported [11]. The solid one was recrystallized from methanol. Dark red crystals m.p. 83°C, yield 80%.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.35 (d, 2H, Ar-**H**), 7.92 (t, 4H, Ar-**H**), 6.85 (d, 2H, Ar-**H**), 6.1 (s, 1H, $C\mathbf{H}_2$), 5.6 (s, 1H, $C\mathbf{H}_2$), 4.38 (m, 2H, $OC\mathbf{H}_2$), 3.75 (m, 2H, $NC\mathbf{H}_2$), 3.56 (m, 2H, $NC\mathbf{H}_2$), 1.94 (s, 3H, $C\mathbf{H}_3$), 1.24 (m, 3H, $C\mathbf{H}_3$). UV-VIS (THF): $\lambda = 475$ nm.

4-((2-Methacryloyloxy)-4'-(4-(phenylazo)-1-naphthylazo)benzene (M2). A solution of 4-[4-(phenylazo)-1-naphthylazo]phenol (1.5 g, 4.2 mmol) and triethylamine (0.64 g, 6.3 mmol) was dissolved in THF (40 ml). The solution was kept in an ice bath for 10 min.

A solution of distilled methacryloyl chloride (0.66 g, 6.3 mmol) in THF (10 ml) was added slowly to the reaction mixture. After the addition of methacryloyl chloride, solution was stirred for 12 h at ambient temperature. The solvent was removed by rotary evaporation and the residue was washed with a solution of sodium carbonate (0.8 g) in water (40 ml). After removing the solvent, the resulting material was purified by column chromatography (silica gel, ethyl acetate/hexane 1/8). Red solid residue, yield: 75%, m.p. 90°C.

^{1}H NMR (500 MHz, DMSO-d6): 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, $C\mathbf{H}_2$), 5.9 (s, 1H, $C\mathbf{H}_2$), 2.07 (s, 3H, $C\mathbf{H}_3$). UV-VIS (THF): $\lambda = 325, 428$ nm.

4-((2-Methacryloyloxyethyl)ethylamino)-4′-(4-nitrophenylazo)azobenzene(M3). Azomonomer **M3** was synthesized in the same way as azomonomer **M2**. Dark purple crystals; yield 60%; m. p. 160°C.

^{1}H NMR (500 MHz, $CDCl_3$): 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, $C\mathbf{H}_2$), 5.61 (s, 1H, $C\mathbf{H}_2$), 4.38 (t, 2H, $OC\mathbf{H}_2$), 3.75 (t, 2H, $NC\mathbf{H}_2$), 3.55 (q, 2H, $NC\mathbf{H}_2CH_3$), 1.97 (s, 3H, $C\mathbf{H}_3$), 1.28 (s, 3H, $C\mathbf{H}_3$). UV-VIS (THF): $\lambda = 340, 502$ nm.

4′-[(2-Methacryloyloxyethyl)ethylamino]-4-cyanoazobenzene (M4). **M4** was obtained as described for **M2**. Red solid residue, yield: 87%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89, 7.87 (d, 4H, Ar-**H**), 7.75, 7.73 (d, 2H, Ar-**H**), 6.82, 6.8 (d, 2H, Ar-**H**), 6.1 (s, 1H, $C\mathbf{H}_2$), 5.6 (s, 1H, $C\mathbf{H}_2$), 4.36 (m, 2H, $OC\mathbf{H}_2$), 3.7 (m, 2H, $NC\mathbf{H}_2$), 3.55 (m, 2H, $NC\mathbf{H}_2$), 1.94 (s, 3H, $C\mathbf{H}_3$), 1.25 (m, 3H, $C\mathbf{H}_3$). UV-VIS (THF): $\lambda = 275, 446$ nm.

Polymerization. Polymers were synthesized by free-radical polymerization. The polymerization was carried out in 10 wt% toluene solution of **M1** and methylmethacrylate (MMA) with monomers initial mole ratios 1:3. The polymerization was performed using AIBN as a free radical initiator (1 wt% of monomer) at 80°C 35 h in argon atmosphere. Previously initial mixture was degassed with repeated freeze-pump-taw cycles. The polymerization was stopped by pouring the reaction mixture into methanol. This procedure was repeated several times to ensure removal of unreacted methacrylic monomers and finally the polymer **P1** dried in vacuo at 50°C overnight. In cases of copolymerization **M2** with MMA, **M3** with MMA and **M4** with MMA the same synthetic procedure was used in DMF, 1,4-dioxane and toluene solution accordingly. The copolymerization ratios of units in the corresponding polymers (structure) were calculated on the basis of the integrated peak areas of ^{1}H NMR spectra in DMSO-d_6 for **P1**, **P3**, **P4** and in pyridine-d_5 for **P2**. The glass transition temperatures have been measured by differential scanning calorimetry at 125°C, 110°C, 140°C and 120°C for the copolymers **P1**, **P2, P3,** and **P4** respectively.

3. Results and Discussion

The 4-(N-ethyl-N-(2-hydroxyethyl)amino)-4′-(4-nitrophenylazo)azobenzene was synthesized by a diazo coupling reaction between N-ethyl-N-(2-hydroxyethyl)aniline and a diazonium salt of 4-(4-nitrophenylazo)aniline. The 4′-[(2-hydroxyethyl)ethylamino]-4-cyanoazobenzene was prepared by coupling the diazonium salt of 4-aminobenzonitrile with 2-(*N*-ethylanilino)ethanol according to the procedure published previously [11]. The 4′-[(2-hydroxyethyl)ethylamino]-4-nitroazobenzene and 4-[4-(phenylazo)-1-naphthylazo]phenol are commercially available (Aldrich).

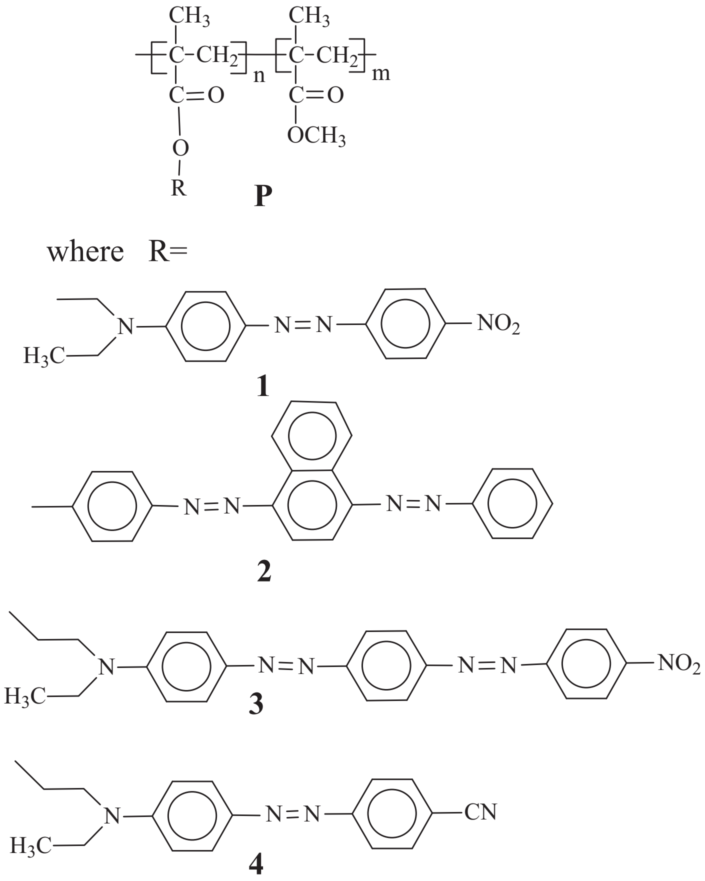

Figure 1. Chemical structures of azobenzene polymers.

The azobenzene methacrylate monomers were synthesized by reaction the azobenzene alcohols with methacryloyl chloride in the presence of triethylamine as nucleophilic catalyst and hydrochloric acid acceptor. The polymers (Fig 1.) were synthesized by radical polymerization using AIBN as radical initiator. The structures of obtained polymers were confirmed by ^{1}H NMR spectra. The compositions of the copolymers were well controlled as the initial ratio of the azobenzenes monomers and MMA. However practically for all copolymers were observed MMA saturation due to high-active polymerization ability of MMA. It should be noted that polar substituents in azobenzene compounds as -CN and -NO_2 can act as retarding agents of free radical polymerization reaction. Therefore, long reaction time is needed to syntheses of polymers with high yield.

In Figure 2 characteristic absorption spectra of the investigated systems can be seen. As shown in the figure, the π- π^* band of the **P1**, **P3** and **P4** systems is shifted to the red, compared to the **P2**. This is due to the electron-donor and electron-acceptor substituents in the synthesized azobenzene polymers **P1**, **P3**, **P4** which are increasing the charge transfer character of the π- π^* transition [12]. The fact that the **P3** system exhibits maximum

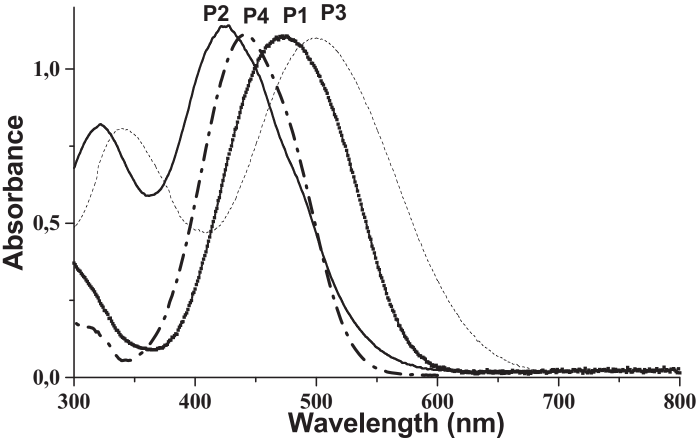

Figure 2. UV-Vis spectra of P1, P2, P3, P4 in thin solid films.

absorption at the longest wavelength (500 nm) among the investigated compounds, it reflects the highest charge-transfer interaction occurring between the electron-donor group (amino) and electron-acceptor group (nitro), which is characteristic for the "pseudo-stilbene" types in Rau's classifications [13]. This enhancement of the charge transfer efficiency, if compared to the **P1** system, can be attributed to the additional phenyldiazene fragment in the side chain [14].

For optics and photonics, the "pseudo-stilbene" molecules are of particular interest. Azobenzene polymers **P1**, **P3, P4** are characterized by a highly asymmetric electron distribution due to the substitution with strong electron donating and withdrawing groups. Such a substitution pattern gives rise to a strong nonlinear optical response, which can be transformed to a macroscopic level by poling the sample using either static electric fields or light fields [15]. The common photochemical properties of all azobenzene compounds are their possibility for photoisomerization through rotation about N-N bond and via the inversion of one or both of the nitrogens through a linear sp-hybridized transition state in which the double bond was retained. Moreover, such compounds have a short *cis*-lifetime and a significant overlap between the spectra of the *trans* and *cis*-forms.

4. Conclusions

We designed and synthesized polymers with different size of the conjugated system between donor and acceptors. The significant photochemical properties combined with the possibility to further modify it, by changing the conjugation, the electron-acceptor and electron-donor groups, suggests that these systems can prove to be important candidates for a variety of photonic/opto-electronic applications. Polymers with analogically properties are promising materials for photonic applications as optical data storage, surface-relief holography and optical switching.

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