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New multifunctional sulfonamide-containing azobenzene chromophores: Synthesis and photochromic properties

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ABSTRACT

The work presents synthesis and characterization of novel sulfadimethoxine and sulfabenzamide azo derivatives as well as the kinetic study of their *trans–cis–trans* isomerization. Spectral properties and kinetic constants were determined for the chromophores dispersed in poly(methyl methacrylate-*co*butyl methacrylate) deposited on glass substrates in form of transparent, thin films. The maximum absorption bands were observed within wavelength in range of 446–457 nm for *N*-disubstituted aminoazobenzene derivatives and 361–362 nm for phenolic chromophores. For the phenolic azo derivatives of sulfadimethoxine and sulfabenzamide the photoisomerization induced with UV light followed the first order kinetics, while for other compounds the process combined of two parallel reactions with different rate constants was observed. The rate constants of thermal relaxation in the dark were usually few times smaller than those determined for photoinduced *trans–cis* isomerization. The change of real part of refractive index upon illumination determined by ellipsometry was within the range of 0.0043–0.0138. © 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Azobenzene-containing chromophores have attracted attention in recent years due to their unique properties arising from reversible conformational changes accompanying light-induced trans--cis-trans isomerization. Illumination of azobenzene derivatives with UV or visible light yields a photostationary composition that is temperature and wavelength dependent [1]. They are one of the most popular class of the photochromic compounds due to simplicity and cost-effectiveness of their synthesis and purification accompanied by versatile, unique properties. These features make azobenzene derivatives promising materials for many applications, including holographic data storage [2,3], liquid crystal displays [4,5], surface relief gratings (SRGs) formation [6-8] and nonlinear optical processes [9-11]. Numerous studies were dedicated to various systems containing azobenzene chromophores. Among the azobenzenes the simple derivatives of *p*-nitroaniline, like Disperse Red dyes, have been most widely investigated [12–16]. However, other more sophisticated structures containing heterocyclic rings were also designed and synthesized. The papers concerning properties of the azobenzene derivatives of sulfisomidine,

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sulfamethoxazole, isoxazole, imidazole and many other heterocyclic compounds have been published [16–26]. These chromophores were successfully incorporated into various systems, like Langmuir–Blodgett films [17,18], vinyl and addition polymers [16,19–22] or hybrid organic-inorganic materials based on silicon [23,24]. Different kinds of properties of materials mentioned above have been investigated, including photochromism, refractive index modulation [19,22], second harmonic generation [17,18] or surface relief grating formation [25,26]. The results of the studies turned out to be promising and encouraged us to continue the investigations in that field.

The aim of this study was to determine susceptibility of the photochromic dyes vs. light in polymer matrix used as a continuous phase. Two kinds of the dyes were selected for the synthesis. The first ones were azo derivatives containing hydroxyphenyl group at the side of electron donor part of the molecule and absorbing in UV range. The second ones were similar derivatives containing aminophenyl group at analogous place and these dyes absorbed light in visible range of the spectrum.

The reversible *trans*—*cis*—*trans* isomerization of the chromophores was investigated using ellipsometric technique and UV—Vis spectroscopy for "guest—host" systems with poly(methyl methacrylate-*co*-butyl methacrylate) as a polymer matrix. Kinetic study was performed to provide full characteristics of photochromic properties for all compounds. Due to the presence of reactive





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hydroxyl group in molecules of all chromophores, they can be easily transformed into vinyl monomers or siloxane precursors and then into macromolecular or hybrid photochromic materials.

2. Materials and methods

2.1. Materials

Sulfabenzamide (TCI Europe), sulfadimethoxine (TCI Europe), phenol (POCH S.A. Gliwice Poland), 2-(methylphenylamino)ethanol (Sigma–Aldrich), 2-(*N*-ethylanilino)ethanol (Sigma–Aldrich), *N*phenyldiethanolamine (Sigma–Aldrich), poly(methyl methacrylate-*co*-butyl methacrylate) ($M_w = \sim 75\,000$) (Sigma–Aldrich), sodium nitrite (POCH S.A. Gliwice Poland), sodium acetate (POCH S.A., Gliwice, Poland) were used as received.

2.2. Synthesis and characterization

2.2.1. 4-[(E)-[4-(benzoylsulfamoyl)phenyl]azo]benzenediazonium chloride (SBACl)

The mixture of sulfabenzamide (4.0 mmol, 1.10 g), concentrated hydrochloric acid (2 ml) and water (9 ml) was heated to 50 $^{\circ}$ C and then cooled to 0 $^{\circ}$ C in an ice-brine bath. The solution of sodium nitrite (4.5 mmol, 0.31 g) in water (1 ml) was added dropwise to the reaction mixture keeping the temperature between 0 and 5 $^{\circ}$ C. The solution of diazonium salt was stirred for 30 min maintaining a low temperature and was further used in coupling reactions.

2.2.2. 4-[(E)-[4-[(2,6-dimethoxypyrimidin-4-yl)sulfamoyl]phenyl] azo]benzenediazonium chloride (SDMCl)

The diazonium salt in the form of SDMCl was synthesized as described above using sulfadimethoxine (4.0 mmol, 1.24 g) instead of sulfabenzamide.

2.2.3. N-[4-[(E)-[4-[(E)-(4-hydroxyphenyl)azo]phenyl]azo]phenyl] sulfonylbenzamide (SBAph)

Phenol (4.5 mmol, 0.42 g) was dissolved in 5 ml of 6 wt % water solution of sodium hydroxide and was cooled to the temperature below 5 °C. Then to the solution of phenol was slowly added solution of diazonium salt (SBACI). The reaction mixture was stirred for 2 h and then was filtered under vacuum. The crude product was washed several times with water and recrystallized from ethanol. SBAph was obtained in a yield of 88%.

¹H NMR (DMSO–*d*₆): 6.84 ppm, d, 2H, (CH in phenylene ring in *ortho* position to hydroxyl group); 7.48 ppm, t, 2H (CH in phenyl ring in *meta* position to carbonyl group); 7.62 ppm, t, 1H (CH in phenyl ring in *para* position to carbonyl group); 7.79 ppm, d, 2H (CH in phenylene ring in *meta* position to hydroxyl group); 7.85 ppm, d, 2H (CH in phenyl ring in *ortho* position to carbonyl group); 7.91 ppm, d, 2H (CH in phenylene ring in *ortho* position to sulfonyl group); 8.11 ppm, d, 2H (CH in phenylene ring in *ortho* position to sulfonyl group); 8.11 ppm, d, 2H (CH in phenylene ring in *meta* position to sulfonyl group); 10.55, s, 1H (OH); 12.62 ppm, br.s., 1H (NH). Elemental analysis calcd for C₁₉H₁₅N₃O₄S: C 59.83%, H 3.96%, N 11.02%, S 8.41%. Found: C 59.50%, H 3.50%, N 10.38%, S 8.09%. M.p.: 263.5–265.2 °C.

2.2.4. N-[4-[(E)-[4-[(E)-[4-[2-hydroxyethyl(methyl)amino]phenyl] azo]phenyl]azo] phenyl]sulfonylbenzamide (SBAm)

The cold solution of 2-(methylphenylamino)ethanol (4.1 mmol, 0.62 g) in water (2 ml) was poured into solution of diazonium salt (SBACl) and stirred for 2 h. Then reaction mixture was neutralized with sodium acetate and filtered under vacuum. The crude product was washed several times with water and recrystallized from ethanol. SBAm was obtained in a yield of 90%.

¹H NMR (DMSO–*d*₆): 3.11 ppm, s, 3H (CH3); 3.57 ppm, dd, 4H (OCH₂CH₂N); 4.80 ppm, s, 1H (OH); 6.84 ppm, d, 2H (CH in phenylene ring in *ortho* position to amino group); 7.48 ppm, t, 2H (CH in phenyl ring in *meta* position to carbonyl group); 7.62 ppm, t, 1H (CH in phenyl ring in *para* position to carbonyl group); 7.79 ppm, d, 2H (CH in phenylene ring in *meta* position to amino group); 7.85 ppm, d, 2H (CH in phenyl ring in *ortho* position to carbonyl group); 7.91 ppm, d, 2H (CH in phenylene ring in *ortho* position to carbonyl group); 7.91 ppm, d, 2H (CH in phenylene ring in *ortho* position to sulfonyl group); 12.63 ppm, br.s., 1H (NH). Elemental analysis calcd for C₂₂H₂₂N₄O₄S: C 60.26%, H 5.06%, N 12.78%, S 7.31%. Found: C 60.20%, H 4.82%, N 12.36%, S 7.50%. M.p.: 159.8–162.3 °C.

2.2.5. N-[4-[(E)-[4-[(E)-[4-[ethyl(2-hydroxyethyl)amino]phenyl] azo]phenyl]azo]phenyl] sulfonylbenzamide (SBAe)

2-(*N*-ethylanilino)ethanol (4.0 mmol, 0.66 g) was dissolved in 2 ml of methanol and cooled to 0 °C. Then it was added to solution of diazonium salt (SBACl) and stirred for 2 h. The reaction mixture was neutralized with sodium acetate and filtered under vacuum. The crude product was washed several times with water and recrystallized from ethanol. SBAe was obtained in a yield of 92%.

¹H NMR (DMSO–*d*₆): 1.13 ppm, t, 3H (CH₃); 3.57 ppm, m, 6H (CH₂); 4.81 ppm, br.s., 1H (OH); 6.84 ppm, d, 2H (CH in phenylene ring in *ortho* position to amino group); 7.48 ppm, t, 2H (CH in phenyl ring in *meta* position to carbonyl group); 7.62 ppm, t, 1H (CH in phenyl ring in *para* position to carbonyl group); 7.79 ppm, d, 2H (CH in phenylene ring in *meta* position to amino group); 7.79 ppm, d, 2H (CH in phenyl ring in *neta* position to amino group); 7.85 ppm, d, 2H (CH in phenyl ring in *ortho* position to carbonyl group); 7.91 ppm, d, 2H (CH in phenylene ring in *ortho* position to sulfonyl group); 8.11 ppm, d, 2H (CH in phenylene ring in *meta* position to sulfonyl group); 12.62 ppm, br.s., 1H (NH). Elemental analysis calcd for C₂₃H₂₄N₄O₄S: C 61.05%, H 5.35%, N 12.38%, S 7.09%. Found: C 61.00%, H 5.31%, N 11.98%, S 7.27%. M.p.: 157.6–160.3 °C.

2.2.6. N-[4-[(E)-[4-[(E)-[4-[bis(2-hydroxyethyl)amino]phenyl]azo] phenyl]azo]phenyl] sulfonylbenzamide (SBAf)

The solution of *N*-phenyldiethanolamine (4.0 mmol, 0.72 g) in methanol (3 ml) was cooled to temperature below 5 °C. Then it was slowly added to the solution of diazonium salt (SBACl) keeping temperature between 0 and 5 °C. The reaction mixture was stirred for 2 h. Product of coupling was precipitated by neutralization of mixture to pH 7 using sodium acetate. The crude product was filtered under vacuum and washed several times with water. SBAF was recrystallized from ethanol. The yield of product was 91%.

¹H NMR (DMSO–*d*₆): 3.43 ppm, t, 8H (CH₂); 4.86 ppm, s, 2H (OH); 6.84 ppm, d, 2H (CH in phenylene ring in *ortho* position to amino group); 7.48 ppm, t, 2H (CH in phenyl ring in *meta* position to carbonyl group); 7.62 ppm, t, 1H (CH in phenyl ring in *para* position to carbonyl group); 7.79 ppm, d, 2H (CH in phenylene ring in *meta* position to amino group); 7.85 ppm, d, 2H (CH in phenylene ring in *ortho* position to carbonyl group); 7.91 ppm, d, 2H (CH in phenylene ring in *ortho* position to sulfonyl group); 8.11 ppm, d, 2H (CH in phenylene ring in *meta* position to sulfonyl group); 12.62 ppm, br.s., 1H (NH). Elemental analysis calcd for C₂₃H₂₄N₄O₅S: C 58.96%, H 5.16%, N 11.96%, S 6.84%. Found: C 58.83%, H 5.04%, N 11.35%, S 7.07%. M.p. 117.0–119.6 °C.

2.2.7. N-(2,6-dimethoxypyrimidin-4-yl)-4-[(E)-[4-[(E)-(4-

hydroxyphenyl)azo]phenyl] azo]benzenesulfonamide (SDMph)

SDMph was synthesized as described in the synthesis of SBAph using SDMCl instead of SBACl. The product was obtained in a yield of 83%.

¹H NMR (DMSO $-d_6$): 3.72 ppm, s, 3H (OCH₃ in 2,6-dimethoxypirimidin-4-yl ring in C6 position); 3.78 ppm, s, 3H

(OCH₃ in 2,6-dimethoxypirimidin-4-yl ring in C2 position); 5.97 ppm, s, 1H (CH in 2,6-dimethoxypirimidin-4-yl ring in C5 position); 6.84 ppm, d, 2H (CH in phenylene ring in *ortho* position to hydroxyl group); 7.77 ppm, d, 2H (CH in phenylene ring in *meta* position to hydroxyl group); 7.87 ppm, d, 2H (CH in phenylene ring in *ortho* position to sulfonyl group); 8.04 ppm, d, 2H (CH in phenylene ring in *ortho* position to sulfonyl group); 9.98 ppm, s, 1H (OH); 11,77 ppm, br.s., 1H (NH). Elemental analysis calcd for C₁₈H₁₇N₅O₅S: C 52.04%, H 4.12%, N 16.86%, S 7.72%. Found: C 52.18%, H 3.67%, N 16.52%, S 7.84%. M.p.: 153.0–155.8 °C.

2.2.8. N-(2,6-dimethoxypyrimidin-4-yl)-4-[(E)-[4-[(E)-[4-[(2-hydroxyethyl(methyl)amino] phenyl]azo]phenyl]azo] benzenesulfonamide (SDMm)

SDMm was obtained according to the procedure described in the synthesis of SBAm using SDMCl instead of SBACl. The yield of product was 85%.

¹H NMR (DMSO– d_6): 3.08 ppm, s, 3H (CH₃N); 3.56 ppm, dd, 4H (NCH₂CH₂O); 3.74 ppm, s, 3H (OCH₃ in 2,6-dimethoxypirimidin-4-yl ring in C6 position); 3.78 ppm, s, 3H (OCH₃ in 2,6-dimethoxypirimidin-4-yl ring in C2 position); 4.80 ppm, s, 1H (OH); 5.95 ppm, s, 1H (CH in 2,6-dimethoxypirimidin-4-yl ring in C5 position); 6.85 ppm, d, 2H (CH in phenylene ring in *ortho* position to amino group); 7.78 ppm, d, 2H (CH in phenylene ring in *meta* position to amino group); 7.88 ppm, d, 2H (CH in phenylene ring in *meta* position to sulfonyl group); 8.04 ppm, d, 2H (CH in phenylene ring in *meta* position to sulfonyl group); 11.78 ppm, br.s., 1H (NH). Elemental analysis calcd for C₂₁H₂₄N₆O₅S: C 53.38%, H 5.12%, N 17.79%, S 6.79%. Found: C 53.12%, H 4.94%, N 16.67%, S 6.82%. M.p.: 177.8–180.7 °C.

2.2.9. N-(2,6-dimethoxypyrimidin-4-yl)-4-[(E)-[4-[(E)-[4-[ethyl(2-hydroxyethyl)amino] phenyl]azo]phenyl]azo]benzenesulfonamide (SDMe)

SDMe was obtained according to the procedure described in the synthesis of SBAe using SDMCl instead of SBACl. The yield of product was 89%.

¹H NMR (DMSO–*d*₆): 1.10 ppm, t, 3H (CH₃); 3.49–3.58 ppm, m, 6H (CH₂–N–CH₂CH₂); 3.71 ppm, s, 3H (OCH₃ in 2,6-dimethoxypirimidin-

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4-yl ring in C6 position); 3.77 ppm, s, 3H (OCH₃ in 2,6dimethoxypirimidin-4-yl ring in C2 position); 4.85 ppm, s, 1H (OH); 5.96 ppm, s, 1H (CH in 2,6-dimethoxypirimidin-4-yl ring in C5 position); 6.83 ppm, d, 2H (CH in phenylene ring in *ortho* position to amino group); 7.76 ppm, d, 2H (CH in phenylene ring in *meta* position to amino group); 7.86 ppm, d, 2H (CH in phenylene ring in *ortho* position to sulfonyl group); 8.04 ppm, d, 2H (CH in phenylene ring in *meta* position to sulfonyl group); 11.78 ppm, br.s., 1H (NH). Elemental analysis calcd for $C_{22}H_{26}N_6O_5S$: C 54.31%, H 5.39%, N 17.27%, S 6.59%. Found: C 54.50%, H 5.22%, N 16.77%, S 6.25%. M.p.: 135.8–137.9 °C.

2.2.10. 4-[(E)-[4-[(E)-[4-[bis(2-hydroxyethyl)amino]phenyl]azo] phenyl]azo]-N-(2,6-dimethoxy-pyrimidin-4-yl)benzenesulfonamide (SDMf)

SDMf was obtained according to the procedure described in the synthesis of SBAf using SDMCl instead of SBACl. The yield of product was 83%.

¹H NMR (DMSO–*d*₆): 3.57 ppm, m, 8H (NCH₂CH₂O); 3.72 ppm, s, 3H (OCH₃ in 2,6-dimethoxypirimidin-4-yl ring in C6 position); 3.78 ppm, s, 3H (OCH₃ in 2,6-dimethoxypirimidin-4-yl ring in C2 position); 4.86 ppm, s, 2H (OH); 5.97 ppm, s, 1H (CH in 2,6dimethoxypirimidin-4-yl ring in C5 position); 6.84 ppm, d, 2H (CH in phenylene ring in *ortho* position to amino group); 7.77 ppm, d, 2H (CH in phenylene ring in *meta* position to amino group); 7.87 ppm, d, 2H (CH in phenylene ring in *ortho* position to sulfonyl group); 8.04 ppm, d, 2H (CH in phenylene ring in *meta* position to sulfonyl group); 8.04 ppm, d, 2H (CH in phenylene ring in *meta* position to sulfonyl group 2); 11.77 ppm, b.s., 1H (NH). Elemental analysis: calcd for C₂₂H₂₆N₆O₆S: C 52.58%, H 5.21%, N 16.72%, S 6.38%. Found: C 52.00%, H 5.41%, N 16.25%, S 6.53%. M.p.: 163.6–165.4 °C.

2.3. Preparation of the films

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The guest-host thin polymer films containing azo dyes were prepared by spin coating technique. The synthesized chromophores were dissolved in 1.2 ml of tetrahydrofuran in an amount of 12 mg. Then 28 mg of poly(methyl methacrylate-*co*-butyl methacrylate) was added to each photochromic solution. The polymer mixtures containing azo dyes were ultrasonicated for 15 min and filtered through syringe filter with a pore size of 0.45 µm. The

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materials were deposited onto glass plates in form of thin transparent films. The resulting films were kept in dark before measurements. The films were illuminated with UV tube lamp (8 W power) or with white light filtered to remove radiation below 400 nm. The white light power was 2 mW per square centimeter.

2.4. Measurements

¹H NMR and ¹H – ¹H COSY NMR spectra were recorded with 300 MHz BRUKER Advance DRX-300 apparatus using DMSO– d_6 as solvents and TMS as an internal standard.

UV–Vis spectra were recorded with Hitachi U 1900 spectrophotometer.

Melting points were determined with Electrothermal 9100 apparatus.

Ellipsometer EL X-02C of DRE Ellipsomerterbau GmbH (Germany) operated at an incident angle of 70° and using a linearly polarized laser beam of 632 nm and ca. 3 mW power was used to measure the changes of refractive index of thin photochromic films before and after illumination with light. The measurements were carried out in air at room temperature.

3. Results and discussion

3.1. Photoisomerization characteristics

All chromophores were synthesized through the well–known reaction path given in Fig. 1. The synthesis consisted of two types of reaction occurring at temperatures below 5 °C. In the first one the diazotization of a primary amine to diazonium salt took place (Fig. 1a). The second reaction was a coupling of the diazonium salt with a tertiary amine or phenol (Fig. 1b). The dyes so obtained in good yields of 83–92% were colored crystalline solids. The purities and structures of synthesized chromophores were confirmed by ¹H NMR. The ¹H NMR peaks assignments were verified with use of ¹H – ¹H COSY NMR spectroscopy.

Kinetic aspects of *trans*—*cis*—*trans* isomerization of sulfonamide chromophores were studied using UV—Vis spectroscopy. The azobenzene derivatives of sulfabenzamide and sulfadimethoxine were dispersed in poly(MMA-*co*-BMA) matrix and were examined as thin films deposited onto glass substrates. Chromophore to polymer host weight ratio and preparation conditions were the same for all samples.

All chromophores underwent reversible *trans*-*cis* isomerization during illumination with light. Examples of spectral changes after 10 min of irradiation and 20 min of thermal relaxation in the dark are presented in Figs. 2 and 3. The maximum absorption band of phenol derivatives (SBAph and SDMph) was observed at 361–362 nm, while for other derivatives it was placed within visible range of wavelengths at ca. 450 nm. The exact values of λ_{max} are presented in Table 1. To explain the influence of chemical structure of the chromophore molecule on the position of maximum absorption band, the approximate values HOMO and LUMO values were calculated. The HOMO–LUMO gap was chosen as an indicator of electron donor–acceptor interaction due to simplicity of its reliable estimation with quantum chemical methods.

The geometries of SBAph, SBAf, SBAm and SBAe were optimized using MOPAC2009 program with PM6 semi-empirical method [27]. The optimized structures were further used to determine the energy of highest occupied molecular orbital (HOMO), which according to Koopmans' theorem [2], is a good estimation of molecule ionization potential. The estimated values of ionization potentials were found to be equal to 9.38, 8.72, 8.64 and 8.58 eV, ascribed to SBAph, SBAf, SBAm and SBAe, respectively. The



Fig. 2. Spectral changes of SDMf in p(MMA-co-BMA) (- \Box -) after 10 min of illumination with white light (- \bigtriangledown -) and after 20 min of thermal relaxation in the dark (- \blacktriangle -) recorded at 25 °C.

HOMO–LUMO gap for phenol derivatives was ca. -7.6 eV while for the other compounds it was in the range of -6.98 to -7.09 eV.

These results indicate that 2-(*N*-ethylanilino)ethanol is the strongest electron donor, what is in good agreement with measured data, as the maximum absorption band of chromophores SBAe and SDMe, containing that donor group, is shifted towards longer wavelengths as compared with other amino chromophores. Phenol was found to be much weaker electron donor in comparison to *N*-disubstituted aminophenyl groups resulting in distinct UV-shift of SBAph and SDMph maximum absorption band. The presence of alkyl groups bound to nitrogen atom in aminophenyl group increases the donor strength. And additionally, the electron donor ability of 2-(methylphenylamino)ethanol is more pronounced than that of *N*-phenyldiethanolamine.

The azobenzene-containing chromophores in solution usually obey the first order kinetics described by the following equation [1]:

$$\ln \frac{A_{\infty} - A_t}{A_{\infty} - A_0} = -k_1 t \tag{1}$$



Fig. 3. Spectral changes of SBAph in p(MMA-co-BMA) ($-\Box$ -) after 10 min of illumination with UV light ($-\mathbf{\nabla}$ -) and after 20 min of thermal relaxation in the dark ($-\mathbf{\Delta}$ -) recorded at 25 °C.

Table 1

Kinetic data for *trans-cis* photoisomerization determined by UV–Vis measurements for chromophores in p(MMA-*co*-BMA) matrix.

Sample	λ _{max} [nm]	α	$k_1 imes 10^3 [s^{-1}]$	$1 - \alpha$	$k_2 \times 10^3 [s^{-1}]$
SDMm	450	0.66	148.5	0.34	9.80
SDMf	448	0.65	81.9	0.35	7.96
SDMe	454	0.59	69.6	0.41	7.16
SBAm	448	0.65	116.7	0.35	4.84
SBAf	446	0.58	74.4	0.42	9.93
SBAe	457	0.85	167.3	0.15	8.30
SBAph	361	1	11.7	_	_
SDMph	362	1	20.8	-	-

where A_{∞} represents absorbance at the photostationary state, A_0 represents absorbance at initial state (before irradiation) and A_t represents absorbance of the sample at time *t*.

The same chromophores incorporated into polymer matrix usually exhibit deviation from simple first-order kinetics; what suggests that in these conditions the photoreaction is a combination of two processes [2]. The *trans*—*cis* photoisomerization results in a change of molecular shape of the azo chromophore around diazo group. In a dense polymeric milieu the molecular movement can be hindered and therefore this influence should be taken into account as a slow part of the material response. The fraction of each process can be estimated from the following equation:

$$\frac{A_{\infty} - A_t}{A_{\infty} - A_0} = \alpha \cdot \exp(-k_1 \cdot t) + (1 - \alpha) \cdot \exp(-k_2 \cdot t)$$
(2)

where k_1 is the rate constant of the fast reaction step, k_2 is the rate constant of the slow reaction step and α describes the fraction of fast photoisomerization stage in total conversion of the system [2].

Equation (2) was used to determine the kinetic constants for *trans*-*cis* isomerization induced by irradiation with white or UV light. All parameters determined for photoisomerization process are presented in Table 1.

The kinetic behavior of phenolic chromophores (SBAph and SDMph) was different from that of other compounds. *Trans–cis* isomerization of these molecules dispersed in poly(MMA-*co*-BMA) matrix followed first-order kinetics and could be described by equation (1), while for other samples the deviation from first-order kinetics was observed and the *trans–cis* isomerization was described with equation (2). The *trans–cis* isomerization of azo chromophores involves a change of molecular shape of the chromophores. In solutions of organic solvents, usually of low



Fig. 4. Kinetics of sulfadimethoxine derivatives photoisomerization induced by illumination with white (SDMm, SDMe, SDMf) or UV (SDMph) light at 25 $^{\circ}$ C.



Fig. 5. Kinetics of sulfabenzamide derivatives photoisomerization induced by illumination with white (SBAm, SBAe, SBAf) or UV (SBAph) light at 25 $^\circ$ C.

concentration, the change of shape is not hindered by the solvents and therefore the first order kinetics is observed. In our case, the concentration of the chromophore in polymer matrix is, by no accident, high to ensure good photochromic response. The molecular movement of the chromophore molecules in such dense environment must be hindered by rheological properties of the material, particularly if photoreactions take place at the temperature below T_g . It is also probable that polar dye molecules interact not only with copolymer chains of the matrix but also between themselves. Due to the presence of hydroxyl group(s) in dye molecules the interactions in materials by formation of hydrogen bonds between material components should also be considered. However the system is still limited by free volume available in rigid polymer matrix, therefore the rate of photoreaction and photoconversion is not large.

The kinetic behavior for pairs of chromophores containing the same donor and different acceptor groups is comparable. Considering the compounds with amino donor groups, the fraction of fast photoisomerization stage in total conversion of the system is significantly larger than that of the slow process. The rate constant of fast process (k_1) has the smallest values for SDMe and SBAf samples, while the highest values are observed for SDMm and SBAe. The plots presented in Figs. 4 and 5 show that the deviation from the first order kinetics is similar for all the systems except SBAm, where the deviation is even more pronounced due to the smallest value of slow process rate constant (k_2).

As it was mentioned, the dyes SDMph and SBAph containing phenol rest in the molecule isomerize according to first order kinetics, as shown in Figs. 4 and 5. The explanation of this phenomenon may be as follows. The reaction rate of the first stage is comparable with that of the second stage, ascribed to rheological

Table 2

Kinetic data for *cis-trans* thermal relaxation in the dark determined by UV–Vis measurements for chromophores in p(MMA-*co*-BMA) matrix.

Sample	A_{∞}/A_0	α'	$k_1'\times 10^3[\rm s^{-1}]$	$1 - \alpha'$	$k_2^\prime \times 10^3 [\mathrm{s}^{-1}]$
SDMm	0.754	0.41	4.64	0.59	0.185
SDMf	0.776	0.36	5.34	0.64	0.241
SDMe	0.792	0.64	5.20	0.36	0.287
SBAm	0.786	0.49	7.65	0.51	0.175
SBAf	0.814	0.40	8.05	0.60	0.151
SBAe	0.864	0.74	62.3	0.26	0.360
SBAph	0.529	0.12	4.16	0.88	0.101
SDMph	0.516	0.05	3.46	0.95	0.058



Fig. 6. Kinetics of sulfabenzamide derivatives thermal relaxation in the dark at 25 °C.

material movement, so that the whole process might be treated as it were first order reaction. Evidence that we have to do also with slower reaction stage in the case of these dyes could be found in next section, describing relaxation kinetics.

The kinetics of thermal relaxation occurring in the dark is described by the following equation [2]:

$$\frac{A_0 - A_t}{A_0 - A_\infty} = \alpha \cdot \exp(-k'_1 \cdot t) + (1 - \alpha) \cdot (-k'_2 \cdot t)$$
(3)

where k'_1 is the rate constant of the fast reaction stage, k'_2 is the rate constant of the slow reaction stage, α describes the fraction of fast process in total conversion of the system, A_0 stands for initial absorbance value (before irradiation), A_t is absorbance at time *t* and A_{∞} describes absorbance at photostationary state.

The values derived from estimation of experimental data for relaxation process with equation (3) as well as A_{∞}/A_0 ratios are presented in Table 2. The rate constants for thermal relaxation process are significantly smaller than those determined for light-induced photoisomerization process. The fraction of fast process in total conversion of the system is dominating only for chromophores containing ethyl(2-hydroxyethyl)amino group (SBAe and SDMe), for other systems the fraction of the slow process is prevailing. Values of rate constant k'_1 referring to fast process are



Fig. 7. Kinetics of sulfadimethoxine derivatives thermal relaxation in the dark at 25 °C.

Table 3

Changes of real part of refractive index of photochromic films.

Sample	SBAph	SBAm	SBAe	SBAf	SDMph	SDMm	SDMe	SDMDf
$\Delta n_{\rm r}$	0.0115	0.0122	0.0043	0.0125	0.0108	0.0086	0.0113	0.0138

higher for sulfabenzamide derivatives, while the rate constants of slow reaction k'_2 are generally higher for sulfadimethoxine derivatives. Both kinds of rate constants have the smallest values for phenolic chromophores; SBAph and SDMph. Plots presenting the kinetics of thermal relaxation are shown in Figs. 6 and 7.

3.2. Refractive index modulation

Ellipsometry is an effective and nondestructive method, which allows estimating variations of refractive index and thickness of thin films occurring during photochromic cycles. Ellipsometry is based on measurement of a change in polarization of light reflected from a material surface. The linearly polarized light reflects from the sample and changes its polarization into elliptical one. The parameters measured by ellipsometry are called ellipsometric parameters Ψ and Δ . Ψ indicates amplitude and Δ is phase shift of polarized light. The change in light polarization is defined as:

$$\rho = \tan(\Psi)\exp(i\Delta) = \frac{r_p}{r_s} \tag{4}$$

where r_p and r_s are the complex Fresnel reflection coefficients for polarized light parallel and perpendicular to the plane of incidence, respectively. Ψ and Δ are used to describe the optical properties which determine how light interacts with a material. The complex refractive index (\tilde{n}) consists of the real part (n_r) and imaginative part of refractive index (*ik*) where *k* is extinction coefficient.

$$n = n_{\rm r} + ik \tag{5}$$

The measurements of ellipsometric parameters were carried out using thin photochromic polymer films during periodic illumination with light. The changes of Ψ and Δ were observed for all chromophores what allowed determining the changes of refractive indices of the film before and after illumination. The changes of the refractive indices (Δn_r) were in the range from 0.0086 for SDMm to 0.0138 for SDMf (Table 3). The course of modification of parameter Ψ , which include four photochromic cycles, is shown on Fig. 8. Each cycle consists of *trans*—*cis* isomerization and thermal relaxation process. *Trans*—*cis* isomerization was observed under illumination with diode light of wavelength 395 nm (growth curve). Thermal relaxation occurred in the absence of illumination (decay curve).



Fig. 8. Ellipsometry of SDMm. The changes of Ψ parameter of film during four photochromic cycles.

4. Concluding remarks

The sulfonamide-containing azobenzene chromophores were synthesized in good yields with an easy procedure. All compounds investigated in a "guest—host" system in poly(methyl methacry-late-*co*-butyl methacrylate) polymer matrix underwent reversible *trans*—*cis* photoisomerization. The kinetic study based on UV—Vis measurements of the compounds in question indicated that the kind of electron-donor group affected the rate of isomerization and thermal relaxation processes as well as the position of maximum absorption band. The reaction run of hydroxyphenyl containing dyes (absorbing in UV) followed first order kinetics as the rate of photoreaction (first stage) was probably of the same range as that ascribed to material rheological behavior (slow stage).

The rate constants for *trans*—*cis* isomerization were found to be higher for sulfadimethoxine derivatives than for sulfabenzamide-containing chromophores except for the SBAe sample, for which the isomerization rate constant had the highest value. For the thermal relaxation in the dark the results were reverse — the process was faster for the sulfabenzamide derivatives. The refractive index modulation observed during illumination was moderate but the change of dielectric properties of materials was distinct qualifying the dyes as potentially usable in holographic applications.

Due to the presence of reactive hydroxyl group in chemical structure of the chromophores, they can be further used for the synthesis of polymer or hybrid organic—inorganic materials.

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