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**The novel photoresponsive oligomers containing azo derivatives of sulfamerazine
for spontaneous surface relief grating inscription**

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Abstract

In this work, a novel photoresponsive materials has been successfully developed. We have synthesized the series of azopolymers containing derivatives of sulfamerazine and studied their photochromic properties. The polymers were obtained from methacrylate azomonomers, butyl methacrylate and isobornyl methacrylate by radical polymerization. Spectral properties and photoisomerization kinetic constants were determined for thin transparent films, using UV-Vis spectroscopy. The maximum absorption of the films was observed at 432-440 nm. The obtained materials showed ability to reversible *trans-cis* photoisomerization. Reversibility of the process was confirmed during ellipsometric measurements. The change of the real part of the complex refractive index induced by laser irradiation was between 0.010 and 0.053. Additionally, some properties of described polymers and azobenzene derivatives were calculated and were utilized in order to better understand the differences in the photochromic behaviour of the new materials. Moreover, we determined the suitability of the obtained azopolymers for spontaneous surface relief grating inscription. Spontaneous surface relief grating recording on the thin azopolymer films was carried out using set-up with one laser beam. The spontaneous SRG was successfully recorded in all investigated polymers.

Keywords: azopolymers; *trans-cis* photoisomerization; surface relief grating

1. Introduction

In the past decade, fast development of nonlinear optics and optoelectronics is observed. The amount of stored and transformed information has rapidly increased and it causes the necessity to create new materials with higher density of information recording [1-3]. Hence, the photoresponsive materials have increasing interest in materials science and technology [4,5]. Among the photoactive materials, the photochromic polymers have a strong position [6]. In almost all of cases, these polymers contain covalently linked derivatives of azobenzene. The chromophores can be built into the main chain or into the side chain of the polymer. It is also possible to form the guest-host systems, where azo dye is randomly dispersed into a polymer matrix without forming the covalent bond between matrix and azo compound. The photochromic polymers have great interest because of their attractive properties and applications in many fields, such as optical data storage [7], holographic memories [8,9], optical switches [10,11] or surface relief gratings [12,13]. Aromatic azo compounds are widely used as dyes, pigments and pH indicators [14,15]. Most of the interesting properties of azopolymers are directly related with the *trans-cis* photoisomerization of the azobenzene units in the polymeric structures [16]. Under light irradiation *trans* isomer undergo a transformation into less stable *cis* isomer. During the thermal relaxation, decline of the *cis*-form and return to the *trans*-form is observed. The thermal relaxation occurs in the dark or under light illumination with the appropriate wavelength. Reversible *trans-cis* photoisomerization induces a number of changes the physicochemical properties of the material [17].

The photochromic groups incorporated in the side chain of polymer create new opportunities for technological applications in optoelectronics as optical information storage devices. Because of the remarkable photochromic properties azopolymers have been the subject of many studies concerning the potential application in data storage and other optical technologies [18,19]. In these kind of polymers, surface relief gratings inscription can be observed at the micrometer scale [20,21]. In the literature, many techniques for the formation of this photoinduced phenomena were described [1, 22-28]. Briefly, SRG can be inscribed on the azopolymer surface by interfering two coherent laser beams of appropriate polarization [3] or by one single beam method [23,25]. Surface grating inscription has been studied since 1990' and published by Tripathy's [29] and Natansohn's group [30].

The possibility and efficiency of SRG inscription depends on structure of azopolymers and their physicochemical properties. Parameters like type of azobenzene compound and its

content, average molecular weight and glass transition temperature have a strong influence on this process. As a general tendency, SRGs are inscribed at room temperature on azobenzene-containing polymers with glass transition temperature in the range of 100-190 °C [31]. In SRG formation process, the average molecular weight of polymers is also important. Generally, the higher molecular weight of polymer causes the lower modulation depth. Due to the increase of viscosity of the polymers with the increasing average molecular weight, the SRG recording is less difficult in the low-molecular weight polymers [32-34]. Moreover, properties of thin films like thickness and homogeneity play an important role in SRG inscription process. A general trend is noticeable: recording SRG in thinner films is possible at shorter exposure and lower intensity of the laser. Furthermore, the depth of inscribed SRG depends on film thickness [22]. It has also been seen that amplitude of modulation increases linearly with time at the beginning of the illumination and reaches saturation at certain depth which depends on the film thickness [33]. The SRG inscription process is related to mass transport phenomenon, thus depends on the mobility of the polymer chains and free volume of the polymer [34,35]. Therefore, polymer physicochemical properties, i.e. viscosity, glass transition temperature and molecular weight plays the key role in SRG formation.

Current investigation shows that materials containing azo derivatives can exhibit the excellent optical properties and photoresponsive variations. The unique photochromic properties are based on the reversible photoinduced *trans-cis* isomerization.

Recently, spontaneous surface relief grating formation was described in numerous papers for various materials containing azobenzene derivatives in their structures. For example, Noga et al. observed the willow structure formation on the surface of supramolecular complex of 4-hydroxy-4'-dimethylaminoazobenzene and poly(4-vinylpyridine) using a single coherent laser beam of linear polarization [36]. In the same year, Mazaheri et al. investigated nucleation and growth of spontaneous surface relief gratings on a Disperse Red 1 (DR1) glass-forming derivative [37]. In another publication, Mazaheri et al. evaluated an influence of temperature on the relaxation kinetics of spontaneous pattern formation in highly photoactive azobenzene copolymer containing heterocyclic sulfonamide moieties [38].

Azobenzene chromophores and polymers containing heterocyclic sulfonamide moieties like sulfamethoxazole, sulfisomidine, sulfamerazine or isoxazole were designed and synthesized in our group [39-44]. These materials have very good optical properties and seem to be promising candidates for novel attractive applications.

Numerous studies were dedicated to various systems of azobenzene derivatives because of their potential applications in many fields. The chromophores were used to obtain a siloxane-

based hybrid organic-inorganic materials [44,45] polyurethane and methacrylic polymers [17,42] the guest-host structures [44,45] or Langmuir-Blodgett films [43]. Moreover, studies of the photochromism, refractive index modulation [40,42], second harmonic generation [46] or nanoobjects formation [47] were carried out. The promising results encourage us to continue the investigation in that field.

In this work, we present the synthesis and characterization of series of novel photoresponsive methacrylic homopolymers and copolymers. Subsequently, these polymers were used for the spontaneous surface relief grating inscription. The polymers were obtained by radical polymerization in presence of AIBN. The azobenzene chromophore were incorporated as a side chain. We investigated the photochromic properties using UV-Vis spectroscopy and ellipsometry and determined relationship between structure of the macromolecular materials and ability to reversible *trans-cis* photoisomerization. The influence of the type of azo-derivatives and non-chromophoric compounds on the photochromic properties was studied. Furthermore, kinetics of *trans-cis* photoisomerization and the thermal relaxation was estimated. This research was also focused on spontaneous SRG formation on azopolymers functionalized with azobenzene derivatives of sulfamerazine. In our study, the one laser beam was used to inscribe spontaneous SRG on the surface of the obtained azopolymer thin films. The surface modulation of polymer thin films was characterized by atomic force microscopy. Moreover, the diffraction efficiency, periodicity and modulation depth were determined.

2. Experimental section

2.1 Materials

Sulfamerazine, 2-(methylphenylamino)ethanol, 2-(N-ethylanylino)ethanol, azobisisobutyronitrile (AIBN, 98%), γ -butyrolactone, CDCl_3 , DMSO- d_6 , methacrylic anhydride, 4-(dimethylamino)pyridine, 4-methoxyphenol were purchased from Aldrich and were used without further purification. Butyl methacrylate and isobornyl methacrylate were purchased from Aldrich and were purified from the inhibitor by washing with a 10% sodium hydroxide aqueous solution and then with deionized water until neutralization. After purification the monomers were dried over anhydrous MgSO_4 . Tetrahydrofuran, pyridine, DMSO, chloroform, sodium nitrite, anhydrous sodium acetate, concentrated hydrochloric acid, glacial acetic acid were purchased from POCH (Poland).

2.2 Synthesis of azo dyes

The azo dyes were synthesized by coupling of the diazonium salt of sulfamerazine with 2-(methylphenylamino)ethanol (SMERm) or 2-(N-ethylamino)ethanol (SMERe). The products were obtained with yields in range of 88-93%. The preparation procedure and characterization details of SMERm and SMERe were described in our previous paper [44]. In our recent work, dye containing derivatives of sulfamerazine was used to form hybrid systems. We observed a high photoactivity of these systems. Moreover, using the obtained sols we succeeded to produce photochromic nanofibers utilizing electrospinning technique. Hence, we used these dyes to obtain the photosensitive monomers and after this the photochromic polymers.

2.3 Synthesis of methacrylic monomers

2.3.1 Synthesis of 2-[N-methyl-4-[(E)-[4-[(4-methylpyrimidin-2-yl)sulfamoyl]phenyl]azo]anilino]ethyl 2-methylprop-2-enoate (M-SMERm)

In a 50 ml flask, 4.3 g (0.01 mol) of 4-[(E)-[4-[N-methyl-(2-hydroxyethyl)amino]phenyl]azo]-N-(4-methylpyrimidin-2-yl)benzenesulfonamide (SMERm), 4-(dimethylamino)pyridine (0.12 g) and 4-methoxyphenol (0.006 g) were dissolved in 20 ml of anhydrous pyridine. Then, methacrylic anhydride (0.013 mol, 2.0 g), was gradually added dropwise. The reaction mixture was purged with nitrogen and heated under reflux for 15 min. Afterward, the resultant mixture was cooled and poured into an excess amount of water. The precipitated product was filtered under vacuum, washed several times with water and dried at 40 °C. The yield of monomer M-SMERm was 95%.

¹HNMR (DMSO-d₆, TMS, ppm): 1,83, s, 3H (-CH₃C=C); 2,33, s, 3H (CH₃ in pyrimidine ring at C2 position); 3,10, s, 3H (CH₃-N-); 3,83, s, 2H (-N-CH₂-); 4,32, t, 2H (-CH₂O-); 5,65, t, 1H (-CH=C); 5,97, s, 1H (-CH=C); 6,90-6,93, m, 3H (CH in pyrimidine ring at C5 position and protons in benzene ring, *ortho* position to amine group); 7,81, d, *J*=8,9 Hz, 2H (protons in benzene ring, *meta* position to amine group); 7,89, d, *J*=8,6 Hz, 2H (protons in benzene ring, *meta* position to N=N group); 8,12, d, *J*=8,5 Hz, 2H (protons in benzene ring, *ortho* position to N=N group); 8,33, d, *J*=5,1 Hz, 1H (CH in pyrimidine ring at C6 position); 12,0, s, 1H (-NH-SO₂).

2.3.1.1 Synthesis of 2-[N-ethyl-4-[(E)-[4-[(4-methylpyrimidin-2-yl)sulfamoyl]phenyl]azo]anilino]ethyl 2-methylprop-2-enoate (M-SMERe)

According to the procedure described in the synthesis of M-SMERm, monomer M-SMERE was obtained. 4.4 g (0.01 mol) of 4-[(E)-[4-[N-ethyl-(2-hydroxyethyl)amino]phenyl]azo]-N-(4-methylpyrimidin-2-yl)benzenesulfonamide (SMERE) was used instead of SMERm. The yield of M-SMERE was 96 %.

^1H NMR (DMSO- d_6 , TMS, ppm): 1,86, s, 3H ((-CH₃)C=C); 2,33, s, 3H, (CH₃ in pyrimidine ring at C2 position); 3,35, s, 2H, (CH₃CH₂N-); 3,52-3,56 (m, 2H, CH₃CH₂N-); 3,77, t, 2H (-N-CH₂-); 4,32, t, 2H, (-CH₂O-); 5,68, s, 1H (-CH=C); 6,02, s, 1H (-CH=C); 6,89-6,93, m, 3H (CH in pyrimidine ring at C5 position and protons in benzene ring, *ortho* position to amine group); 7,79, t, $J=3,4$ Hz, 2H (protons in benzene ring, *meta* position to amine group); 7,89, d, $J=8,4$ Hz, 2H (protons in benzene ring, *meta* position to N=N group); 8,33, d, $J=5,2$ Hz, 2H (protons in benzene ring, *ortho* position to N=N group); 8,58, d, $J=4,2$ Hz, 1H (CH in pyrimidine ring at C6 position); 12,10, s, 1H (-NH-SO₂).

2.4 Synthesis of homopolymers and copolymers

The methacrylate homopolymers and copolymers were obtained by radical polymerization in presence of AIBN. In a 50 ml flask, the initiator (10% by weight towards monomers) and 1.0 g of monomer [and co-monomer in proportions 1/1 (mol/mol) for copolymers] were placed and the air was removed with nitrogen stream. Then, 15 ml of the mixture of solvents: THF/ γ -butyrolactone=7/3 (v/v) was added. The reaction mixture was heated under reflux and nitrogen atmosphere for 72 h. After this time, the mixture was cooled and poured into an excess amount of water. The precipitate was collected by filtration under vacuum, washed with water and dried at 50 °C. The yield of resultant polymers was 85-96 %. The structures of the obtained polymers were confirmed by ^1H NMR.

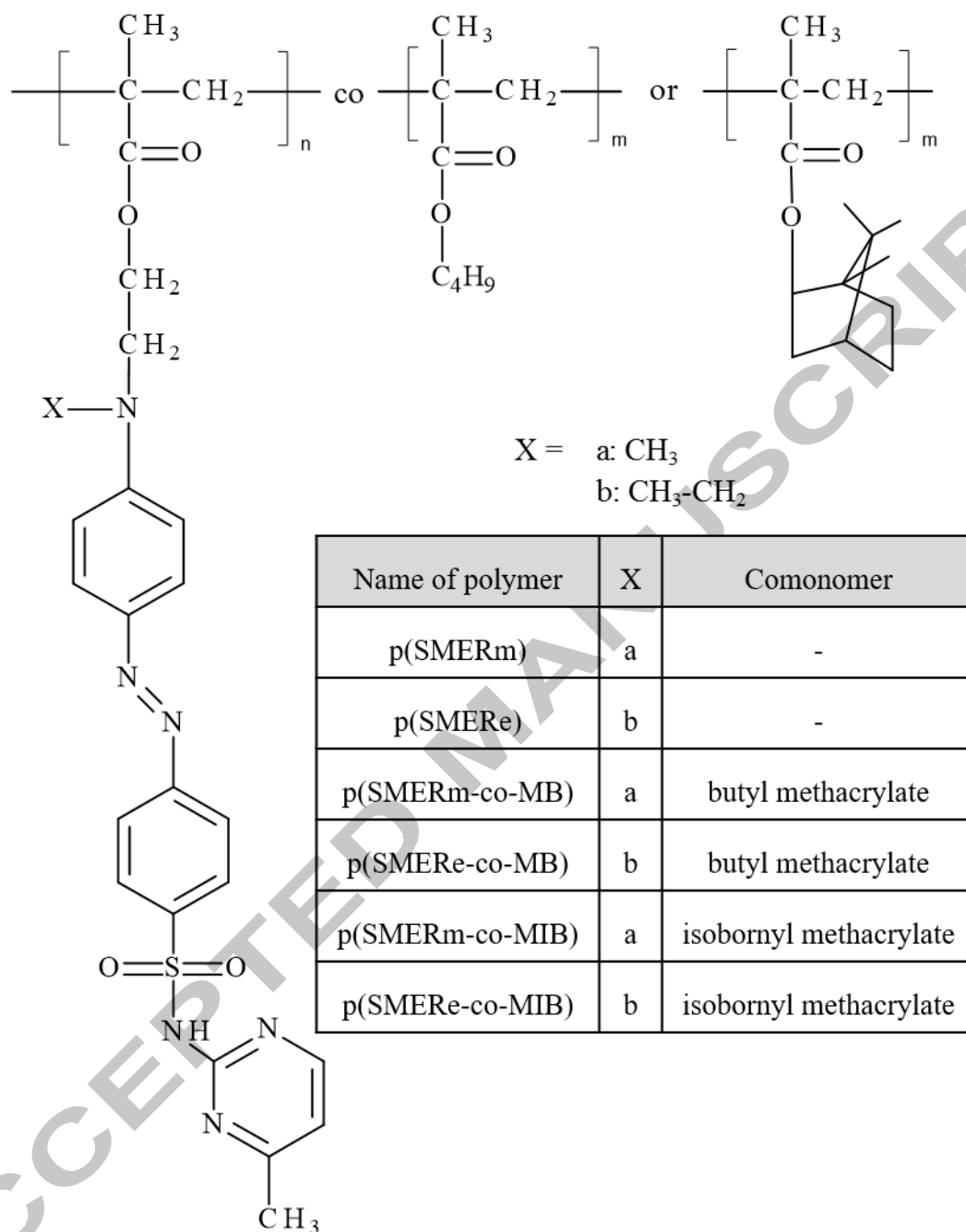


Figure 1. Chemical structure of the synthesized azopolymers.

2.4.1 ¹HNMR analysis of poly(2-[N-methyl-4-[(E)-[4-[(4-methylpyrimidin-2-yl)sulfamoyl]phenyl]azo]anilino]ethyl 2-methylprop-2-enoate), [p(SMERm)]

¹HNMR (DMSO-d₆, TMS, ppm): ~1,45 ((-CH₃)C-C); ~1,70-2,00 (protons in the main chain of polymer); ~2,30 (CH₃ in pyrimidine ring at C2 position); ~3,10 (CH₃N-); ~3,60 (-CH₂N-); ~4,30 (-CH₂O-); ~6,89 (CH in pyrimidine ring at C5 position); ~7,60-8,00 (protons in benzene ring, *ortho* and *meta* position to amine group); ~8,10-8,40 (protons in benzene ring,

ortho and *meta* position to N=N group), ~8,52 (CH in pyrimidine ring at C6 position); ~11,9 (-NH-SO₂).

2.4.2 ¹HNMR analysis of poly(2-[N-ethyl-4-[(E)-[4-[(4-methylpyrimidin-2-yl)sulfamoyl]phenyl]azo]anilino]ethyl 2-methylprop-2-enoate), [p(SMERE)]

¹HNMR (DMSO, TMS, ppm): ~1,13 ((-CH₃)C-C); ~1,90-2,00 (protons in the main chain of polymer); ~2,30 (CH₃ in pyrimidine ring at C2 position); ~3,35, (CH₃CH₂N-); ~3,52-3,56, (CH₃CH₂N-); ~4,20 (-CH₂N-); ~4,30 ppm, (-CH₂O-); ~6,91 (CH in pyrimidine ring at C5 position); ~7,60-7,90 (protons in benzene ring, *ortho* and *meta* position to amine group); ~8,00-8,20 (protons in benzene ring, *ortho* position to N=N group); ~8,30 (protons in benzene ring, *meta* position to N=N group); ~8,59 (CH in pyrimidine ring at C6 position); ~12,0 (-NH-SO₂).

2.4.3 ¹HNMR analysis of poly(2-[N-methyl-4-[(E)-[4-[(4-methylpyrimidin-2-yl)sulfamoyl]phenyl]azo]anilino]ethyl 2-methylprop-2-enoate-co-butyl methacrylate), [p(SMERm-co-MB)]

¹HNMR (CDCl₃, TMS, ppm): ~0,97-1,40 (protons in butyl methacrylate mer); ~1,44 (methylene protons of chromophore mer); ~1,94 (methylene protons of nonchromophore mer); ~2,07 (protons in the main chain of polymer); ~2,45 (CH₃ in pyrimidine ring at C2 position); ~3,15 (CH₃N-); ~4,17, (protons in butyl methacrylate mer); ~4,32 (-N-CH₂-); ~4,40 (-CH₂O-); ~6,84 (CH in pyrimidine ring at C5 position); ~7,89-7,93 (protons in benzene ring, *ortho* and *meta* position to amine group); ~8,25 (protons in benzene ring, *ortho* position to N=N group); ~8,49 (protons in benzene ring, *meta* position to N=N group); ~8,50 (CH in pyrimidine ring at C6 position); ~11,90 (-NH-SO₂).

2.4.4 ¹HNMR analysis of poly(2-[N-ethyl-4-[(E)-[4-[(4-methylpyrimidin-2-yl)sulfamoyl]phenyl]azo]anilino]ethyl 2-methylprop-2-enoate-co-butyl methacrylate), [p(SMERE-co-MB)]

¹HNMR (DMSO, TMS, ppm): ~0,89-1,36 (protons in butyl methacrylate mer); ~1,42 (methylene protons of chromophore mer); ~1,85 (methylene protons of nonchromophore mer); ~1,90-2,01 (protons in the main chain of polymer); ~2,33 (CH₃ in pyrimidine ring at C2 position); ~3,53 (CH₃CH₂N-); ~3,72 (CH₃CH₂N-); ~4,05 (protons in butyl methacrylate mer); ~4,22 (-N-CH₂-); ~4,35 (-CH₂O-); ~6,89 (CH in pyrimidine ring at C5 position); ~7,79-7,89 (protons in benzene ring, *ortho* and *meta* position to amine group); ~8,10-8,12

(protons in benzene ring, *ortho* position to N=N group); ~8,30 (protons in benzene ring, *meta* position to N=N group); ~8,62 (CH in pyrimidine ring at C6 position); ~11,90 (-NH-SO₂).

2.4.5 ¹HNMR analysis of poly(2-[N-methyl-4-[(E)-[4-[(4-methylpyrimidin-2-yl)sulfamoyl]phenyl]azo]anilino]ethyl 2-methylprop-2-enoate-co-isobornyl methacrylate), [p(SMERm-co-MIB)]

¹HNMR (DMSO, TMS, ppm): ~0,81-1,40 (protons in isobornyl methylacrylate mer); ~1,45 (methylene protons of chromophore mer); ~1,77 (methylene protons of nonchromophore mer); ~2,34 (protons in the main chain of polymer); ~2,53 (CH₃ in pyrimidine ring at C2 position); ~3,09 (CH₃N-); ~3,61 (-N-CH₂-); ~4,27 (-CH₂O-); ~6,83 (CH in pyrimidine ring at C5 position); ~7,81-7,90 (protons in benzene ring, *ortho* and *meta* position to amine group); ~8,11 (protons in benzene ring, *ortho* position to N=N group); ~8,32 (protons in benzene ring, *meta* position to N=N group); ~8,50 (CH in pyrimidine ring at C6 position); ~11,80 (-NH-SO₂).

2.4.6 ¹HNMR analysis of poly(2-[N-ethyl-4-[(E)-[4-[(4-methylpyrimidin-2-yl)sulfamoyl]phenyl]azo]anilino]ethyl 2-methylprop-2-enoate-co-isobornyl methacrylate), [p(SMERE-co-MIB)]

¹HNMR (CDCl₃, TMS, ppm): ~0,88-1,39 (protons in isobornyl methylacrylate mer); ~1,57 (methylene protons of chromophore mer); ~1,96 (methylene protons of nonchromophore mer); ~2,11 (protons in the main chain of polymer); ~2,45 (CH₃ in pyrimidine ring at C2 position); ~3,54 (CH₃CH₂N-); ~3,69 (CH₃CH₂N-); ~4,31 (-N-CH₂-); ~4,39 (-CH₂O-); ~6,84 (CH in pyrimidine ring at C5 position); ~7,89-7,92 (protons in benzene ring, *ortho* and *meta* position to amine group); ~8,25 (protons in benzene ring, *ortho* position to N=N group); ~8,48 (protons in benzene ring, *meta* position to N=N group); ~8,60 (CH in pyrimidine ring at C6 position); ~11,90 (-NH-SO₂).

2.5 Azopolymer thin films preparation

Thin films were prepared from the azopolymer solution by spin-coating technique. The synthesized polymers were dissolved in THF (40 mg/1.2 ml), ultrasonicated for 30 min. and filtered through syringe filter. For spin-coating Laurell'sWS-400-B – 6NPP-LITE spin coater was used and the spin-up speed was set at 1200 rpm for 40 s. After deposition the films were dried at 50 °C for 24 h.

2.6 Characterization methods

2.6.1 Computer simulations

For quantum chemical calculations Gaussian 09 software was used [48]. Geometry of repeating units occurring in polymers described in this work was optimized using RHF method and 3-21g basis set. The same method and basis set was used to calculate the first hyperpolarizability of azobenzene-containing molecules, characterizing their nonlinear optical properties. That combination gave very reasonable results in our previous works [41,49]. Materials Studio package was used to calculate selected properties of polymers using Synthia module. The calculations were performed in order to explain better the differences observed between new materials in question.

2.6.2 ^1H NMR spectroscopy

^1H NMR spectra were recorded with a NMR Bruker AvanceTM600 MHz spectrometer using CDCl_3 and DMSO-d_6 as solvent and tetramethylsilane as an internal standard.

2.6.3 Differential scanning calorimetry

Glass transition temperatures of the polymers were determined with a Mettler Toledo 821e DSC apparatus. The heating and cooling rate were 10 K/min.

2.6.4 Average molecular weights

Average molecular weights of the polymers were determined by GPC. The measurements were carried out using azopolymer solutions in DMF with the addition of 5 mmol/L LiBr. Polystyrene standards were used as reference.

2.6.5 UV-Vis spectroscopy

UV-Vis spectra were recorded on HITACHI U-1900 Spectrophotometer. The measurements were carried out for the thin films prepared by spin-coating technique. Before measurements, the samples were stored in the dark at room temperature overnight to ensure that all of the azobenzene units were in the *trans* configuration. The polymer thin films were irradiated with laser beam with 445 nm wavelength.

All measurements were performed at room temperature.

2.6.6 Ellipsometry

Ellipsometric measurements were performed with EL X-02C Ellipsometer, DRE-Dr, Ellipsometerbau GmbH (Germany) operating at an incident angle of 70 °C and using linearly polarized laser beam of 632 nm and ca. 3 mW power.

All measurements were carried out at room temperature.

2.6.7 Thickness measurements

The thickness of the analysed thin polymer films were measured using Dektak 32 Profilometer.

2.6.8 Laser irradiation

A linearly polarized Ar⁺ laser beam at 473 nm and 400mW/cm² power was used as the light source for surface relief grating inscription. All experiments were performed at room temperature under air-ambient conditions.

For *trans-cis* isomerization studies using UV-Vis and ellipsometry the 445 nm laser with 50 mW maximum power was used for illumination.

2.6.9 Atomic Force Microscopy

After samples surface illumination with argon laser during one hour, the AFM observations were performed to characterize surface of the polymer thin films. The microscopic measurements were carried out using Nanoobserver from CS Instruments. The measurements were conducted using Contact mode.

3. Results and discussion

3.1 Synthesis

The methacrylic monomers (M-SMERm or M-SMERE) were used to obtain the photochromic homopolymers or copolymers by radical polymerization. The chemical structures of the synthesized polymers are shown in Figure 1. Obtained polymers contain two types of azobenzene chromophore: 4-[(E)-[4-[methyl(2-hydroxyethyl)amino]phenyl]azo]-N-(4-methylpyrimidin-2-yl)benzenesulfonamide (SMERm) or 4-[(E)-[4-[ethyl(2-hydroxyethyl)amino]phenyl]azo]-N-(4-methylpyrimidin-2-yl)benzenesulfonamide (SMERE) moieties. The copolymers contain butyl methacrylate or isobornyl methacrylate as

nonchromophoric part. All of the methacrylate polymers and copolymers were synthesized with high yields (84-96%) and purity, therefore were used without any further purification. Structures of the investigated polymers were confirmed by $^1\text{H NMR}$ spectroscopy. Series of the synthesized polymers showed signal characteristic for methyl groups in pyrimidine ring (~ 2.30 ppm), methyl and ethyl group at nitrogen atom (~ 3.10 ppm and ~ 3.50 ppm, respectively) and protons at benzene ring ($\sim 7.60 - 8.40$ ppm). Broad multiplets of methylene protons of nonchromophoric mer were visible at $0.80-1.90$ ppm.

Both of the synthesized monomers showed the vinyl proton signals characteristic for protons at C atoms in a double bond ($\text{CH}_2=\text{CH}$) at ~ 5.65 ppm and ~ 6.00 ppm. On spectra recorded for the polymers these signals not occurred. It may be further confirmation that monomers were reacted completely.

The average molecular weights of the obtained materials determined by GPC were between 1200 and 9300. They were rather low indicating that they were oligomers. It is consistent with literature data for similar materials [50-53]. During synthesis, the high content of the initiator was used (10% by weight towards monomers). This may be associated with these obtained results. However, reduction of amount of the initiator could significantly influence the polymerization efficiency. The low degree of polymerization in discussed oligomers strongly affects the measured polydispersity values. For copolymer p(SMERm-co-MIB) which contained isobornyl methacrylate as co-monomer, the molecular weight was the highest and it was 9300. The glass transition temperatures T_g of the obtained polymers were in the range of $70-116$ °C. The T_g of copolymers was lower than that of the homopolymers. These results are consistent with the literature data [54]. The lowest T_g was for copolymer which contained butyl methacrylate as nonchromophoric part. All values of T_g are presented in Table 1. Incorporation of nonchromophoric comonomer enable to modify the physical properties of the obtained materials.

Table 1. Selected properties of the obtained polymers

Polymer	λ_{max}		Absorbance change [%]	Δn_f	Film thickness [nm]	T_g [°C]	M_w [g/mol]	M_w/M_n
	S ^a	F ^b						
p(SMERm)	445	432	25	0.010	484	116	1200	4.7
p(SMERm- co-MB)	448	436	34	0.053	526	70	4500	2.7
p(SMERm- co-MIB)	445	432	21	0.028	468	103	9300	4.3

p(SMERE)	452	436	23	0.013	481	90	1200	5.6
p(SMERE-co-MB)	452	440	31	0.023	526	80	6400	3.9
p(SMERE-co-MIB)	451	436	25	0.031	498	85	4600	3.1

S^a - the azopolymer solution,

F^b - the azopolymer thin film,

Δn_r - change of the real part of complex refractive index

3.2 Computer simulations

The geometry optimization of repeating units present in polymers described in this work was performed using ab initio method RHF and 3-21g basis set. Basic properties derived from geometry optimization and dipole electric field polarizabilities and hyperpolarizabilities calculation results are presented in Table 2. The optimized structures of azobenzene-containing repeating units are shown in Figure 2.

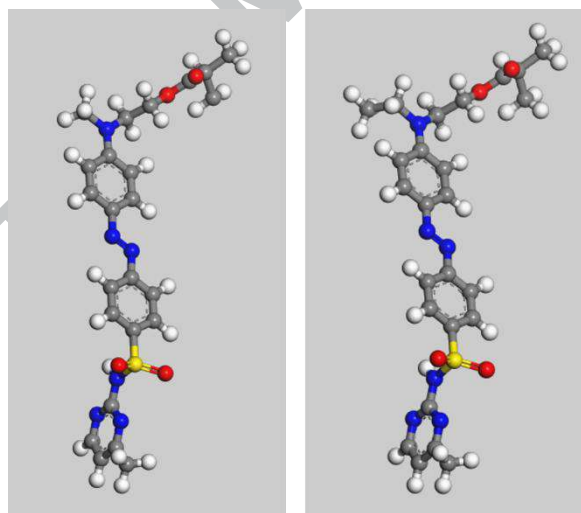


Figure 2. Optimized structures of trans isomers of M-SMERm (left) and M-SMERE (right)

Table 2. Basic properties of trans and cis isomers of sulfamerazine azo derivatives

	mSMERm		mSMERE	
	trans	cis	trans	cis
μ [Cm] $\cdot 10^{30}$	29.9	6.71	30.2	6.92
Molar volume [cm ³ /mol]	379.64	326.47	381.14	296.355

α^0 [$C^2m^2J^{-1}$] $\cdot 10^{40}$	51.5	47.2	53.4	49.1
β^0 [$C^3m^3J^{-2}$] $\cdot 10^{50}$	17.1	6.47	18.2	7.00
ΔHF [kJ/mol]	82.12		82.04	

The calculated values of dipole moments, molar volumes, polarizabilities and first hyperpolarizabilities were similar for both compounds due to the very small difference in their chemical structure. The most distinct differences between trans and cis isomers were observable in case of dipole moment and first hyperpolarizability values.

Additional, physicochemical properties calculated using Synthia module for in Materials Studio package, basing on group additive methods, are presented in Table 3. Properties were determined for the temperature 298 K and the value of molecular weight of homo- and copolymers equal to 10 000 amu.

Table 3. Properties of homopolymers and copolymers determined using Synthia module in Materials Studio software.

Polymer	T_g [$^{\circ}C$]	Coefficient of volumetric thermal expansion [ppm/K]	Density [g/ccm]	C_p of solid at 298K [J/(mol·K)]	Thermal conductivity at 298K [J/(K·m·s)]	Refractive index at 298K	Young's modulus [GPa]
p(SMERm)	82.8	272.5	1.28	579.3	0.159	1.587	8.25
p(SMERm-co-MB)	72.6	280	1.22	397.1	0.156	1.557	5.97
p(SMERm-co-MIB)	87	269.6	1.20	458.1	0.152	1.558	6.35
p(SMERE)	76.1	277.3	1.26	605	0.158	1.583	8.16
p(SMERE-co-MB)	67.7	283.6	1.21	410	0.155	1.555	5.93
p(SMERE-co-MIB)	82.4	272.8	1.19	470.9	0.151	1.556	6.32

3.3 Photoisomerization study

A significant part of this research was focused on investigation of the photoresponsive properties occurring in the obtained materials. For the UV-Vis measurements, the azopolymer thin films and the azopolymer solution in DMSO were prepared.

Before further spectroscopic measurements, the thicknesses of the azopolymer thin films were determined. The thicknesses of the analysed films were comparable and were found to be in the range of 460-530 nm. The summarized results are presented in Table 1.

To ensure that all of the azobenzene units were in the *trans* configuration, the samples were kept in the dark at room temperature overnight. After this, the reversible *trans-cis* photoisomerization of the azobenzene moiety in the synthesized polymers was verified. The maximum absorption band of the synthesized polymers was located in the range of 432-440 nm for the thin films and 445-452 nm for the azopolymer solutions in DMSO (Table 1). The measurements for the thin azopolymer films were carried out before illumination, after laser irradiation and after the thermal relaxation conducted in the dark. Figure 3 shows the UV-Vis spectra of homopolymer p(SMERE) thin film after exposure to the laser beam at 445 nm for different irradiation time. The changes for the other azopolymers are quite similar to these spectra.

Laser irradiation caused the *trans-cis* photoisomerization of the azo group, resulting in a strong decrease in absorbance at ~440 nm. Hence, the change of the absorbance after irradiation with laser was studied. Based on the resulting spectra, the degree of the *trans-cis* photoisomerization was estimated (Table 1). The highest change of absorbance was observed for butyl methacrylate copolymers: p(SMERM-co-MB) and p(SMERE-co-MB) and it was ~30% in the both cases. For homopolymers and copolymers containing isobornyl methacrylate as nonchromophoric comonomer the changes of absorbance were lower (~20-25%). After about 6-10 minutes irradiation (depends on the sample) no spectral changes were observed and the samples reached a photostationary state. After this time, no further significant changes were observed in spectra. The samples were left in the dark and unstable *cis* isomer relaxed thermally to the thermodynamically stable *trans* form.

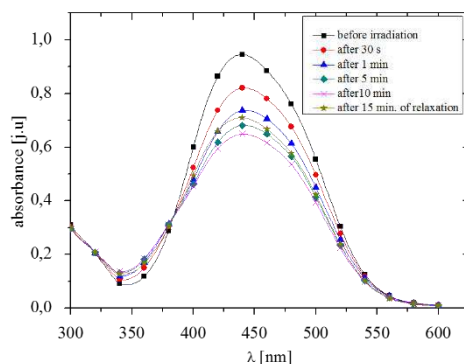


Figure 3. UV-Vis spectral changes of p(SMERE) thin film during irradiation with 445 nm for 0.5, 1, 5, 10 min. and after 15 min. of the thermal relaxation.

Moreover, the kinetics of the *trans-cis* photoisomerization process and the thermal relaxation was studied. According to the exponential equations, the rates of changes in the obtained polymers during the both process were determined. All kinetic parameters are given in Table 4.

Kinetics of the photoinduced *trans-cis* isomerization process could be described by the second-order kinetics expression [49]. The experimental results can be fitted by the following equation (1):

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

where k_1 is the rate constant of the fast reaction step and k_2 is the rate constant of the slow reaction step of the *trans-cis* photoisomerization, α describes the fraction of fast photoisomerization stage in total conversion of the system, A_0 is an initial absorbance (before irradiation), A_{∞} is absorbance in the photostationary state and A_t represents absorbance measured at time t .

Table 4. Kinetic data for *trans-cis* photoisomerization and *cis-trans* thermal relaxation in the dark determined by UV-Vis measurements for the photochromic polymers thin films.

Polymer	Photoisomerization <i>trans-cis</i>					Thermal relaxation	
	A_{∞}/A_0	α	$k_1 \cdot 10^{-3}$ [s ⁻¹]	$1-\alpha$	$k_2 \cdot 10^{-3}$ [s ⁻¹]	α'	$k_1' \cdot 10^{-4}$ [s ⁻¹]
p(SMERM)	0.75	0.73	19.0	0.27	223.2	0.78	1.7

			(±1.1)		(±154.4)		(±0.7)
p(SMERm-co-MB)	0.66	0.61	57.2 (±8.5)	0.39	11.6 (±2.4)	0.82	1.9 (±0.6)
p(SMERm-co-MIB)	0.79	0.49	3.8 (±1.1)	0.51	4.8 (±1.4)	0.84	1.6 (±0.6)
p(SMERE)	0.77	0.45	13.1 (±2.0)	0.55	60.1 (±9.0)	0.75	2.4 (±0.5)
p(SMERE-co-MB)	0.69	0.64	45.8 (±5.2)	0.36	12.0 (±2.1)	0.78	2.0 (±0.8)
p(SMERE-co-MIB)	0.75	0.53	9.9 (±4.0)	0.47	34.4 (±15.7)	0.79	2.6 (±0.4)

For the homopolymers p(SMERm) and p(SMERE) rate constants of the fast reaction step (k_1) of the *trans-cis* isomerization were found to be $19.0 \cdot 10^{-3} \text{ s}^{-1}$ and $13.1 \cdot 10^{-3} \text{ s}^{-1}$, respectively. The kinetic behaviour of the copolymers strongly depends on the type of nonchromophoric comonomer and is comparable for pairs of the copolymers containing the same comonomer. It was interesting that the rate constants of the fast process for copolymers containing butyl methacrylate as comonomer have the highest values ($57.16 \cdot 10^{-3} \text{ s}^{-1}$ for p(SMERm-co-MB) and $45.78 \cdot 10^{-3} \text{ s}^{-1}$ for p(SMERE-co-MB)), while the smallest values are observed for copolymers with isobornyl methacrylate. These results might be caused by limited free volume available in polymer chain, because the free volume around the chromophore plays an important role for the *trans-cis* photoisomerization process. Probably, the chromophore group in butyl methacrylate copolymers have greater freedom to move during isomerization cycle. In turn, the large size of the side groups of isobornyl methacrylate comonomer limits the movements of the azobenzene groups in polymer chain. The molecular movement of the chromophores and the mobility strongly depends on the free volume available around the chromophore molecule [34,55]. The photoisomerization rates exhibited comparable relationship between the two series of polymers described in this work. Surprisingly, the highest photoisomerization rates were observed for homopolymers, possessing the largest values T_g of calculated elastic moduli and densities, as presented in Table 3. The intermediate values were observed for butyl methacrylate copolymers, and the lowest for isobornyl methacrylate copolymers. The photoisomerization rates seems to depend on the average molecular weights of polymers (Table 1). The M_w 's of the homopolymers (more

precisely oligomers) were much lower than those determined for copolymers, what can affect the chromophore moieties mobility.

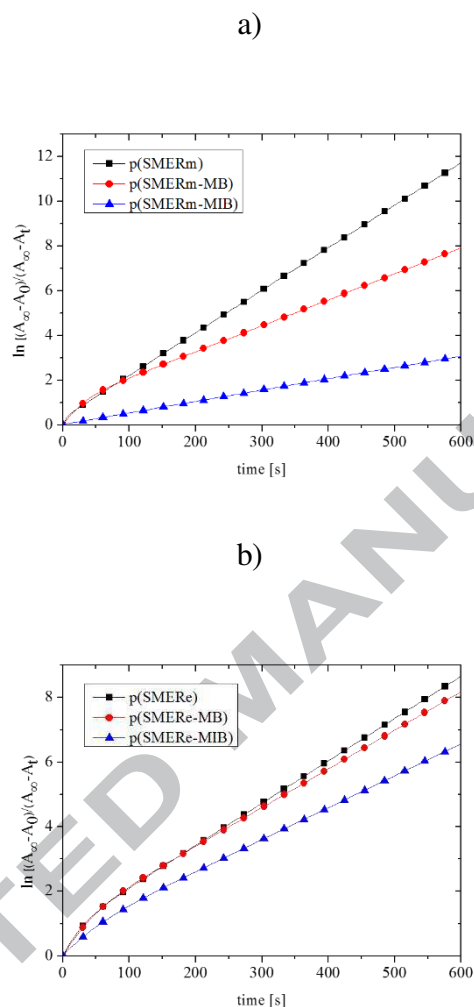


Figure 4. Kinetics of the *trans-cis* photoisomerization induced by illumination with laser: a) polymers containing SMERm azo-derivative b) polymers containing SMERe azo-derivative.

Subsequently, kinetic aspects of the *cis-trans* isomerization of the azo group in the obtained polymers were studied. The thermal relaxation process was analysed by the first-order kinetics expression in equation (2):

$$(A_0 - A_t)/(A_0 - A_\infty) = \alpha' \cdot \exp(-k_1' \cdot t) \quad (2)$$

where k_1 is rate constant related to the *cis-trans* isomerization, α describes the fraction in total conversion of the system, A_0 is an initial absorbance (before irradiation), A_∞ is absorbance in the photostationary state and A_t represents absorbance measured at time t . All investigated

polymers relaxed with a similar rate. Values of rate constants of the thermal relaxation are in the range of $1.6 - 2.6 \cdot 10^{-4} \text{ s}^{-1}$.

In this experiment we observed that the *trans-cis* photoisomerization induced by light illumination is significantly faster process than the thermal relaxation at ambient temperature. These relationship can be explained with the fact that the thermal relaxation process occurs at ambient conditions without any external stimuli. The comparison of kinetics of the thermal relaxation is presented in Figure 5.

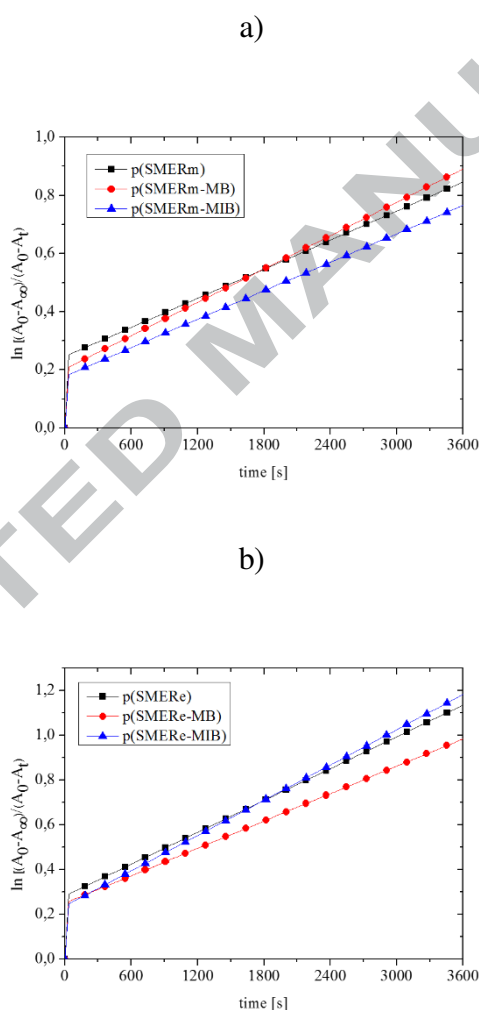


Figure 5. Kinetics of thermal relaxation in the dark: a) polymers containing SMERm azo-derivative, b) polymers containing SMERE azo-derivative.

Afterwards, the ellipsometric investigations were carried out. Ellipsometry is an optical method for measurements of optical parameters of thin layers by evaluation of polarization state of reflected light. Ellipsometry technique enable to determine two parameters: Ψ and Δ .

The Ψ parameter indicates intensity ratio of reflected polarized light and the Δ parameter is defined as phase shift of polarized light. This method made it possible to observe changes of the both parameters during irradiation with laser. These changes are used to calculate refractive index changes of the samples (3):

$$n = n_r + ik \quad (3)$$

where n_r is defined as the real part of refractive index and ik represents imaginary part of refractive index, k is extinction coefficient.

The measurements were performed in a continuous way using the thin photochromic polymer films. All samples were illuminated for the same period of time, this is 3 minutes. After that, the samples were allowed to relax thermally for 6 minutes. The light source used in experiment was laser with wavelength 445 nm and power of 18mW. After sample illumination, significant changes of the both ellipsometric parameters and the real part of refractive index were observed for all materials. Depending on the polymer, the change of refractive index was in the range of 0.010-0.053. The changes of the real part of the complex refractive index are presented in Table 1. Similar changes of both ellipsometric parameters during illumination were observed for all investigated samples. Relationships between change of Ψ and Δ parameters during irradiation are shown in Figure 6 and 7.

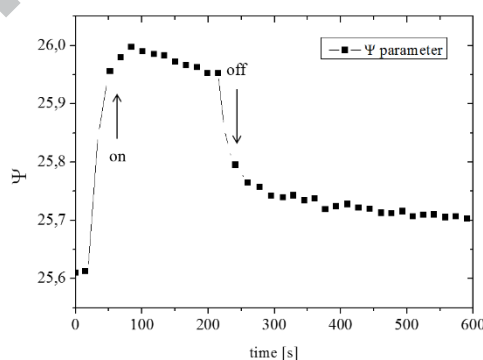


Figure 6. Change of the ellipsometric parameter Ψ of the homopolymer p(SMERE) under irradiation with laser beam ($\lambda = 445\text{nm}$).

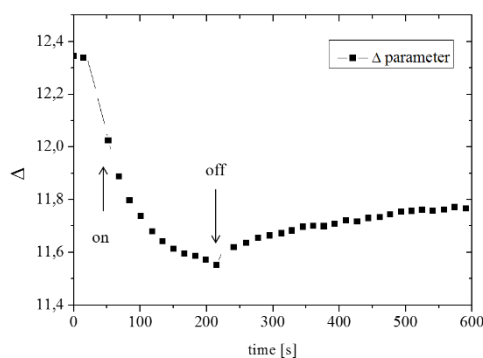


Figure 7. Change of the ellipsometric parameter Δ of the homopolymer p(SMERE) under irradiation with laser beam ($\lambda=445\text{nm}$).

The ellipsometric measurements enabled us to confirm the photochromic properties and ability to *trans-cis* photoisomerization of the azobenzene derivatives in the synthesized polymers.

3.4 Surface Relief Grating formation

The potential use of synthesized polymers as holographic recording materials was examined by surface relief grating formation. The experimental setup uses only one laser beam with controlled polarization in a one-step irradiation process to photoinduce a spontaneous SRG. A linearly polarized Ar^+ laser beam at 473 nm and $400\text{mW}/\text{cm}^2$ power was used as the light source. Each sample of the azopolymer thin film was illuminated for 1 hour. All of the samples were irradiated for the same time. The wavelength of laser beam used for a spontaneous SRG inscription was located in the range of the absorption band of the synthesized polymers.

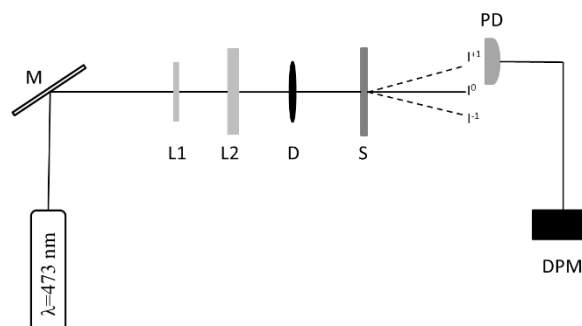
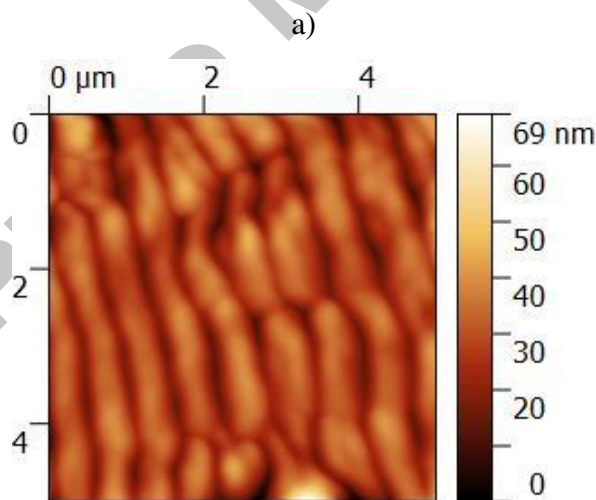
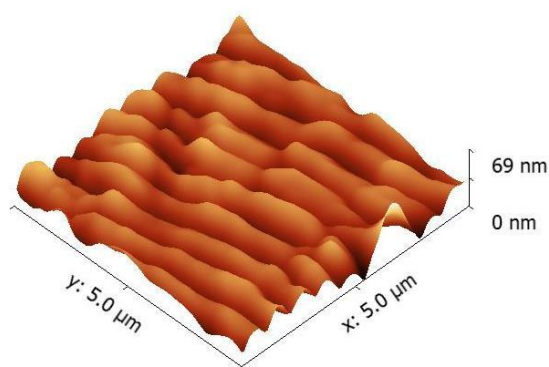


Figure 8. Scheme of the experimental set-up for recording surface relief grating with one beam method: M-mirror, L1, L2 – lenses, D - diaphragm, S - sample, PD - detector, DPM - Digital Power Meter. Recording was conducted with laser $\lambda = 473\text{nm}$.

In all of the investigated polymer films, the surface relief grating was successfully inscribed. The surface profile of the grating of the homopolymer p(SMERE) is shown in Figure 9. The SRGs for the other azopolymers are quite similar to results presented in Figure 9. The parameters of the recorded spontaneous SRG were determined by AFM imaging and are given in Table 5.



b)



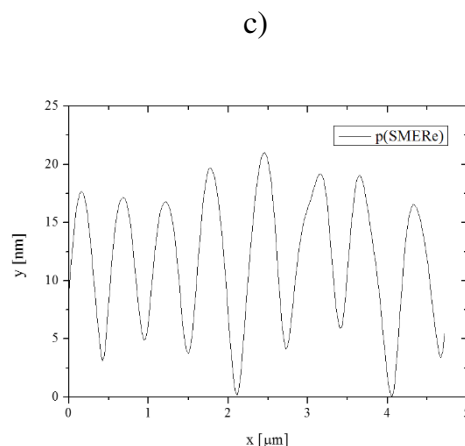


Figure 9. AFM images of homopolymer p(SMERE) film surface a) relief grating, b) three-dimensional view of grating, c) relief grating profile.

We observed that the type of nonchromophoric comonomer plays an important role in the spontaneous SRG formation process. It is related to these physicochemical properties such as molecular weight and glass transition temperature. The characteristic polymer properties for a series of synthesized polymers with azo derivatives of sulfamerazine are summarized in Table 1.

The surface patterns inscribed on the thin films were imaged with an atomic force microscope. After 1 hour recording, we can observe a modulation with an average pitch (periodicity) $\Lambda=475\text{-}900$ nm, depending on the sample. The AFM measurements of the surface gratings show a depth (amplitude) of the modulation in the range of 15-85 nm. The periodicity of patterns depends on the incident angle of the laser beam and can be modified by changing the angle. The period can be estimated following the empirical law:

$$\Lambda = \frac{\lambda}{n_r(1 - \sin(\theta))} \quad (4)$$

where Λ is the period of patterns, n_r is the refractive index of the material, λ is the wavelength and θ describes an incident angle [1,3,25].

According with the above equation, the refractive index influences the period of patterns. Hence, the differences of the periodicity between homopolymers and copolymers were observed. The calculated values of refractive index for homo- and copolymers as well as periods of spontaneous surface relief gratings inscribed on the surface of azopolymer thin films are found to be in good agreement with the empirical equation (4). According to that equation, the grating period is inversely proportional to the refractive index of the material in question. Therefore, for copolymers, in case of which we determined lower values of

refractive index, we observed larger periods of spontaneous surface relief gratings. For homopolymers the results are opposite but still remain in accordance with the equation (4). The experimental conditions (incident angle, wavelength, polarization and intensity of the laser beam) were the same for all the samples.

Moreover, after illumination with laser, experimental diffraction efficiencies η were determined according to the formula [56]:

$$\eta = (I_1/I_0) \cdot 100\% \quad (5)$$

where I_1 is the intensity of the diffracted light in the first order diffraction and I_0 the intensity of the incident light.

As a general tendency, the diffraction efficiencies were higher for copolymers (6-14%) than for homopolymers (2-4%). In case of copolymer p(SMERm-co-MIB) the largest diffraction efficiency was observed (~14%). For copolymer p(SMERE-co-MB) it was only slightly less: ~9%.

In case of surface relief grating inscription we noticed the opposite relationship between the polymer surface modulation depth and the polymer type comparing to results related to photoisomerization kinetics. The polymers susceptibility to laser irradiation in terms of spontaneous SRG inscription efficiency seems to correlate with their properties estimated by computer simulations. The modulation depth was the lowest for homopolymers, which according to the calculated results are the stiffest materials among all other (they have distinctly higher values of density and Young modulus than the copolymers, refer to Table 3). Another interesting difference between homopolymers and copolymers is molar heat capacity, which in case of homopolymers was significantly higher than for copolymers. This property may also affect the material susceptibility to efficient spontaneous SRG formation. The highest modulation depths observed for copolymers containing isobornyl methacrylate can be explained by the advantageous influence of large nonchromophoric side groups, which efficiently separate the chromophore molecules and make them more accessible to laser radiation.

Table 5. Periodicity (Λ) and amplitude (A) of surface modulation and the diffraction efficiency (η) for SRG inscription in the azopolymer thin films.

Polymer	p(SMERm)	p(SMERm-co-MB)	p(SMERm-co-MIB)	p(SMERE)	p(SMERE-co-MB)	p(SMERE-co-MIB)
A [nm]	20	30-55	85	15-25	40	70

Λ [nm]	475	785	865	525	890	900
η [%]	4.3	6.4	13.9	2.1	8.5	2.1

4. Conclusion

In summary, a series of novel photochromic polymers containing azo derivatives of sulfamerazine have been successfully synthesized and characterized. All polymers were obtained with satisfactory yields exceeding 85%. Furthermore, their photoisomerization and holographic behaviour was reported. Obtained polymer materials containing chromophores were irradiated with laser with a wavelength within the absorption band, leads to a *trans-cis* isomerization of the dye molecules. All of the obtained polymers exhibited similar photoresponsive behaviour. The reversible *trans-cis* photoisomerization of all investigated polymers was monitored by UV-Vis spectroscopy. Moreover, based on UV-Vis measurements, the kinetic study was carried out. Photoisomerization of the azobenzene derivatives chromophores was reversible in all investigated materials. The observation of this phenomenon in ellipsometric measurements confirmed photochromic properties of the synthesized polymers. The determined change of refractive index during illumination with laser was in the range of 0.010-0.053. All of the measured azopolymer thin films exhibited an ability to form surface relief gratings upon irradiation with one laser beam with 473 nm wavelength. Spontaneous SRGs were formed on the polymer films by irradiating linearly polarized Ar⁺ laser for 1 hour. Surface relief gratings have been inscribed on polymer films at identical recording conditions. In all cases spontaneous SRGs were formed successful and characterized by regular sinusoidal surface modulation. Depends on the polymer, the diffraction efficiency was in the range of 2.1-13.9%. Based on these preliminary results, we suppose that this kind of the photoresponsive materials may find the potential applications in photonics for information recording by holographic procedures. However, further investigation will be carried out.

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Materials Studio software was utilized within the Biovia Polish Country WideLicense.

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1. A series of highly photoactive polymers containing azo derivatives of sulfamerazine was described.
2. Photoisomerization behavior has been extensively studied in thin azopolymer films.
3. The synthesized polymers show an ability to self-organize into regular, periodical surface relief structures during illumination with single laser beam.
4. The new computational approach to explain the polymers behavior under illumination was also proposed.

Graphical abstract

