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Kinetics of Refractive Index Changes in Polymeric Photochromic Films

*Ewelina Ortyl, Stanisław Kucharski**

Institute of Organic and Polymer Technology, Technical University of Wrocław,
50-370 Wrocław, Poland
E-mail: kucharski@itots.ch.pwr.wroc.pl

Summary: Methacrylate copolymers containing, in side chain azobenzene groupings with heterocyclic sulfonamide substituents: *N*-(2,6-dimethylpyrimidin-4-yl)sulfamoyl (sulfisomidine) and *N*-(5-methylisoxazol-3-yl) sulfamoyl (sulfamethoxazole) were investigated. The materials undergo reversible *trans-cis* isomerisation during illumination with light. This results in changes of dipole moment, polarizability and refractive index. Ellipsometric measurements showed a distinct decreasing refractive index during illumination with light corresponding to absorption band (*ca.* 450 nm). Depending on the polymer, the change of real part of refractive index in spin-coated films was between 0.016 and 0.031. The dynamics of growth and decay of refractive index changes, was described by biexponential function approach.

Keywords: azobenzene polymers; ellipsometry; photochromic polymers; refractive index modulation; *trans-cis* isomerisation

Introduction

Polymers containing the azobenzene moiety in side chain or built in the main chain have been attracting much attention as active materials in optical data storage and holographic applications [1]. The ability of the azobenzene grouping to reversibly *trans-cis* (or E-Z) izomerize has been known for a long time and described in numerous papers [2-4]. Under illumination with visible or UV light, corresponding to the maximum of absorption band, the more stable *trans* form undergoes transformation to the less stable *cis* form. The reverse *cis-trans* reaction takes place as a thermal relaxation and is relatively slow. The photoisomerisation of the azobenzene grouping is particularly interesting because its consequence is a change of refractive index.

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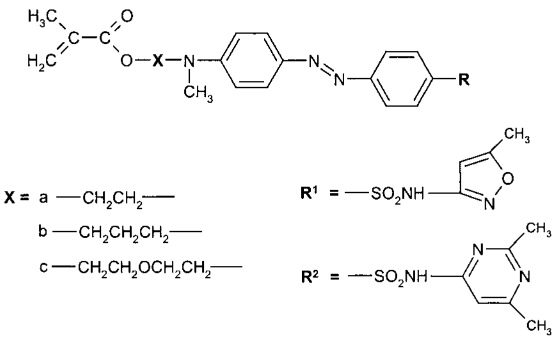

CODE	X	R
MET-1	a	R^1
MET-2	b	R^1
MET-3	c	R^1
IZO-1	a	R^2
IZO-2	b	R^2
IZO-3	c	R^2

Fig. 1. Chromophoric monomers.

Results and discussion

We calculated changes of some molecular properties which take place under light irradiation of chromophoric monomers (Fig. 1). Syntheses of monomers were described previously [5]. We started with optimization of geometrical structures of the isolated molecules of the compounds with GAUSSIAN 98 [6] program using *ab initio* RHF (restricted Hartree-Fock) options with a split-valence 3-21G basis set. The optimized geometry was used to calculate dipole moment (μ), static polarizability (α^0) and first hyperpolarizability (β^0), for both *trans* and *cis* form of the monomers, and potential energy difference, ΔE, between them (Table 1). For both sulfisomidine and sulfamethoxazole azobenzene derivatives the values of μ, α^0 and β^0 were higher for *trans* form. The differences between dipole moments of *cis* and *trans* isomers increased with increasing length of the aliphatic spacer joining nitrogen atom with methacryloyl group. For monomer IZO-3, which has the longest spacer, the dipole moment difference was the highest, 6.41 D. This difference was considerably lower for monomers with short spacers, IZO-1 and MET-1, 1.88 D and 4.69 D, respectively. In both homologous series of monomers, the decrease in static polarizability and first hyperpolarizability was more pronounced with increasing length of spacer. The differences in potential energy, ΔE, between *trans* and *cis* form of the compounds also increase with increasing length of aliphatic spacer. For IZO-3 monomer, ΔE has the highest value equal to 104.6 kJ/mol.

Table 1. Dipole moments, polarizability, first hyperpolarizability and potential energy difference (ΔE) of the *trans* and *cis* structures calculated by GAUSSIAN.

Compound	μ (D)		$\alpha^0 \times 10^{24}$ (cm^3)		$\beta^0 \times 10^{30}$ (esu)		ΔE (kJ/mol)
	cis	trans	cis	trans	cis	trans	
IZO-1	8.34	10.22	43.12	47.02	10.17	40.80	64.27
IZO-2	5.25	10.58	43.85	49.65	3.88	49.27	92.18
IZO-3	3.98	10.39	45.40	51.65	3.39	52.65	104.61
MET-1	5.52	10.21	40.40	43.92	13.94	45.29	81.23
MET-2	4.24	8.79	41.39	46.42	10.46	53.49	81.58
MET-3	3.73	9.22	41.92	48.21	2.42	50.83	92.45

One of the consequences of the *trans-cis* isomerisation of the azobenzene grouping is the refractive index change. But investigation of these photoinduced phenomena is not easy as there is a problem with isolation of the pure form of *cis* isomer, which is unstable at room temperature, where the measurements are usually carried out. For these reasons we calculated refractive indices for the isolated molecules of their pure *trans* and *cis* forms. We utilized two models, which relate the index of refraction to the polarizability of the molecule [7-9].

In the first model we used the transformated Lorentz-Lorenz equation (Eq. 1):

$$n(\omega) = \sqrt{\frac{3 + 8\pi N\alpha(\omega)}{3 - 4\pi N\alpha(\omega)}} \tag{1}$$

Equation (1) may be approximated by the Lorenz form. In the second model we used the Lorenz expression (2):

$$n(\omega) = \sqrt{1 + 4\pi N\alpha(\omega)} \tag{2}$$

In both equations (1) and (2), N is average number of molecules per unit volume and $\alpha(\omega)$ is the isotropic average polarizability of the isolated molecule, is equal to $^1/_3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$. The volume occupied by an isolated molecule was calculated using Cerius2 program. The values of refractive indices calculated according to Eq. (1) and (2) and differences between both isomers (Δn) are given in Table 2. The most interesting for us were the values of Δn. The highest value of Δn was observed for IZO-3 monomer which was 0.0392.

Table 2. Refractive indices and refractive index changes calculated utilizing two models: Lorenz and Lorentz-Lorenz.

Comp.	Molecule volume (Å^3)		n Lorenz		Δn Lorenz	n Lorentz-Lorenz		Δn Lorentz-Lorenz
	cis	trans	cis	trans		cis	trans	
IZO-1	627.53	639.37	1.3649	1.3870	0.0221	1.4871	1.5280	0.0409
IZO-2	652.42	668.88	1.3580	1.3901	0.0321	1.4748	1.5338	0.059
IZO-3	686.3	691.3	1.3531	1.3923	0.0392	1.4659	1.5381	0.0722
MET-1	551.01	558.48	1.3860	1.4099	0.0239	1.5261	1.5724	0.0463
MET-2	581.53	582.12	1.3762	1.4148	0.0386	1.5078	1.5823	0.0745
MET-3	602.35	616.98	1.3690	1.4076	0.0386	1.4945	1.5680	0.0735

Our aim was to compare the calculated refractive index change for monomers with the measured ones for polymers containing the same chromophoric groups. We used ellipsometry for the determination of film thicknesses and refractive index changes during illumination. Ellipsometry measurement yields two quantities Δ and Ψ, which are sensitive to optical parameters of the sample [10]. From the measured values, it is possible to calculate the complex dielectric function expressed by complex refractive index (3):

$$n = n_\mathrm{r} + \mathrm{i}k \tag{3}$$

The refractive index change, Δn_r, we calculated according to equation (4):

$$\Delta n_\mathrm{r} = n_\mathrm{r}^0 - n_\mathrm{r}^{\mathrm{photostat.}} \tag{4}$$

where n_r^0 is the real part of complex refractive index (3) measured before illumination with light and $n_\mathrm{r}^{\mathrm{photostat.}}$ is the real part of the refractive index measured in the photostationary state. Natansohn *et* al. have observed a biexponential kinetic process in their azobenzene systems [11]. We have found that biexponential functions also well describe the dynamics of growth and decay of refractive index changes in our polymers.

The biexponential functions are

$$\Delta n_\mathrm{r} = A\{1-\exp(-k_\mathrm{a}t)\} + B\{1-\exp(-k_\mathrm{b}t)\} \tag{5}$$

for photoinducing, and

$$\Delta n_\mathrm{r} = C\exp(-k_\mathrm{c}t) + D\exp(-k_\mathrm{d}t) + E \tag{6}$$

for the relaxation process in the absence of illumination. In Eqs. (5) and (6) Δn_r is the change of real part of refractive index observed at time t; k_a, k_b, k_c and k_d represent the rate constants with the amplitudes of A, B, C and D respectively. E is the fraction of refractive index modulation conserved for a long time. All values of the constants are given in Tables 3a and 3b. The rate constants of the fast-growth process and stability of the photoinduced refractive index changes (E) depend on the kind of chromophore side group as well as on the kind of the comonomer used: butyl 2-methacrylate (MB) and 2-ethylhexyl acrylate (AI).

But for IZO-3/20MB polymer the refractive index change, Δn_r, was the highest (0.031).

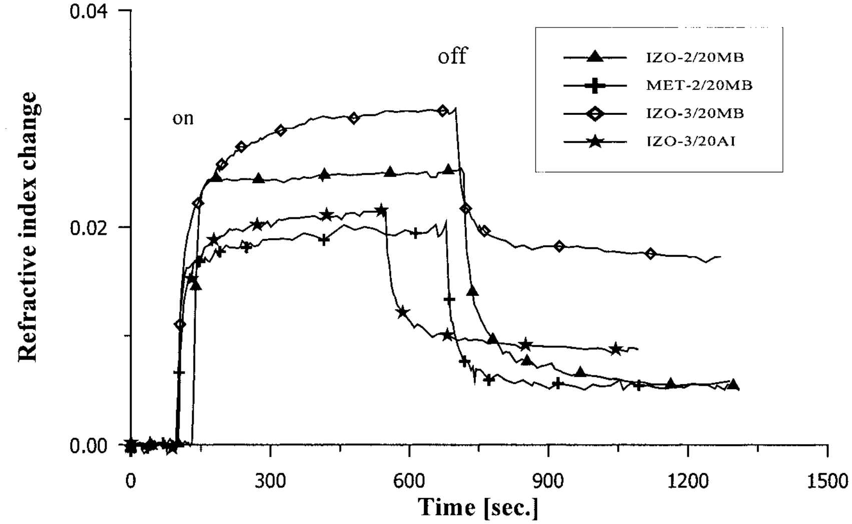

Fig. 2. Typical growth and decay processes of photoinduced refractive index modulation. The light source used for sample illumination was white light of ca. 2 mW cm^{-2} power (from 410 nm on).

Table 3a. Kinetic data for the photoinduced refractive index modulation – growth process.

Polymer	A	k_a	B	k_b	Δn_r
IZO-3/20MB	0.0180	0.0875	0.0127	0.0103	0.031
IZO-3/20AI	0.0176	0.085	0.0036	0.007	0.021
IZO-2/20MB	0.0225	0.085	0.0026	0.007	0.025
MET-2/20MB	0.0168	0.085	0.003	0.006	0.020
MET-3/20AI	0.0144	0.1308	0.0015	0.001	0.016

Table 3b. Kinetic data for the photoinduced refractive index modulation – decay process.

Polymer	C	k_c	D	k_d	E
IZO-3/20MB	0.00842	0.1476	0.00492	0.01436	0.01751
IZO-3/20AI	0.0085	0.1180	0.0041	0.0093	0.0087
IZO-2/20MB	0.01125	0.09444	0.00773	0.00924	0.00541
MET-2/20MB	0.00746	0.2305	0.00748	0.02800	0.00544
MET-3/20AI	0.01417	0.05467	0.00083	0.01347	0.00178

Conclusions

The methacrylate polymers containing azobenzene grouping with sulfonamide substituents in side chains undergo a reversible *trans-cis* isomerisation during illumination with light corresponding to their maximum absorption band. This photoinduced transformation results in change of physicochemical properties of materials, such as refractive index.

The observed decrease in refractive indices of polymers during illumination was in fair agreement with the values calculated for monomers. The refractive index modulation, Δn_r, measured by ellipsometry was in the range of ca. 0.016 – 0.031. Biexponential functions well described the kinetics of refractive index change in these polymers: they give good fits to the growth curves as well as to the relaxation ones.

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