

KINETICS OF REFRACTIVE INDEX MODULATION IN POLYMERIC PHOTOCHROMIC FILMS

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INTRODUCTION

Incorporating photochromic molecules, such as azobenzene or other chromophores, into organic systems leads to photoresponsive materials, the properties of which can be manipulated by light [1]. Methacrylate polymers and copolymers containing azobenzene fragments in side chains are intensively investigated with hope for their potential application as active materials in information storage devices: optical data storage and holographic applications [2].

The key physical process involved in this phenomena is the ability of azobenzene molecules to reversible trans-cis (or E-Z) photoisomerisation. Under illumination with visible or UV-light, corresponding to maximum absorption band, more stable trans form undergoes transformation to the cis form, which is less stable. Thermal relaxation usually causes reverse transformation from cis to trans form [3].

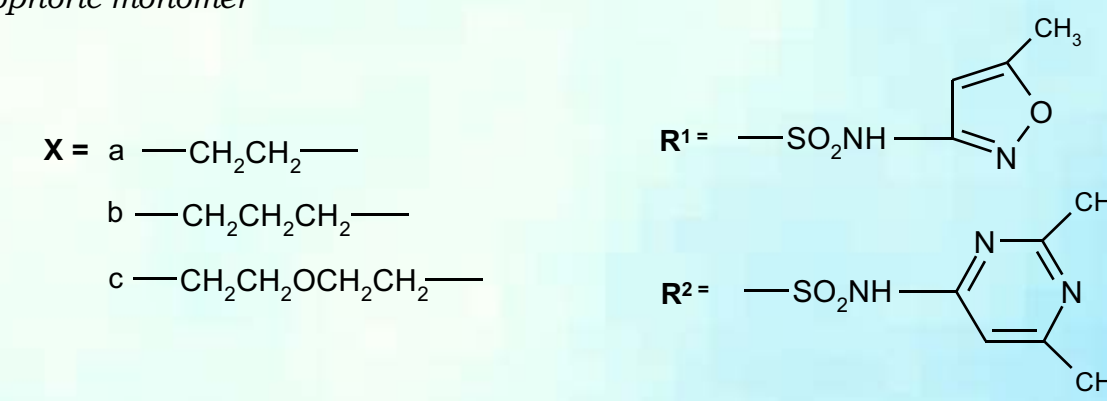
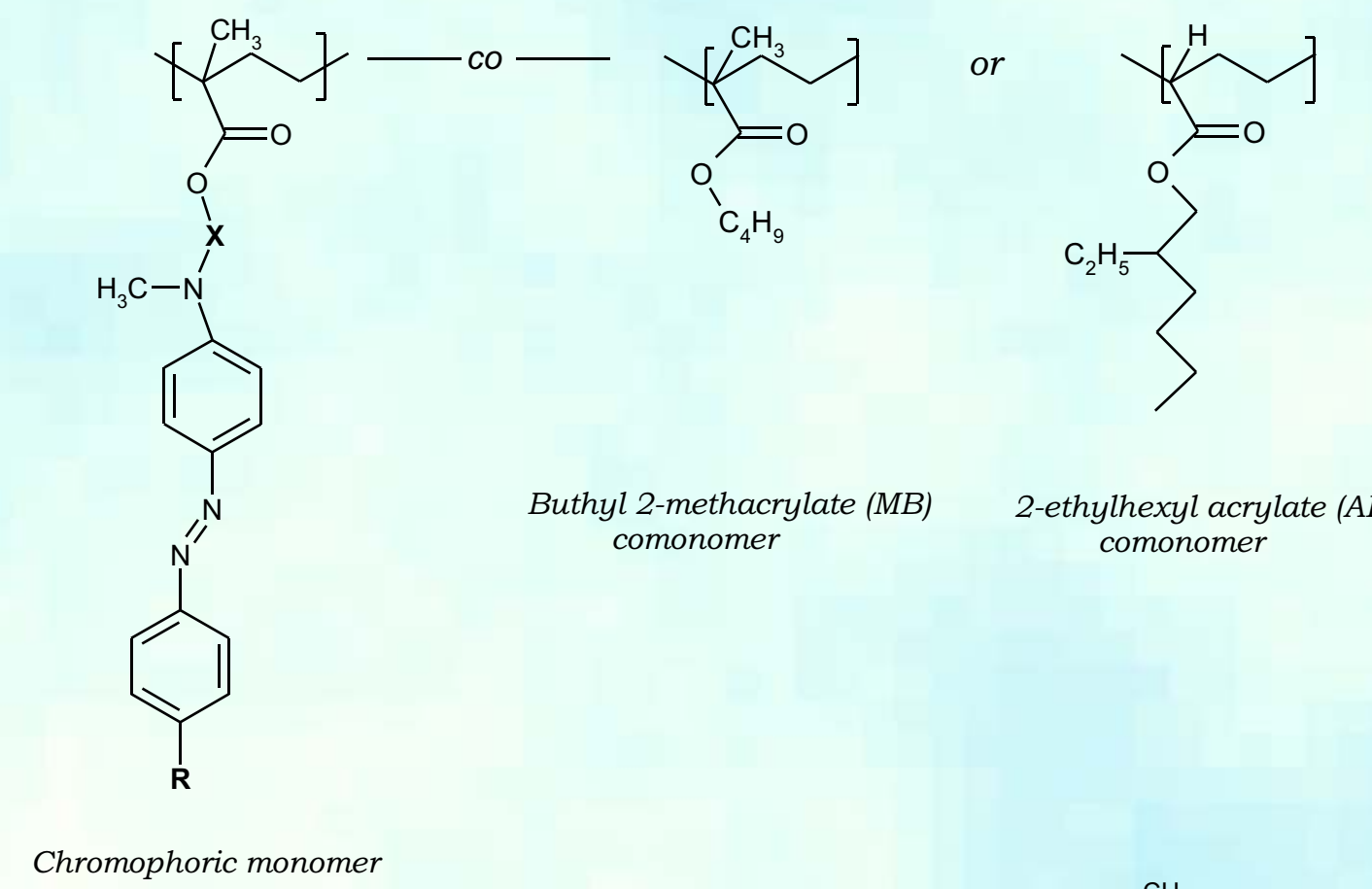
During the photoisomerisation the change of absorption spectra of molecule is observed. Besides, trans-cis isomerisation of azobenzene derivatives results in changes of geometrical structure and physicochemical properties of materials such as: dipole moment, dielectric permittivity and refractive index. Just these changes of molecular properties, and especially that called refractive index modulation, are of particular interests for practical applications in various photonic devices.

We present differences between trans and cis form and relationship between structure and photochromic properties of methacrylate chromophoric monomers containing azobenzene groups with heterocyclic sulfonamide substituents: 4-amino-N-[2,6-dimethylpyrimidin-4-yl]-benzenesulfonamide and 4-amino-N-[5-methylisoxazol-3-yl]-benzenesulfonamide, and polymers with these chromophoric groups in side-chain.

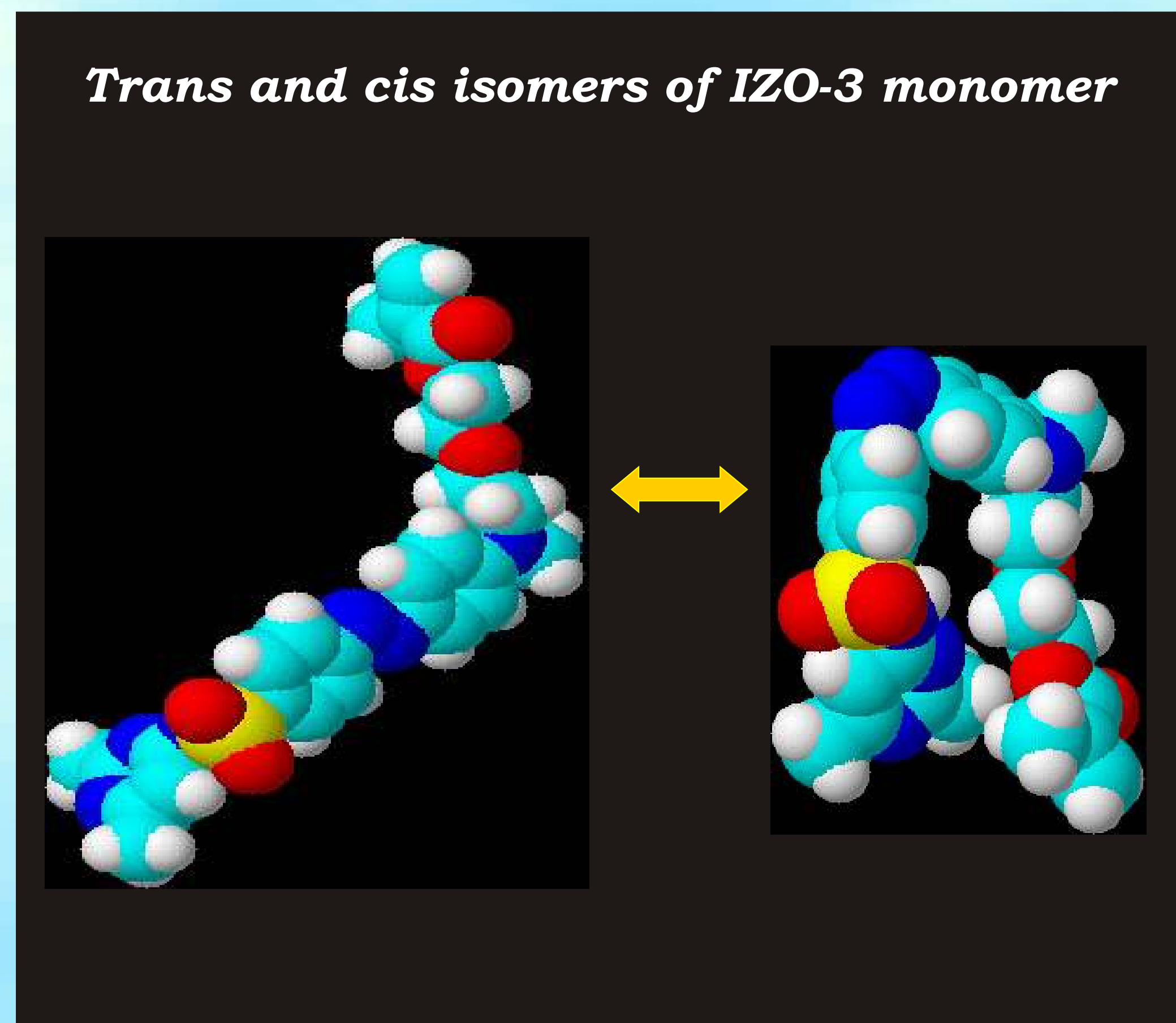
The polymers were prepared by free radical polymerizations of the corresponding chromophoric monomers and comonomers: butyl 2-methacrylate (MB) and 2-ethylhexyl acrylate (A) in the presence of AIBN as an initiator [4].

We used quantum chemical methods to calculate: dipole moment, polarizability, potential energy, UV spectrum and refractive index changes during photoirradiation. We also evaluated kinetics of refractive index changes under influence of light in homopolymer and copolymers containing above-mentioned chromophores. Our aim was to find a reference of calculated refractive index changes for monomers with measured ones for polymers containing the same chromophore groups.

CHEMICAL FORMULAS OF POLYMERS

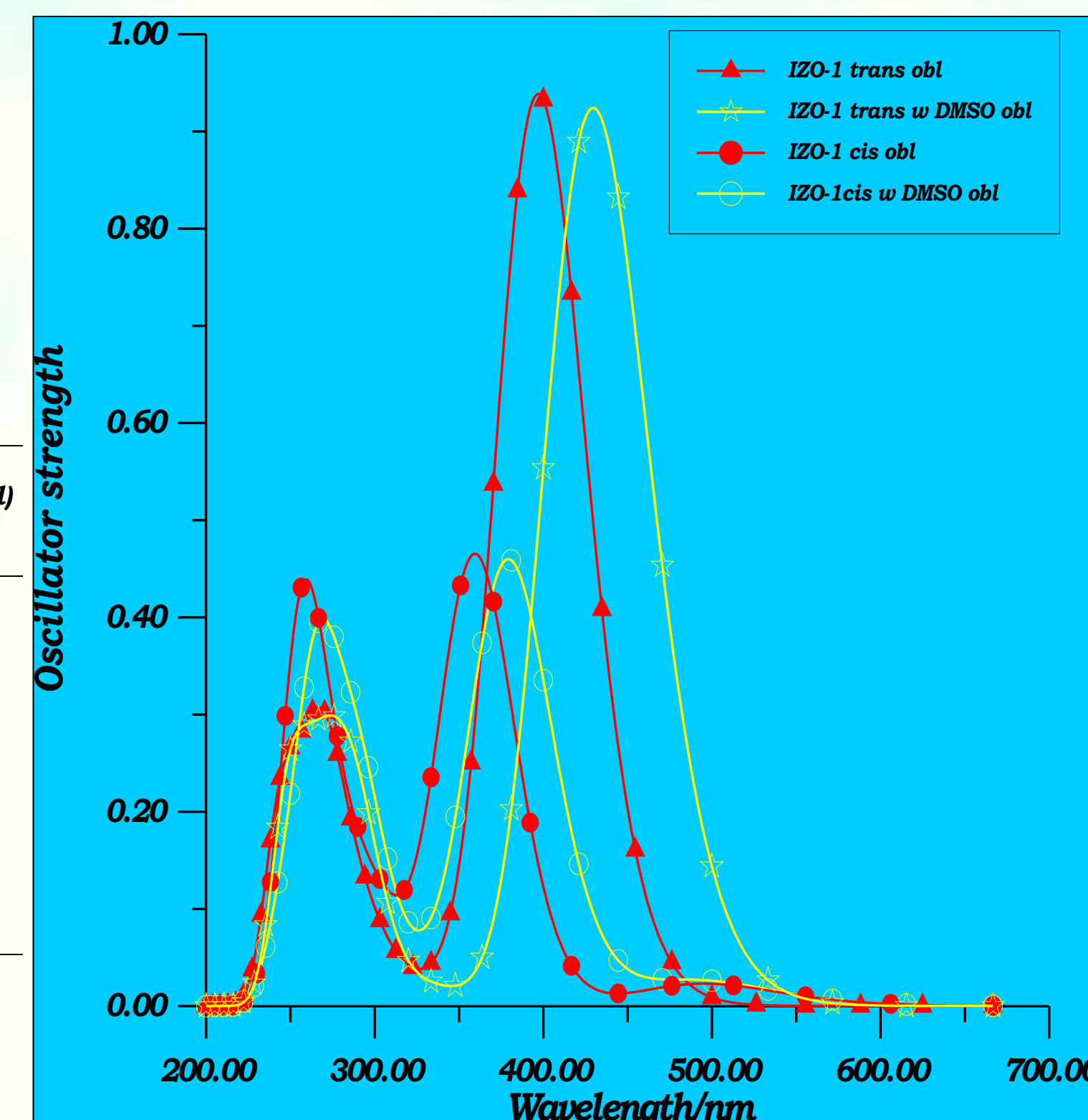


SYMBOL	X	R
MET-1	a	R ¹⁺
MET-2	b	R ¹⁺
MET-3	c	R ¹⁺
IZO-1	a	R ²⁺
IZO-2	b	R ²⁺
IZO-3	c	R ²⁺



The calculated UV-VIS spectra of IZO-1 compound for the isolated molecule and that in solution for pure trans and cis forms.

The agreement between measured and calculated spectra is relatively good.



The dipole moment, polarizability, first hyperpolarizability and potential energy differences

We calculated dipole moment (μ), polarizability (α) and first hyperpolarizability (β^0), for both trans and cis form of the chromophoric monomers in their pure forms, and potential energy difference (ΔE) between them to show changes which take place under light influence.

Compound	$\mu / 10^{-30}$ (C m)		$\alpha / 10^{24}$ (cm ³)		$\beta^0 / 10^{-30}$ (esu)		ΔE (kJ/mol)
	cis	trans	cis	trans	cis	trans	
IZO-1	27.84	34.10	43.12	47.02	10.17	40.80	64.27
IZO-2	17.53	35.29	43.85	49.65	3.88	49.27	92.18
IZO-3	13.28	34.65	45.40	51.65	3.39	52.65	104.61
MET-1	18.43	34.06	40.40	43.92	13.94	45.29	81.23
MET-2	14.14	29.31	41.39	46.42	10.46	53.49	81.58
MET-3	12.43	30.77	41.92	48.21	2.42	50.83	92.45

Calculation of refractive index changes

We calculated the refractive indices utilizing two different models. Both of them relate the index of refraction to the polarizability of the molecule [5]. In the first model we used the transformed Lorentz-Lorenz equation:

$$n(\omega) = \sqrt{\frac{3 + 8pNa(\omega)}{3 - 4pNa(\omega)}}$$

This is the optical analog of the Clausius-Mossotti equation, which relates the low-frequency dielectric function to the polarizability. The Lorentz - Lorenz relation may be approximated with Lorentz form. So in the second model we used Lorentz expression:

$$n(\omega) = \sqrt{1 + 4pNa(\omega)}$$

where: N is average number of molecules per unit volume and $a(\omega)$ is the mean polarizability of the isolated molecule and is equal to $1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$. Volume occupied by isolated molecule was calculated using Cerius2 program.

Monomer	Volume/molecule (Å ³)		n Lorentz		Δn Lorentz	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

KINETICS OF REFRACTIVE INDEX MODULATION

Kinetics of the refractive index modulation during light illumination we monitored by ellipsometry.

In our experiments the measurements were carried out using a linearly polarized laser beam of 632 nm and ca. 3 mW power (standard equipment of the ellipsometer). Thin films of the polymers were obtained by dissolving the samples in THF (2-2.5%) and then spin-coated onto clear glass plates. Thickness of the polymeric films, measured by ellipsometry, was ca. 300-400 nm. The light source used for sample illumination was white light of ca. 2mW cm⁻² power (from 410 nm on).

Ellipsometric measurement yields two quantities, D and Ψ , which are sensitive to the optical parameters of the sample [6]. From these measured values it is possible to calculate the film thickness and complex dielectric function expressed by complex refractive index:

$$n = n_r + ik$$

The refractive index change, Δn_r , was calculated according to equation:

$$\Delta n_r = n_r^0 - n_r^{photostat}$$

where n_r^0 is the real part of refractive index measured before illumination with light and $n_r^{photostat}$ is the real part of refractive index measured at photostationary state.

We have found that biexponential functions well describe the dynamics of growth and decay of refractive index changes in our polymers. The biexponential functions are:

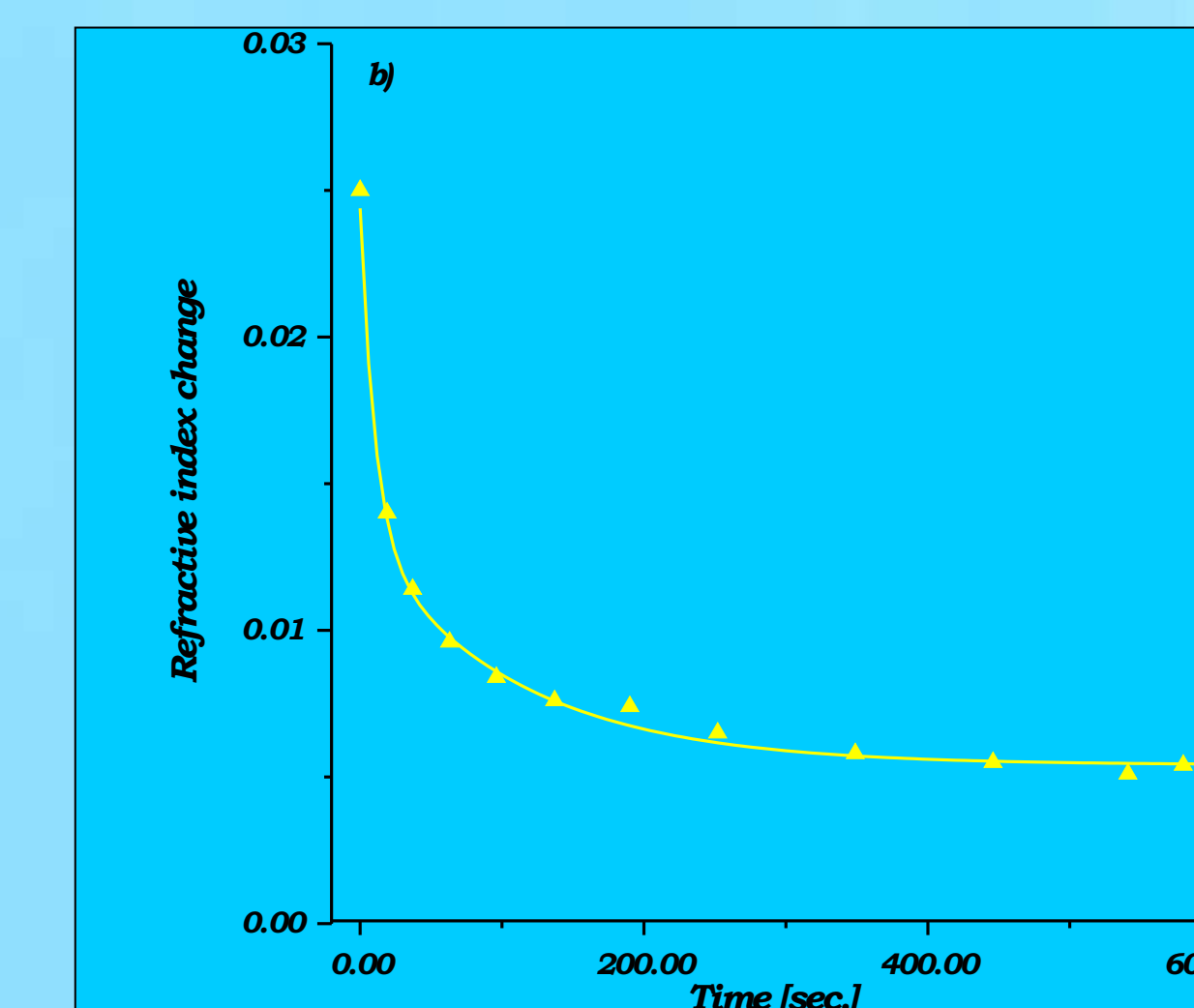
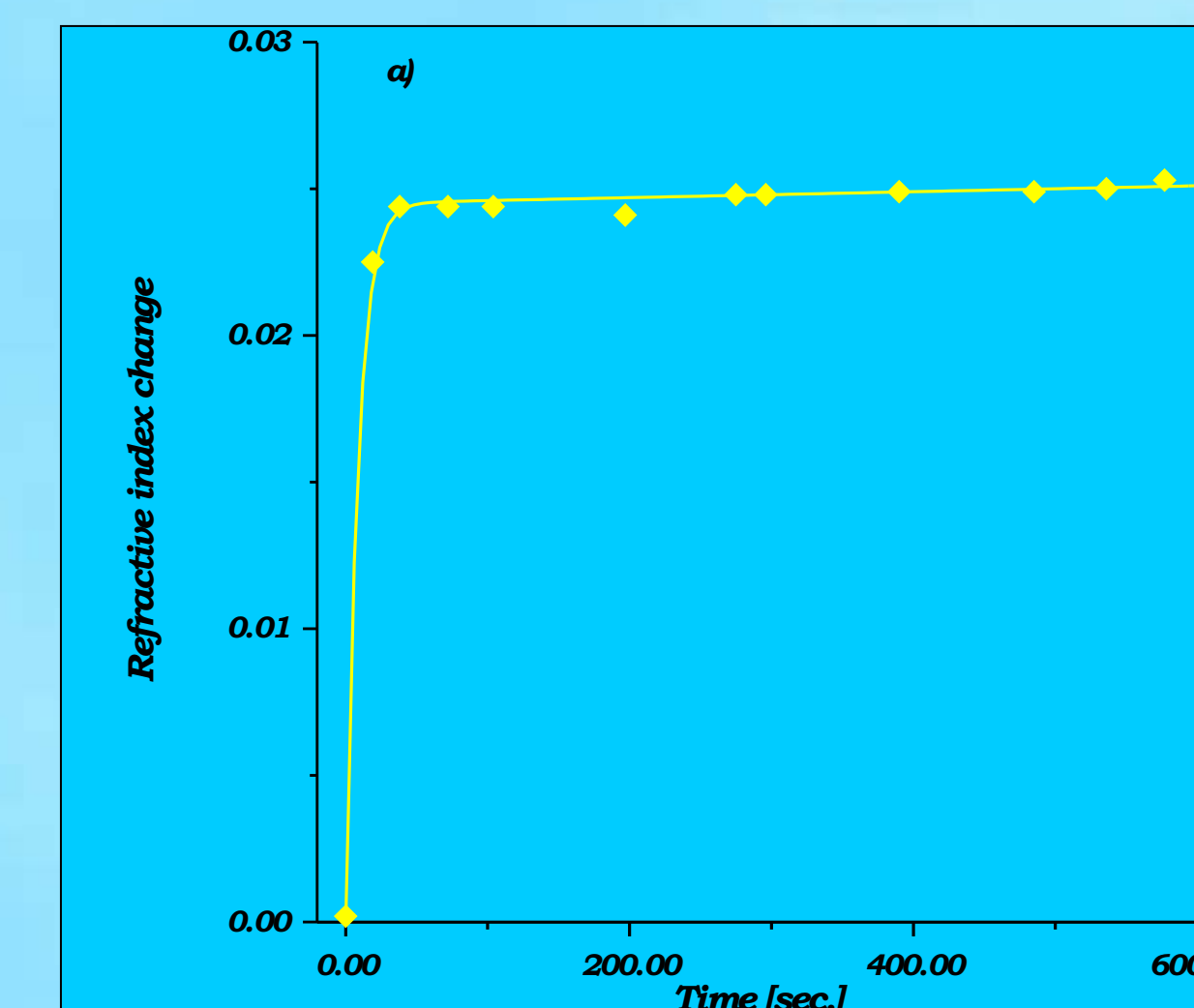
$$\Delta n_r = A\{1 - \exp(-k_a t)\} + B\{1 - \exp(-k_b t)\}$$

for photoinducing and:

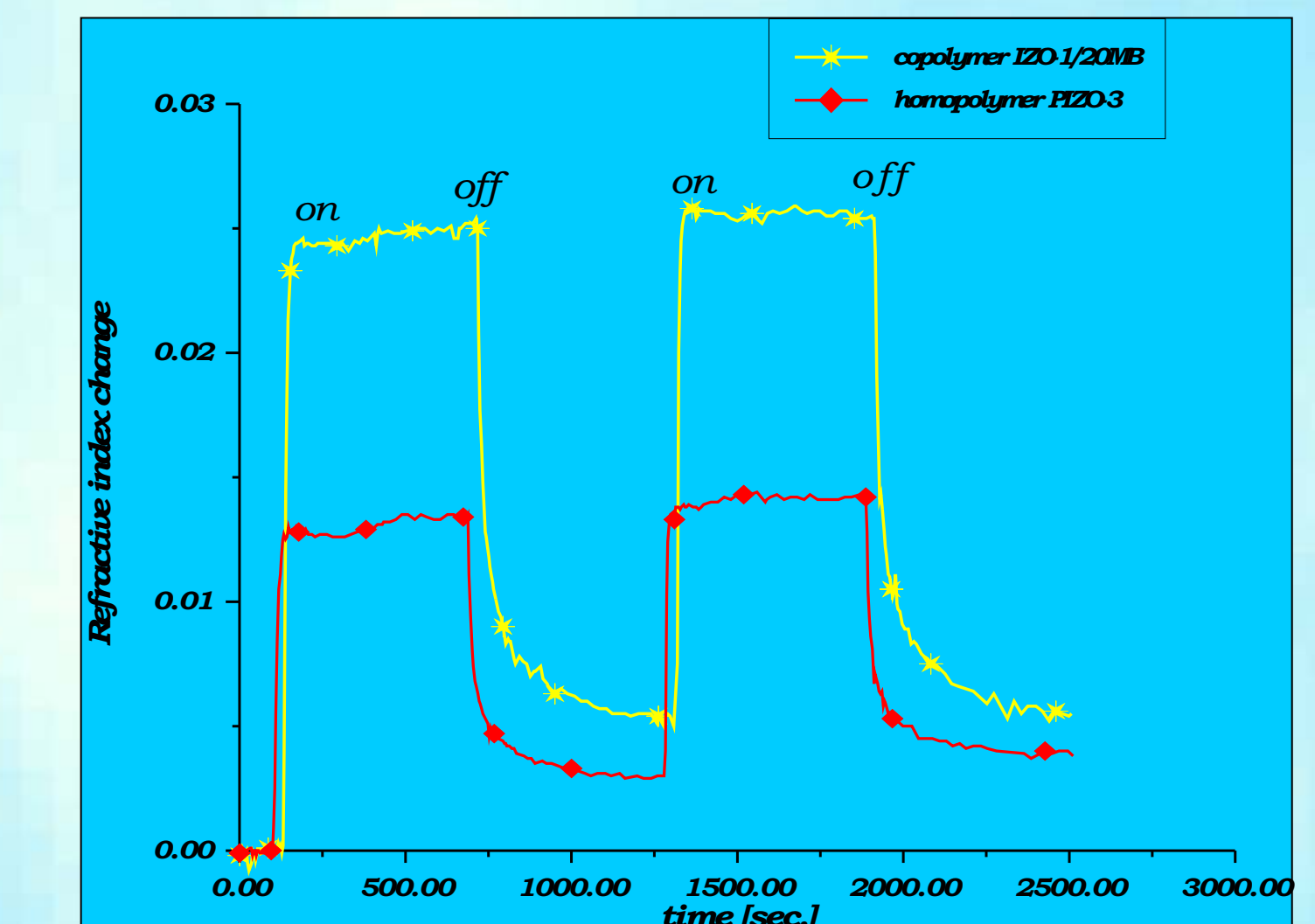
$$\Delta n_r = C \exp(-k_c t) + D \exp(-k_d t) + E$$

for the relaxation process in the absence of illumination.

In equations 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.



Refractive index change for IZO-2/20MB. The solid line is a fit to biexponential functions a) for growth-light on; b) for decay after the light was turned off



CONCLUSIONS

- ✓ The methacrylate monomers and polymers containing azobenzene with sulfonamide substituents 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.
- ✓ Quantum chemical calculations showed significant differences in UV-VIS spectra, dipole moments, polarizability, first hyperpolarizability and refractive index between both cis and trans form of the chromophore monomers.
- ✓ The illumination of spin-coated polymer films during ellipsometry measurements resulted in a change of refractive index in the range of 0.016 and 0.031.
- ✓ Biexponential functions well described the kinetics of refractive index change in these polymers. The rate constants of the growth process and stability of the photoinduced refractive index changes were found to be depended on the kind of chromophore side group as well as on the kind of comonomer used.
- ✓ All these properties make these polymers potentially attractive as optical active materials for information recording by holographic procedures.

References

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