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Photochemical transformations of chromophoric methacrylates under the influence of light and laser radiation

Stanisław Kucharski,*[a] Ryszard Janik,[a] Philip Hodge,[b] Dave West[c] and Kaleemullah Khand[c]

[a]*Institute of Organic and Polymer Technology, Technical University of Wrocław, 50-370 Wrocław, Poland. E-mail: kucharski@itots.ch.pwr.wroc.pl*
[b]*Department of Chemistry, University of Manchester, Manchester, UK M13 9PL*
[c]*Department of Physics and Astronomy, University of Manchester, Manchester, UK M13 9PL*

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Methacrylate type polymers of 2-methyl-2-[4-({4-[(5-methylisoxazol-3-yl-amino)sulfonyl]-phenyl}diazenyl)phenylamino]ethyl methacrylate (**PMMI**), 2-*n*-butyl-2-[4-({4-[(5-methylisoxazol-3-ylamino)-sulfonyl]phenyl}diazenyl)phenylamino]ethyl methacrylate (**PMBI**) and 2-*n*-butyl-2-[4-({4-[(1,3-thiazol-2-ylamino)sulfonyl]phenyl}diazenyl)phenylamino]ethyl methacrylate (**PMBT**) were obtained. The polymers were deposited as thin films onto glass plates either by the Langmuir–Blodgett technique or by spin coating. On illumination with both unpolarized and linearly polarized light *trans–cis* isomerisation of the azobenzene group took place as evidenced by a drop of the absorbance of the maximum absorption peak at *ca.* 450 nm. The samples illuminated with *p*-polarized light showed essentially no drop of absorbance when observed in an s-polarized UV-VIS spectrophotometer beam.

Degenerate four wave mixing experiments carried out with two 512 nm writing beams and a 632 nm probe beam showed formation of a diffracted beam with 4 and 7% efficiency for **PMBI** and **PMMI**, respectively; both were methylisoxazole derivatives with methyl and butyl groups, respectively, at the tertiary nitrogen atom. Refractive index modulation of the **PMMI** film was equal to 0.004. The illumination of the samples in ellipsometric measurements resulted in a change in the refractive index of the films in the range of 0.012 due to *trans–cis* isomerisation.

Introduction

Azobenzene derivatives are generally able to undergo *trans–cis* isomerisation reversibly. This is one of the best known photochemical reaction systems. On absorption of light in the UV-VIS range, the more stable *trans*-form is excited from the ground state S_0 level to a higher level state with the subsequent formation of the *cis*-form. The mechanism of the transformation involves either a dihedral –N=N– rotation or an –N=N– inversion. It is assumed that the first mechanism is involved when the molecule is excited to the S_2 state, and that inversion takes place when the molecule is excited to the S_1 state.[1–3] Since the *trans*- and *cis*-forms have different absorption bands, the reverse *cis–trans* isomerisation can be induced by illumination at the characteristic absorption of the *cis*-form. It can, however, also occur thermally. The latter is a slower process but it generally produces the *trans*-isomer in theoretical yield. The reversibility of the *trans–cis* isomerisation in repeated cycles with no destruction of the primary material is a key feature of azobenzene derivatives which makes them interesting for the writing and storage of information by optical methods.[4–9] The latter depends on the fact that the absorption spectra, refractive indices, relative permittivities *etc.* of the two forms differ.

Data on reaction rates, reversibility and yields of *trans–cis* isomerisations in dilute solutions are relatively easily obtained by UV-VIS spectrophotometry,[1,2,17] but from the point of view of material engineering more important studies are those carried out using Langmuir–Blodgett films (L–B),[10–13] or spin-coated films of either the pure solid material or the material dispersed in a polymer matrix.[14–16] Polymeric materials containing azobenzene groups in the main chain or in side chains are of particular interest because many of their properties are easily tuned by a proper choice of the monomer and/or co-monomers. The most frequently used azobenzene derivatives for *trans–cis* isomerisation studies are those with amino and nitro substituents in the *para* positions, *i.e.*. those of the Dispersed Red type.[14–21] They have a strong absorption band at *ca.* 485 nm.[14–16]

The aim of the present work was to prepare methacrylate polymers with side chain azobenzene groups with, in place of the usual nitro substituents, the sulfonamide moieties shown in Fig. 1. These chromophores show nonlinear optical properties[22–25] and their amphiphilic derivatives are able to form Langmuir–Blodgett films.[23] Our goal was to investigate the *trans–cis* isomerisation of the materials shown in Fig. 1, in the form of both L–B films and spin-coated films using unpolarized and polarized light. The latter would give us the possibility of producing interference domains in films using laser light, and as a consequence, would be promising for the formation of patterns necessary for the optical writing and storage of information by optical methods. For these purposes polymers having rather low degrees of polymerization were selected (Table 1).

Experimental

Materials

The polymers were prepared by free radical polymerizations of the corresponding monomers. The syntheses and properties of the monomers are described elsewhere.[26] In each case a solution of the chromophoric methacrylate (5.0 g) in a mixture of THF: γ-butyrolactone (70 : 30 v/v) with AIBN (0.5 g) as an initiator was heated under reflux (*ca.* 346 K) under nitrogen for

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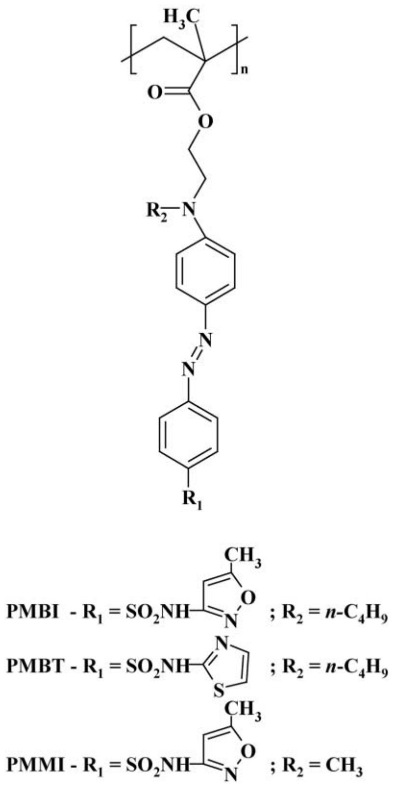

Fig. 1 Chemical formulae of the polymers.

Table 1 Characteristics of the polymers

Polymer	Yield (%)	$\bar{M}_n$	$\bar{M}_w$	T_g/K	UV-VIS λ_{max}	UV-VIS log (ε_{max}/ dm^3 mol^{-1} cm^{-1})[a]
PMMI	73	13400	15900	396	446	4.41
PMBI	64	13100	15500	378	452	4.43
PMBT	85	20600	36400	326	448	4.41

[a] ε_{max} per monomer unit in DMSO.

72 h. Then, the cooled mixture was poured into cold water (200 cm^3). The polymer precipitated out and was filtered off, washed several times with water and dried. The crude product was freed from monomer by washing it in a Soxhlet apparatus with ethanol until the washings were colorless. The polymer was then dried and powdered. The ^{1}H NMR spectra of the polymers in DMSO-d$_6$ solutions showed the absence of proton signals of the vinyl group at *ca.* 5.6–6.0 ppm; the broad signals of other protons had nearly the same values of chemical shifts as those of the monomers.[26]

The glass transition temperatures of the polymers were determined using a Mettler-Toledo Differential Scanning Calorimeter. The speed of sample heating was 20 K min^{-1}. Molecular masses of the polymers were determined using a GPC instrument equipped with a LC-6A Shimadzu pump, a 7225 Rheodyne injector with a 20.2 µl loop and a UV detector. The system was calibrated in the range 440–45700 using polystyrene samples of narrow dispersity (Aldrich).

Langmuir–Blodgett films

The surface pressure isotherms were recorded using a NIMA 622D2 two-barrier trough with a subphase temperature of 295 K. The sub-phase was doubly-distilled water additionally passed through 0.2 µm Millipore filter. Solutions (*ca.* 3 mmol dm^{-3}) in chloroform (**PMMI**, **PMBI**) or in chloroform–DMSO (9 : 1 v/v) were used to spread monolayers on the water surface. After allowing 15 min for solvent evaporation the barriers were started at a speed of 5 mm min^{-1}. The deposition of the films onto glass plates was achieved by horizontal deposition (“touch and carry method’) at a surface pressure of 15 mN m^{-1}.

Spectrophotometry

UV-VIS spectra were recorded using a Varian CARY 1 spectrophotometer.

4-Wave mixing equipment (4WM)

A Coherent Ar+ laser was used in the 4WM experiments. The two 512 nm writing beams had 25 mW power and a beam diameter of 2 mm. The reading beam of 632 nm had 0.3 mW power and a 1 mm spot diameter.

Ellipsometry

Ellipsometer EL X-02C of DRE Ellipsometerbau GmbH (Germany) was used for the determination of film thicknesses and refractive indices. A linearly polarized laser beam of 3 mW at an incident angle of 70° was used in measurements.

Results and discussion

Monolayer films

The polymers used in the present study form monolayers at the air/water interface. The isotherms are classical in shape and there is no film collapse below 40 mN m^{-1}. Only **PMMI** shows an inflection of the isotherm at *ca.* 30 mN m^{-1}, see Fig. 2. The lengths of the side chains of the monomers are comparable with the lengths of normal C_{16}–C_{17} aliphatic chains and are *ca.* 2.0 nm long. Compression of the monolayers probably caused close packing of the flat *trans*-azobenzene side groups to give a smooth film on the surface of the water. This would probably facilitate deposition of the film onto a solid glass support. In fact, deposition of a monolayer of the **PMBT** film onto the glass on the upstroke was 100% efficient but it was impossible to obtain multilayer structures because further deposition steps, in particular those on downstrokes, caused peeling of the material deposited previously. In the case of **PMBI** and **PMMI** even the deposition of a single monolayer was problematic. In these circumstances it was decided to try horizontal deposition of the “touch and carry’ type. This involves touching the glass plate to the monolayer on the water surface and then moving it

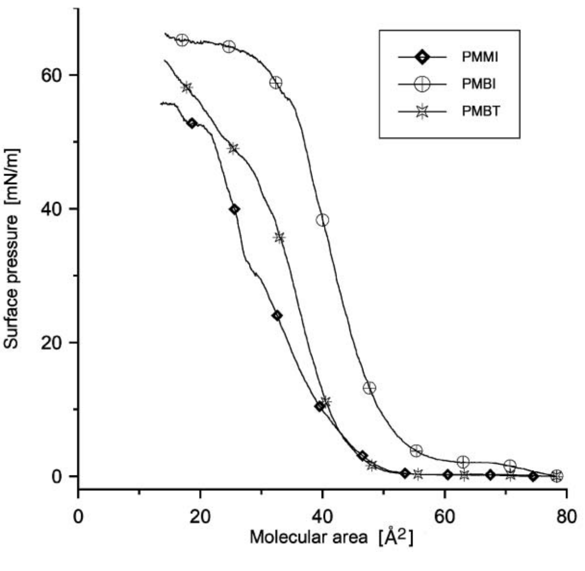

Fig. 2 Surface pressure isotherms of polymers.

sidewise. In this way, with a *ca.* 15 min waiting period between consecutive touches, it was possible to deposit multilayers. At surface pressures of 15 to 18 mN m^{-1} the transfer ratio was nearly 100% and it worked well up to 15 steps (15 monolayers transferred).

trans–cis Isomerisation

The azo-sulfonamide chromophores used in this study each show a strong absorption band in the visible region at *ca.* 450 nm. They are pseudo-stilbene type azobenzene derivatives and are able to undergo reversible *trans–cis* isomerisation by illumination (usually of their solutions) with a light band strongly absorbed by these compounds. Recently, solutions of the methacrylic monomers were investigated,[22,26] and it was shown that the isomerisations were reversible and that the reverse *cis–trans* transformation took place by thermal relaxation. Having prepared the polymers shown in Fig. 1 from the monomers, the isomerisation behaviour of the chromophores in the solid state could be studied, with the material either as Langmuir–Blodgett films or as spin-coated films.

LB films could be obtained for **PMBT** by the "touch and carry' technique and illumination of a 9-layer structure caused the spectrum of the sample to change due to *trans–cis* isomerisation. Isomerisation also took place when the sample was illuminated with white light from which radiation below 400 nm was filtered off. It was found that the absorption band of the *cis*-form was at *ca.* 385 nm, so cutting off this radiation region avoided the reverse photochemical *cis–trans* isomerisation. As shown in Fig. 3, the absorption band of the *trans*-form has its maximum absorption at 454 nm and the absorption band is relatively broad, reaching also to the green light region. Absorption in the red light region is very weak. Using filters to obtain a light beam with a narrow transmission band corresponding to the maximum absorption band of the *trans*-isomer reduces the intensity of the incident light and so increases the amount of time needed to achieve the photostationary state. Of course, blue light radiation with the same amplitude (power) would be more effective than the unfiltered white light. The main part of our experiment was carried out using linearly polarized light for illumination. The UV-VIS spectra were recorded with a polarized recording beam using the same polarizing filter for illumination and spectra recording. Fig. 3 shows the polarized spectra of the LB films of **PMBI**. The illumination was carried out with a p-polarized beam of white light. The decrease in the p-polarized absorption is evident while the spectrum recorded in the s-polarization plane was identical with that recorded before illumination.

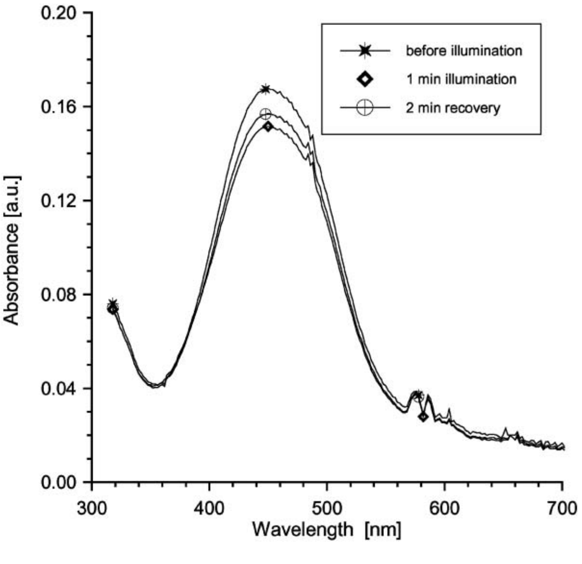

Fig. 3 Polarized UV-VIS spectra of **PMBT** Langmuir–Blodgett film containing 9 monolayers. p-Polarized illumination and p-polarized spectra recording were used.

The polymer films obtained by spin coating had micrometer scale thickness whereas the LB films had nanometer (molecular) scale thickness. The former show stronger absorption and in this case the power of the incident beam is important as this increases the rate of *trans–cis* isomerisation. The spin-coated samples of the **PMMI** and **PMBI** polymers isomerized by the p-polarized light beam show good responses to the radiation. Essentially a 2 min period of illumination with a *ca.*20 mW cm^{-2} light beam was sufficient to achieve the photostationary state of the *trans–cis* system. Fig. 4 and 5 show the change in the polarized absorption spectra of **PMBI** and **PMMI** (respectively) caused by illumination and the thermal relaxation recovery from the *cis*- to *trans*-form. The absorbance drop of **PMBI** from the *trans* to the photostationary state was *ca.* 22%, that of **PMMI** was 19% and of **PMBT** *ca.* 14%. It was found that isomerisation of **PMBI** and **PMMI** was reversible and that the cycles of photochemical *trans–cis* and thermal *cis–trans* isomerisation could be repeated many times without any signs of the material showing fatigue. This was not the case with **PMBT** where probably a side reaction takes place on

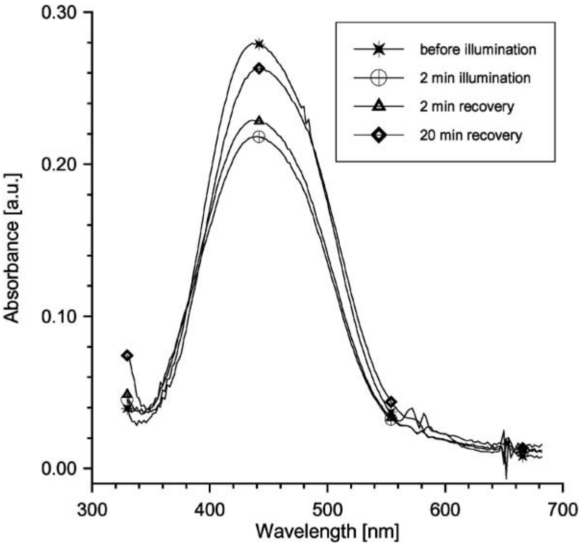

Fig. 4 Polarized UV-VIS spectra of **PMBI** spin-coated film.

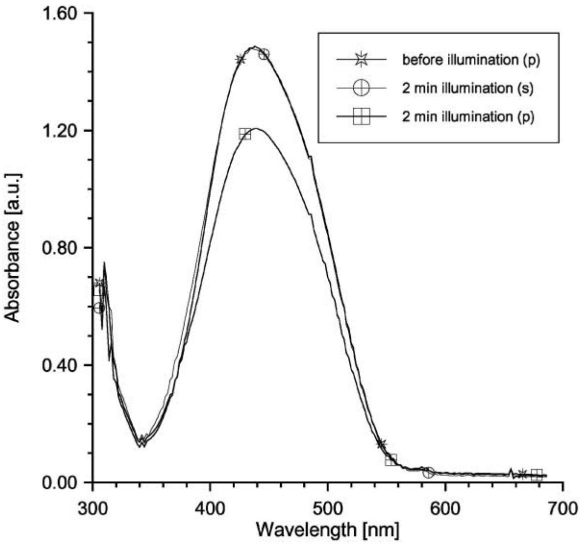

Fig. 5 Polarized UV-VIS spectra of **PMMI** spin-coated film.

illumination and so the thermal recovery of the *trans* form is not always complete.

The isomerisation of the polymers in question changes the properties of the material and isomerisation with polarized light changes the properties selectively. The changes in material are more pronounced in those places which lie in the polarization plane. One could imagine that the chromophore fragments affected by light change their orientation from *trans* to *cis* producing repeated areas rich in *trans* and rich in *cis* forms. This patterned polymer surface could be utilized for the storage of information.

In spin-coated polymer layers the *trans–cis* isomerisation is relatively fast. Using a light power of 20 mW cm^{-2}, on vertical illumination the photostationary state is reached after *ca.* 2 min, though visible effects can be observed after a few seconds. The reverse thermal *cis–trans* relaxation is much slower and takes about 1 hour to reach the original state defined by the starting absorbance. However, this could be accelerated by irradiation with a light beam of a wavelength corresponding to the absorbance band of the *cis* form.

Four wave mixing

The *trans*- and *cis*-forms of the present azo chromophores differ in shape, magnitude and direction of the dipole moment, in polarizability and in hyperpolarizability, all of which result in a photoinduced anisotropy of the films. The *trans*-form is more extended and one may assume that among the components of the polarization tensor a dominant one is that which is parallel to the molecular axis. If polarized light is used to induce *trans–cis* isomerisation then the probability of a given molecule being transformed (pumped) from *trans* to *cis* is highest for the molecules lying parallel to the light polarization plane. The *cis* shaped chromophores have a smaller polarizability and a blue shifted absorption spectrum (maximum at *ca.* 385 nm) and the photoinduced anisotropy is a result of so called angular hole burning around *trans*-oriented molecules (although other phenomena were also suggested[2,4]).

When two interfering polarized laser beams are used, the photoinduced anisotropy effect can be utilized to produce surface relief gratings. In the system studied the writing beams are those which are absorbed by the material to induce the isomerisation. Two beams of 512 nm were within the absorption band of the present polymers and they were used as writing beams. Their intensities were both 25 mW at beam diameters of 2 mm. The probe beam was of lower intensity. Its power was 0.3 mW, its diameter was 1 mm, and its wavelength was 632 nm. It was, therefore, well beyond the absorption maxima of the polymers. The p-polarized writing beams were found to induce interference beams in a four-wave mixing experiment and in Fig. 6 and 7 the generation of the first order diffraction beam of **PMBI** and **PMMI**, respectively, as a function of time is shown. The shape of the curves is similar, but **PMMI** yields a more intensive diffraction beam. Quantitatively, the diffraction efficiency expressed as the intensity ratio between diffraction and incident beam was 7% and 4% for **PMMI** and **PMBI**, respectively. For the spin-coated film of *ca.* 10 μm the refraction index modulation Δn was 0.004 and 0.003, respectively. In the case of **PMBT** no interference beam was observed.

Ellipsometric measurements

Ellipsometry is a technique which offers precise measurements of film thickness and optical constants. It operates by reflecting light from the material (bulk or thin film) and measuring its polarization change. Linearly polarized light is incident at an oblique angle; in our case at 70° relative to the sample normal. The light interacts with the sample and undergoes a polarization change to elliptically polarized light. The change in the polarization is measured as a ratio of the complex Fresnel reflection coefficients, *R*p and *R*s, for p- and s-polarized light, respectively. The fundamental equation of ellipsometry is given in eqn. (1),

$$\rho = \tan(\Psi)e^{i\Delta} = \frac{R\mathrm{p}}{R\mathrm{s}} \tag{1}$$

where Ψ determines the intensity ratio and Δ determines the phase difference of the reflected p- and s-polarized light. From these measured values it is possible to calculate the film thickness and complex dielectric function expressed by complex refractive index: $n = n_r + ik$, $i^2 = -1$.

Recently, ellipsometry was used to monitor the photoisomerisation process of methacrylate copolymers in Langmuir–Blodgett films.[27] The authors observed no change in the refractive index on sample illumination but they observed a change in monolayer thickness owing to layer interdigitation of sidechains and probable disorganization of the monolayer structure. For an amorphous polymer film deposited by spin-coating the chromophoric side-chain groups are randomly distributed if one may neglect the plate rotary movement as an organizing factor. The molecular volume of the chromophore *trans* and *cis* form is nearly the same when treated as a molecule in the isolated state. This may not be the same in material in the

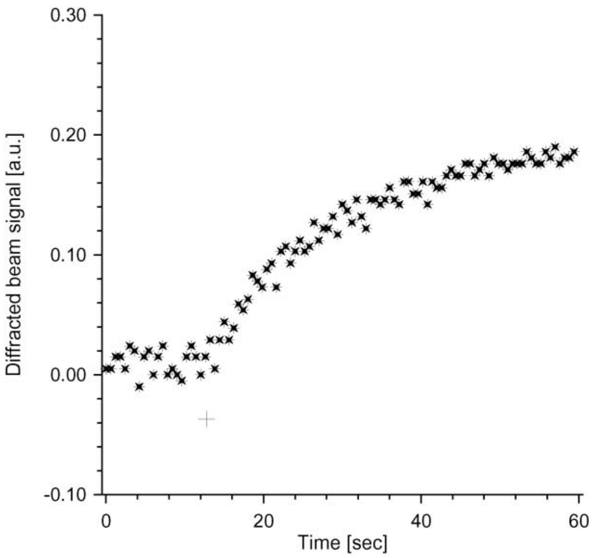

Fig. 6 Interference signal of **PMBI** film. + means start of probing.

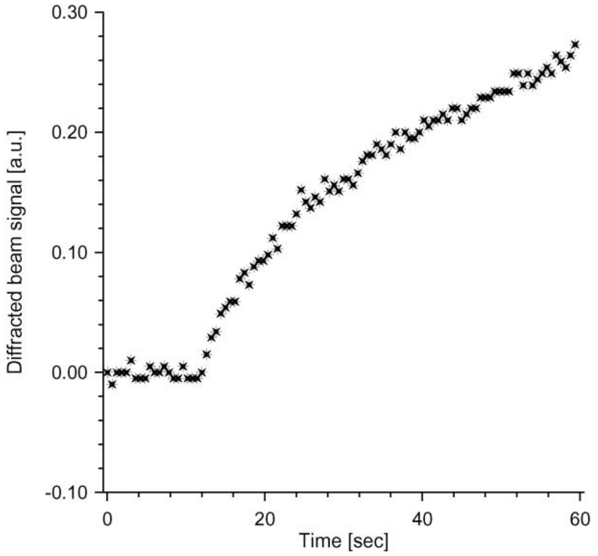

Fig. 7 Interference signal of **PMMI** film. + means start of probing.

Table 2 Change of refractive index on illumination (n_r, real part; k, imaginary part)

	Before illumination		After 5 min illumination with blue light (2 mW cm^{-2})	
Polymer	n_r	k	n_r	k
PMMI	1.6594	0.1127	1.6472	0.1120
PMBI	1.6520	0.1241	1.6397	0.1193
PMBT	1.6029	0.1146	1.5985	0.1008

macroscale and the specific volume of the material may also depend on the intermolecular space not occupied by molecules. But, on the other hand, quantum chemical calculations indicate considerable difference in polarizability and dipole moment values between the isomer forms and this should be manifested in different values of dielectric properties, *i.e.*, different refractive index values.

In our experiments the measurements were carried out using a linearly polarized laser beam of 632 nm and of *ca.* 3 mW power. The spin-coated films were prepared on glass plates treated on the reverse side with an abrasive sand to avoid reflection from the lower plane of the plate. The computer program accompanying the ellipsometer was a tool to fit the ellipsometry measured parameters to the film thickness and its refractive index by carrying out a simulation. The measurements were carried out in two ways. The various parameters were recorded before illumination and after 5 min illumination with blue light of *ca.* 2 mW cm^{-2} power. This period of time was long enough to reach a photostationary state even with such a weak light intensity. The results are summarised in Table 2. For samples of *ca.* 300 nm thickness the illumination changed the character of the material due to the *trans–cis* isomerisation of the polymer side-chain chromophores. For **PMMI** and **PMBI** the change in refractive index (real part) was relatively high and was in the range of 0.012. This was higher than values obtained by 4-wave-mixing but in that case only the first-order interference spot was taken into account. For **PMBT** the change of refractive index was much smaller and this probably explains the fact that no interference spot was observed for this material in 4-wave mixing experiment.

The second type of ellipsometric experiments was carried out by continuous illumination of the sample with blue light while observing the ellipsometric parameters. The results of this experiment are shown in Fig. 8. From left to right we can see the change of these parameters in repeated cycles of switching the illumination on and off. Here one can observe that **PMBI**, having a lower T_g and a butyl group on the tertiary nitrogen atom, reaches on illumination an isomerisation saturation state and recovers to an initial state. The time of the recovery is much longer than the time to reach the isomerisation equilibrium. The next observation is that in the second cycle the time to recover is shorter than in the first one but no tendency to shorten recovery time was observed in subsequent cycles. This may be due either to structural changes of the material which was caused by local movement of molecules changing their shape from the *trans*- to *cis*-form (hole burning?) or to a slight increase in the local temperature. This phenomenon was observed many times in our experiments, and this meant that the material in question would need to be subjected to a structure "softening' to become reversibly isomerisable. Observation of the polymers during continuous illumination indicated that the **PMMI** polymer showed a kind of material fatigue when illumination was prolonged (Fig. 8B), and in the case of **PMBT** it was difficult to find a plateau value of both Ψ and Δ so its *trans–cis–trans* isomerisation could not be assumed to be fully reversible, at least in light of ellipsometric measurements.

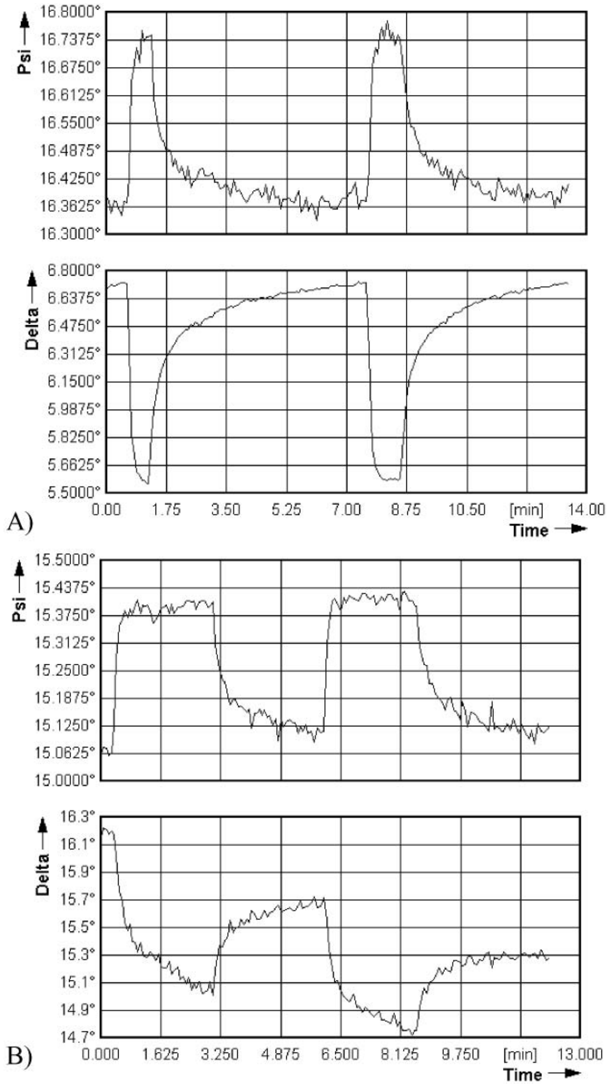

Fig. 8 Variation of ellipsometric parameters with illumination. From left to right: light on–off, on–off. A: **PMBI**, B: **PMMI** (spin-coated films).

Conclusions

The methacrylate polymers containing side-chain chromophores of azobenzene with sulfonamide-type substituents undergo a reversible *trans–cis* isomerisation under the influence of white light (UV region excluded) in an unpolarized or polarized state. The change in the material property due to this transformation is a key feature to be utilized for reversible optical storage. The 4-wave mixing with a 512 nm writing beam and 632 probe beam showed the formation of an interference beam with diffraction efficiencies of 7% and 4% for **PMMI** and **PMBI**, respectively. The refractive index modulation, Δn, was 0.004 and 0.003 for these polymers, *i.e.*, it was rather large. The change in the refractive index of the material under illumination with blue light, determined by ellipsometry, was *ca.* 0.012 for these polymers. All this indicates that these materials may be interesting for optical information storage.

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References

1 H. Rau, *J. Photochem.*, 1984, **26**, 221.

2 H. Rau, in *Photochemistry and Photophysics*, ed. J. F. Rabek, CRC, Boca Raton, FL, 1990, **Vol. II**, Ch. 4, p. 119.

3 Z. Sekkat and W. Knoll, in *Advances in Photochemistry*, ed. D. C. Neckers, D. H. Volman and G. von Buenau, Wiley, Chichester, New York, **Vol. 22**, p. 117.

4 J. A. Delaire and K. Nakatori, *Chem. Rev.*, 2000, **100**, 1817.

5 D. Y. Kim, X. I. Jiang, L. Li, J. Kumar and S. K. Tripathy, *Photonic and Optoelectronic Polymers*, ed. S. A. Janekhe and K. J. Wynne, ACS Symposium Series No. 672, Washington, 1995, p. 251.

6 M. Han, S. Morino and K. Ichimura, *Macromolecules*, 2000, **33**, 6360.

7 T. Seki, K. Fukuda and K. Ichimura, *Langmuir*, 1999, **15**, 5098.

8 T. Yamamoto, M. Hasegawa, A. Kanazawa, T. Shiono and T. Ikeda, *J.Mater. Chem.*, 2000, **10**, 337.

9 B. L. Feringa, R. A. van Delden, N. Koumura and E. M. Geertsma, *Chem. Rev.*, 2000, **100**, 1789.

10 C. Wang, H. Fei, Y. Yang, Z. Wie, Y. Qiu and Y. Chen, *Opt. Commun.*, 1999, **159**, 58.

11 A. Danabalan, D. S. Dos Santos, C. R. Mendonca, L. Misoguti, D. T. Balogh, J. A. Giacometi, S. C. Zilio and O. N. Oliveira, Jr., *Langmuir*, 1999, **15**, 4560.

12 D. Kinoshita, *J. Photochem. Photobiol.*, 1998, **42**, 12.

13 H. S. Blair, H. J. Pague and J. E. Riordan, *Polymer*, 1980, **21**, 1195; H. S. Blair, H. J. Pague and J. E. Riordan, *Polymer*, 1984, **25**, 1347.

14 C. J. Barret, A. L. Natansohn and P. L. Rochon, *J. Phys. Chem.*, 1996, **100**, 8836.

15 T. Buffeteau and M. Pezolet, *Macromolecules*, 1998, **31**, 2631.

16 S. H. Lin, K. Y. Hsu, W.-Z. Chen and W. T. Whang, *Opt. Lett.*, 2000, **25**, 451.

17 A. L. Natansohn, P. L. Rochon, J. Gosselin and S. Xie, *Macromolecules*, 1992, **25**, 2268.

18 M.-S. Ho, A. L. Natansohn, C. J. Barrett and P. L. Rochon, *Can. J. Chem.*, 1995, **73**, 1773.

19 A. L. Natansohn, P. L. Rochon, M.-S. Ho and C. J. Barrett, *Macromolecules*, 1995, **28**, 4179.

20 X. Meng, A. L. Natansohn and P. L. Rochon, *Supramol. Sci.*, 1996, **3**, 207.

21 D. Hore, A. L. Natansohn and P. L. Rochon, *Can. J. Chem.*, 1998, **76**, 1648.

22 S. Kucharski, R. Janik, H. Motschmann and C. Raduege, *New J. Chem.*, 1999, **23**, 765.

23 S. Kucharski, R. Janik and P. Kaatz, *J. Phys. Chem.*, 1997, **101**(44), 8967.

24 S. Kucharski, R. Janik and P. Kaatz, *J. Mater. Chem.*, 1999, **9**, 395.

25 J. Raźna, P. Hodge, D. West and S. Kucharski, *J. Mater. Chem.*, 1999, **9**, 1693.

26 R. Janik, S. Kucharski, A. Kubaińska and B. Łyko, *Polish J.Chem.*, 2001, **75**, 241.

27 H. Knobloch, S. Katholy, J. Hesse, H. Orendi, D. Prescher, R. Ruhman and L. Brehmer, *Mater. Sci. Eng.*, 1998, **C5**, 307.