Photochromism and diffraction grating in cyanoazobenzene polymer films

M. Serwaczak^a, M. Wübbenhorst^b, S. Kucharski^{*a}

^aWrocław University of Technology, Faculty of Chemistry, Department of Polymer Engineering and Technology, Wybrzeże Wyspiańskiego 27; 50-370 Wrocław, Poland

^bCatholic University Leuven, Acoustics and Thermal Physics Section, Department Natuurkunde en Sterrenkunde, B-3001 Heverle, Belgium

ABSTRACT

Two series of photochromic copolymermethacrylates containing cyanoazobenzene chromophores as side chains were described. The series with shorter ethylene spacer between mesogen and main polymethacrylate chain was amorphous, whereas the second one with longer ethoxyethylene spacer was liquid crystalline forming smectic C mesophase above T_g. The materials were deposited on glass substrates *via* spin coating and casting technique to provide thin transparent films. The reversible change of refractive index of the films on illumination with white light was determined by ellipsometry. The difference of real part of the refractive index of the sample was in the range 0.0067-0.0210 depending on the polymer. Formation of diffraction grating was achieved by two beam coupling arrangement using a 532 nm laser diode. The diffraction efficiency for the first order diffraction was in the range of 1.5-2.1% for the homopolymers.

Keywords: photochromic polymethacrylate, cyanoazobenzene mesogens, modulation of refractive index, diffraction grating

1. INTRODUCTION

Polymers with pendant azobenzene moieties in the side chain have received increasing attention due to their photochromic properties and broad range of potential applications especially in the field of optics and optoelectronics. The photochromic polymeric materials can be used as active materials for optical data storage, holographic recording media and other optoelectronic applications [1-3]. It is well known [4-9] that illumination of photochromic materials with linearly polarized light which can be absorbed by the azobenzene dye, activates the photoisomerization of those *trans* azo groups whose dipole moments are parallel to the polarization direction of the light. The azobenzene groups located perpendicularly to the light polarization direction are inert to such photochemical excitation [10]. The reverse *cis-trans* isomerization proceeds as a result of thermal relaxation, and with time, an equilibrium state is established between the populations of *trans* and *cis* isomers.

Using two coherent laser beams crossed on photochromic film results in modification of the film material due to light interference creating *cis*-rich and *trans*-rich zones. A consequence of this phenomenon is formation of a diffraction grating, which can be utilized in data recording by holographic technique.

In the present system, the *p*-cyanoazobenzene chromophore belongs to the pseudostilbene type (according to Rau classification [11,12]), a feature that leads to a strong overlapping in the absorption spectra of the *cis* and *trans* isomers and that increases the rate of the *cis-trans* thermal isomerization. Pseudostilbene are also the best group in term of photoinduced orientation, because the appropriate selected light for photoactivation of the *trans-cis* isomerization will also photoactivate the *cis-trans* isomerization, which will significantly speed up the whole process. The materials in question show a strong absorption band in the visible region with maximum at ca.450 nm due $\pi - \pi^*$ transition of azobenzene groups attributable to its *trans* form. The *trans-cis* photoisomerization of the chromophoric fragments was carried out by UV-Vis spectroscopy under illumination with unpolarized white light and showed the reversibility of the process [13].

The cyanoazobenzene mesogens have been introduced and investigated in homo- or copolymer based systems such as polyacrylates [14-19], polymethacrylates [20-27], and polyesters [14,28]. In our photochromic system, molecule

p-cyanoazobenzene is linked as side chain to the methacrylate main chain by spacer and methyl amino group to give rise to a structural non-centrosymmetry to improve the nonlinear optical properties. Two types of spacer: ethylene and ethoxyethylene (Figure 1) were taken into account. The longer spacer was used with hope to improve the flexibility of the dye moiety and to avoid undesired haze in transparent film. The flexibility of the molecule may also have an effect on response rate of the material on illumination. The investigated photochromic polymethacrylates were not described in available literature.

In this work, which is a continuation of our previous studies on these materials, the main attention will be directed to investigation of the ability to modulation of the refractive index by ellipsometric measurements. The change of refractive index of the films on repeated illumination cycles with unpolarized white light will be monitored. The ability to formation of diffraction grating will be tested by a two beam coupling (TBC) technique. Two crossed 532 nm *p*-polarized laser beams focused on the sample have been used to write diffraction grating.

2. MATERIALS AND METHODS

2.1 Materials

In present work, two series of methacrylate push-pull side-chain cyanoazobenzene polymers with amorphous and liquid crystalline properties, were investigated. The series with shorter ethylene spacer between mesogen and main polymethacrylate chain, pCN (Fig. 1, X=a), was amorphous, whereas the second one with longer ethoxyethylene spacer, pCNO (Fig. 1, X=b), was liquid crystalline. The polymers were synthesized, according to the procedure described in Ref. [29], by free radical homo and copolymerization of the photochromic methyl methacrylate monomers in THF and γ -butyrolaktone as a solvent using 2, 2-azoisobutyronitrile (AIBN) (8% wt) as an initiator. Butyl methacrylate was used as a non-photochromic comonomer. The synthesis, thermal behavior, mesomorphic and photochromic properties of the materials in question were described in details in Ref. [13]. The polymerization reaction yielded homopolymers and statistical copolymermethacrylates, where the azobenzene comonomer content varied from 100 to 30 (wt. %) as taken for reaction and additionally determined by the ¹H NMR analysis. The average molecular mass of the polymers determined by GPC was between 8 000 and 11 000 (Table2.), and it was rather low indicating that the polymers were rather oligomers, what was in agreement with literature data [30, 31]. The thermogravimetric analysis of the investigated polymers indicated their very good thermal stability with initial decomposition temperatures of all the polymers above 230 °C [13].

Fig. 1. Structural formulae of the photochromic pCN (X=a) and pCNO (X=b) polymer series

*stanislaw.kucharski@pwr.wroc.pl; phone +48713202862, fax: +48713203678

2.2. Methods

The thermal properties of photochromic polymers were determined by differential scanning calorimetry (DSC), using a Perkin Elmer DSC 7 instrument. All recorded data were obtained after the first heating run which was performed to erase the thermal history. The scanning rate was $5^{\circ}\text{C min}^{-1}$ and indium was used as a calibration standard. First order transition temperatures were given by peak maximum value and glass transitions by the midpoint of the heat capacity jump.

Ellipsometer EL X-02C of DRE Ellipsometerbau GmbH (Germany) was used for the determination of film thickness and refractive index changes during illumination with unpolarized white light.

Holographic grating writing experiments were performed by two beam coupling (TBC) technique using linearly p-polarized light from green laser diode: 10 mW power at 532 nm wavelength. The angle between the laser beams was 15° and the sample was positioned normal to the bisection line. A diffraction beam was monitored by a Hamamatsu photomultiplier tube, placed on the path of the diffracted beam, and its readings were recorded by a PC computer.

3. RESULTS AND DISCUSSION

3.1 Differential scanning calorimetry

Both polymer pCN and pCNO series possess typical feature of side chain liquid crystalline polymers (SCLCP) i.e., a linear backbone containing the rigid rod like mesogenic groups, the principles of which have been reviewed elsewhere. However, because of the short alkyl spacer, which restricts the mobility of side groups, polymers in pCN series do not form liquid crystalline phase. As a result, its DSC thermogram reveals only a second-order transition. Differential scanning calorimetry data from the second heating mode are summarized in Table 1. All polymers of pCN series are amorphous, as suggested by the absence of melting peaks of the mesomorphic phase in the DSC curves, as well as by the lack of optical anisotropy of the samples.

The DSC investigations reveals for both polymer series the presence of a glass transition, the localization of which depends on the copolymer composition. If we compare the two series, the T_g of the photochromic polymers is seen to decrease with increasing length of the spacer. This kind of behavior, as reported in literature, can be attributed either to the increased decoupling of the side chains from the main chain or to the plasticizing effect of the spacer chain[32]. From comparison of both copolymers series separately, it results that if the fraction of azobenzene block decreases, the T_g shifts generally to lower temperatures. This could be explained by molecular weight effect of the azobenzene polymer.

Table 1. Results of the GPC and DSC analysis of the pCN and pCNO polymer series.

sample	azo block content (wg. %)	Mn (g/mol)	Mw (g/mol)	M_w/M_n	phase transitions ($^{\circ}\text{C}$)
pCNOhomo	100	3190	7996	2.51	g72S148I
pCNO80	80	3218	10081	3.13	g37S150I
pCNO50	50	2932	8075	2.75	g32S166I
pCNO30	30	5881	11356	1.93	g29I
pCNhomo	100	3078	7489	2.43	g102I
pCN80	80	3051	7612	2.49	g82I
pCN50	50	3670	7905	2.15	g60I
pCN30	30	3085	7914	2.57	g32I

g = glass transition, S = smectic phase, I = isotropic phase (isotropic melt)

The homopolymer pCNOhomo and the copolymers containing 80 and 50 weight percent of the side chain photochromic units, form mesophase above T_g , as revealed by melting peak on DSC thermogram. The copolymer with the lowest concentration of the chromophoric units doesn't exhibit liquid crystalline phase due to the high "dilution" of the mesogenic moieties; the stabilizing effect of the polymer backbone is not strong enough to promote the LC order. Thus, pCNO30 is completely amorphous, as indicated by the lack of the first order transition in DSC,

whereas the other copolymers pCNO50 pCNO80 form mesophase above T_g . In fact 50% proves to be enough to overcome the energetically preferred random coil conformation of the polymethacrylate backbone and allow the mesogens to pack in the parallel arrangement needed to form a LC phase.

The optical texture of the mesophase was observed for the polymers via polarizing optical microscope. The optical observations reveal the existence of smectic mesophase in the case of pCNOhomo and pCNO80 polymers. To get more information on the molecular arrangements, molecular packing and types of order in mesophases, the X-ray diffraction analysis was carried out. The results indicate the smectic C phase, in which the side chain mesogens are tilted within layers. The highest tilt angle is observed for the lowest side chain concentration, probably due to more free space between the mesogens, which allows them to be not so restrictedly perpendicular to the main chain direction. With increasing content of the mesogens the space between mesogens is reduced causing more compact order between them in layers and therefore the tilt angle is lower [13].

3.2 Ellipsometric measurements

Ellipsometry is a method, which is applied for determination of refractive index and thickness of thin transparent films [33]. The ellipsometer serves to measure the change of state of polarization of the reflected light from a sample at oblique incidence. The resulting change in polarization after reflection from a surface measured as a ratio of intensities of p- and s polarized light, is expressed by

$$\rho = \tan \psi e^{i\Delta} = \frac{R_p}{R_s} \quad (1)$$

where R_p and R_s are the complex reflectances at oblique incidence for light polarized parallel (p) and perpendicular (s) to the plane of incidence respectively. The physical meaning of ψ and Δ is the amplitude ratio and phase difference of the s and p component after reflection. From measured ψ and Δ values it is possible to calculate thickness of the film and complex refractive index, n which represents the real and imaginary parts of the refractive index:

$$n = n_r - ik \quad (2)$$

Ellipsometry served us as a tool to monitor the *trans-cis-trans* photoisomerization process on light exposure by measuring the changes in the ellipsometric Δ and ψ . The film thickness and refractive index of the films were determined using a simulation program. The measurements were carried out with using red laser beam of $\lambda = 632$ nm, not absorbed by red-colored polymer film. The incidence angle of the beam was 65° . In order to monitor the photoisomerization process, we exposed periodically the sample to white unpolarized light and allowed the sample to relax thermally. The power of the illuminating source was 2 mW/cm^2 . The illumination of samples on ellipsometer table with periodic switching light on (during 3 min) and out (3 min) showed that the process was reversible in the case of polymers with lowest azobenzene block content as presented in Figure 2. The measurement of ellipsometric parameters before and after illumination showed distinct changes of ψ and Δ . By exposing the film to light, an increase of ψ and decrease of Δ was observed, while on relaxation steps both the parameters changed in opposite directions. The most important result was the change of real part of refractive index, Δn_r , which was calculated according to equation:

$$\Delta n_r = n_r^0 - n_r^{\text{photostat.}} \quad (3)$$

where n_r^0 is the real part of refractive index measured before illumination and $n_r^{\text{photostat.}}$ is real part of refractive index measured at photostationary state. From the experiment the change of real part of refractive index was in the range of 0.0067-0.0210, depending on the polymer. It was found that the photoisomerization process was fully reversible for the pCN30, polymer with the lowest concentration of chromophoric mer in the polymer chain. For the polymer with higher chromophoric mer content, the changes were not fully reversible at the time period of 3 min., taken for thermal relaxation. The ellipsometric parameters ψ and Δ were only partly recovering the values from

before illumination, as can be seen from Figure 2. The highest change of the real part of refractive index was recorded for both homopolymers. The thickness of the deposited films was 300–520 nm.

Fig. 2. The ellipsometric parameters ψ and Δ (squares) measured during illumination of pCN30 and pCN50 polymers (lines are guide for eyes)

3.3 Two beam coupling

We performed measurements of holographic grating recording with conventional TBC technique using linearly p-polarized light from a green laser diode (532 nm wavelength) delivering 10 mW of power. The laser output beam was split into two equal power coherent beams. The angle between the laser beams (θ) incident on the sample was 15°. The sample plane was normal to the bisector line. The film thickness of the two samples made by casting technique and used in TBC experiment were ca. 0.6 μm .

Two coherent beams were crossed at the sample giving an interference grating and the grating period calculated from the Eq. 4

$$\Lambda = \frac{\lambda}{2 \cdot n \cdot \sin(\theta/2)} \quad (4)$$

was equal ca. 2 μm for pCNhomo sample.

The diffracted beam intensities were measured in real time and monitored by a photodiode, placed on the path of the diffracted beam. Experimental diffraction efficiencies η were calculated as the power ratio of the first order diffraction beam and the transmitted beam. Diffraction efficiency can be related to the refractive index modulation Δn by following equation:

$$\eta = J_m^2 \left(\frac{2\pi \cdot d \cdot \Delta n}{\lambda \cdot \cos \theta'} \right) \quad (5)$$

where d is the film thickness, θ' is diffraction beam angle, and J_m^2 is Bessel function of the first kind and m th order. The diffraction efficiency determined from TBC was 2.15% for pCNhomo sample and the value of refractive index modulation calculated from Eq. 5 was 0.003.

On switching the laser beams on, the diffraction spots appeared gradually being a function of time. The rise and decay of diffraction signal for the pCNhomo film was shown in Figure 3. At the point where the linearly polarized laser beams were switched on, the intensity of diffracted beam rapidly increased up to a saturation level. When the writing beam was switched off the intensity of the diffraction spot decreased gradually up to its disappearance. This process can be easily repeated by switching the writing beam again.

Figure 3. Time dependence of first order diffraction intensity of pCNhomo film recorded with green laser at 532 nm, $\Lambda = 2 \mu\text{m}$.

4. CONCLUSIONS

Two series of photochromic copoly(meth)acrylates containing cyanobenzene chromophores as side chains, differing in the length of the flexible spacer, were found to show well defined photochromic properties. The films deposited on glass plates showed reversibility of the *trans-cis* photoisomerization of the chromophore fragments as observed by ellipsometry. The modulation of refractive index of the films on illumination with white light was in the range 0.0067–0.0210. The holographic grating was successfully formed in these materials by conventional TBC technique using the 532 nm laser beam. The diffraction efficiency for first order diffraction was in the range of 1.5–2.1%.

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