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An azobenzene-containing side-on liquid crystal polymer

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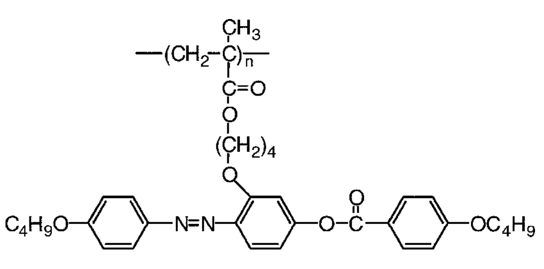
A new azobenzene-containing side-on LC polymer was synthesized. It shows a nematic phase. Its photochemical properties were characterized in solution and in thin film. The N–I phase transition can be induced upon irradiation in the π-π* absorption region of the polymer.

1. Introduction

When the azobenzene group undergoes a *trans–cis* isomerization, there are large changes in its size, shape and polarity. These changes may have important effects on the physical properties of polymers which incorporate the azobenzene group in their structure [1–4]. This *trans–cis* isomerization can be induced by light giving rise to photomechanical and photoviscosity effects, photocontrollable wettability and permeablility etc [1]. In particular, for azopolymers which are liquid crystalline, phase transition (e.g. from nematic to isotropic, N–I) can be provoked by a suitable light pulse. In these LC azopolymers, the more stable *trans*-isomer of azobenzene is mesogenic because of its rod-like shape, while the *cis*-isomer of azobenzene obtained by photoisomerization is not mesogenic, since it has a bent shape and acts as an impurity which disrupts the orientational order. Birefringence and dichroism can also be optically induced and erased in azopolymers which can be NLO materials if well chosen substituents are introduced on the azobenzene group [5–7]. A large domain of possible application has therefore been opened, e.g. in optical storage systems [2], the latest novelty being relief gratings using these polymers [8, 9].

The azopolymers studied up to now have been mostly side group polymers, where the azobenzene units are attached as pendant groups (end-on). There are also some examples of main chain polymers, where the azobenzene units are incorporated into the backbone. We report here the synthesis of a liquid crystal azopolymer with a new architecture: the azobenzene-containing mesogens are linked side-on to a methacrylate backbone, as shown below:



We will present first the polymer synthesis. The characterization of its liquid crystalline and photochemical properties will then be described, and finally we will discuss the photochemically induced N–I transition of this polymer.

2. Synthesis

The polymer was synthesized according to the scheme. NMR spectra were recorded using a Bruker HW 250 MHz or HW 400 MHz spectrometer. Molecular masses and molecular mass distributions were measured using a Waters 510 HPLC pump, Waters Styragel™ HR 5E columns and a Waters™ 410 differential refractometer, on line with a Wyatt miniDAWN light scattering instrument. THF was used as eluent.

2.1. *4-Butoxy-2′,4′-dihydroxyazobenzene (1) [10]*

150 ml of a mixture of PEG200/1,4-dioxane/water (60/30/10) was cooled in an ice bath, and to the mixed solvent were added 5.23 ml (0.0607 mol) of concentrated HCl and 5 g (0.0303 mol) of 4-butoxyaniline. A solution of $NaNO_2$ (2.30 g, 0.0333 mol) in water (10 ml) was added dropwise to the above mixture to form the diazonium salt.

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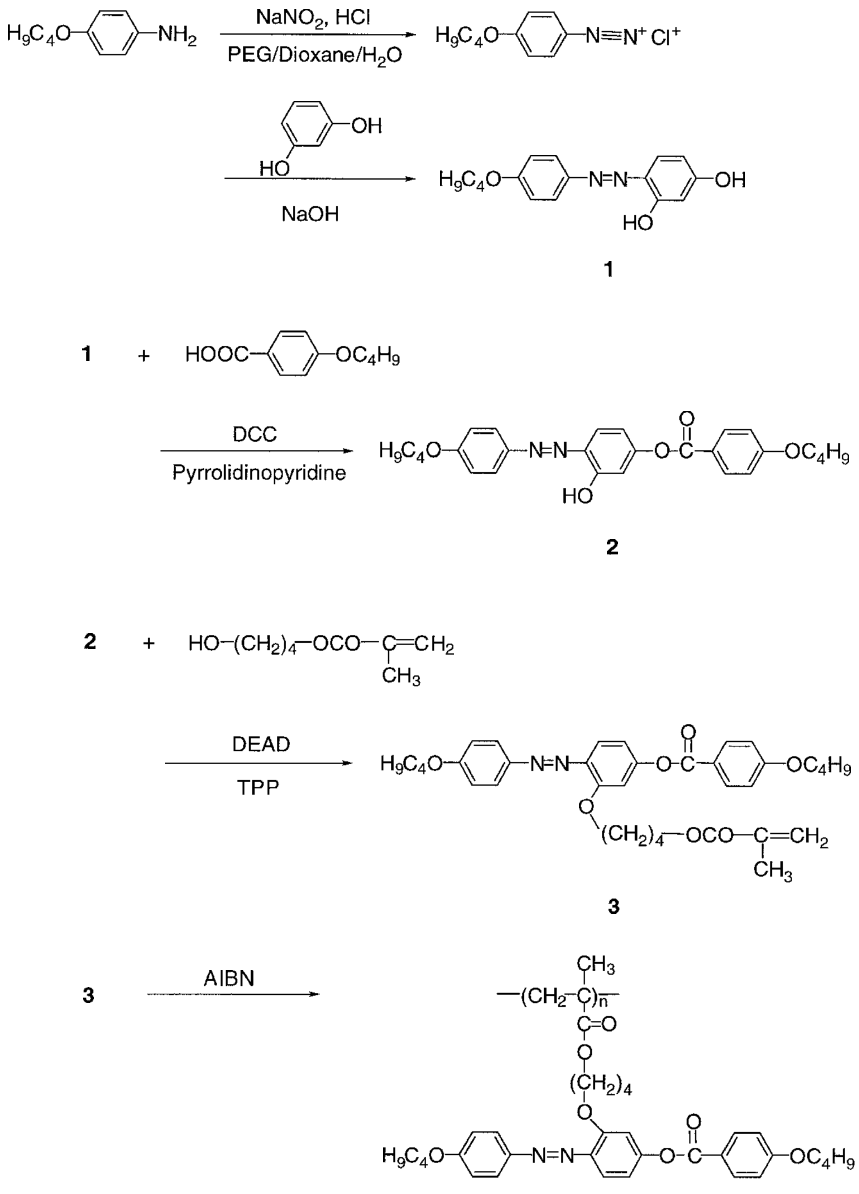

Scheme.

The solution was left stirring at 5°C for 1 h. A solution of resorcinol (10 g, 0.0909 mol) and NaOH (1.33 g, 0.0333 mol) in 150 ml of the mixed solvent PEG200/1,4-dioxane/water (60/30/10) was prepared and poured into the diazonium salt solution. The mixture was stirred during 15 min and water (350 ml) was then added. HCl was added if necessary to make the mixture slightly acid ($pH \approx 5$). The solid product (red powder) was filtered off, washed with water and dried over P_2O_5 in vacuum; yield 8.15 g (94%). For NMR analysis, the pure product was obtained by chromatography on silica gel using heptane/ethyl acetate (80/20) as eluent. ^1H NMR ($CDCl_3$): 0.99 (t, 3H, $\underline{CH_3}$), 1.51 (m, 2H, $\underline{CH_2}$–CH_3), 1.81 (m, 2H, $\underline{CH_2}$–CH_2–O), 4.03 (t, 2H, $\underline{CH_2}$–O), 6.42–7.79 (m, 7H arom.), 13.71 (s, 1H, $\underline{HO}$–*ortho* to –N=N–).

2.2. *4-Butoxy-2′-hydroxy-4′-(4-butoxybenzoyloxy)-azobenzene (2) [10]*

To a solution of compound **1** (6.15 g, 0.0215 mol) in CH_2Cl_2 (150 ml) was added dicyclohexylcarbodiimide (DCC) (5.32 g, 0.0258 mol), 4-pyrrolidinopyridine (0.382 g, 2.58 mmol) and 4-butoxybenzoic acid (4.17 g, 0.0215 mol). The resulting mixture was stirred at room temperature overnight. The solution was filtered and shaken successively with 200 ml of water, 200 ml of 5% aqueous acetic acid and 200 ml of water. The organic solution was then dried with Na_2SO_4. After evaporation of the solvent, the residue was recrystallized twice from toluene/ethanol (20/80) (orange crystals); yield 9.76 g (74%). ^1H NMR ($CDCl_3$): 1.00 (t, 6H, $2\underline{CH_3}$), 1.53 (m, 4H, $2CH_3$–$\underline{CH_2}$), 1.81 (m, 4H, $2CH_2$–$\underline{CH_2}$–O), 4.06 (m, 4H, $2\underline{CH_2}$–O), 6.88–8.15 (m, 11H arom.), 13.2 (s broadened, ~0.5H, corresponding to H in HO– *ortho* to –N=N– which did not exchange completely with D in $CDCl_3$). Elemental analysis: found, C 69.7, H 6.55, N 6.04; calc. for $C_{27}H_{30}N_2O_5$, C 70.1, H 6.49, N 6.06%.

2.3. *4-Butoxy-2′-(4-methacryloyloxybutoxy)-4′-(4-butoxybenzoyloxy)azobenzene (3)*

To an ice cooled solution of phenol **2** (1 g, 2.16 mmol), 4-hydroxybutyl methacrylate (0.43 g, 2.72 mmol) and triphenylphosphine (TPP) (0.85 g, 3.24 mmol) in CH_2Cl_2 (15 ml) was added dropwise diethyl azodicarboxylate (DEAD) (0.56 g, 3.24 mmol). The mixture was stirred at room temperature overnight. After evaporation of the solvent, the residue was purified by chromatography on silica gel using cyclohexane/ethyl acetate (90/10) as eluent. The product was recrystallized from absolute ethanol (yellow crystals); yield 0.9 g (69%). ^{1}H NMR ($CDCl_3$): 1.02 (m, 6H, 2 $\underline{CH_3}$–CH_2), 1.5–2.1 (m, 15H aliph.), 4.0–4.35 (m, 8H, 4 $\underline{CH_2}$–O), 5.57 (m, 1H, olefin. *trans* to COO), 6.13 (m, 1H, olefin. *cis* to COO), 6.9–7.8 (m, 7H, arom. of azobenzene), 7.9–8.2 (m, 4H, arom., O–ϕ–COO). Elemental analysis: found, C 69.3, H 7.03, N 4.61; calc. for $C_{35}H_{42}N_2O_7$, C 69.8, H 6.98, N 4.65%.

2.4. *Side-on azobenzene-containing mesogenic polymethacrylate (**I**)*

In a typical procedure, 0.85 g (1.41 mmol) of monomer **3** and 2.45 mg (1.41×10^{-2} mmol, 1%) of azo-bis-isobutyronitrile (AIBN) were dissolved in 5 ml of toluene. The solution was purged with an argon flow for 30 min to remove oxygen from the solution. Then the flask containing the solution was immersed in an oil bath with a preset temperature of 70°C. After 24 h of polymerization, the solution was poured into 50 ml of diethyl ether. The precipitated polymer **I** was purified twice by dissolution in a small amount of THF and precipitation into a large volume of diethyl ether. The polymer was dried in vacuum for 3 days; yield 0.3 g (35%). ^{1}H NMR ($CDCl_3$): 0.8–1.8 (m, 23H aliph.), 3.9 (m, 8H, 4$\underline{CH_2}$–O), 6.6–8.0 (m, 11H arom.). The signals from olefinic hydrogens have completely disappeared from the NMR spectrum. Molecular mass: M_n = 100 600 (degree of polymerization = 167), M_w = 168 200, polydispersity index I_w = 1.67.

3. Mesomorphic properties

The mesomorphic properties of polymer **I** and its monomer precursor **3** were studied by thermal polarizing optical microscopy and differential scanning calorimetry (DSC). For the microscopic observations, we used a Leitz Ortholux equipped with a Mettler FP82 hot stage and for the calorimetric study, a Perkin-Elmer DSC7.

For monomer **3**, a typical schlieren texture of the nematic phase appears around 85.5°C when cooling from the isotropic phase. Then at 53.5°C crystallization starts. Upon heating, melting is observed at 84°C and then isotropization at 85–86°C. The DSC thermograms of monomer **3** are shown in figure 1, and DSC results (transition temperatures and enthalpies) in the table. In the case of polymer **I**, the nematic phase appears upon cooling at 96.5°C with a more dense texture which remains without significant change down to room temperature. Upon heating, the nematic phase disappears between 93 and 98°C. The DSC results are given in figure 2 and in the table; a melting peak is given upon heating. Upon cooling, a glass forming phase is observed (T_g = 57.4°C) and there is no recrystallization peak. On analysing a sample which had been kept at room temperature overnight, the melting peak had reappeared. This means that the polymer recrystallizes slowly at room temperature and a glass-forming nematic phase is obtained when cooling rapidly (even at 5°C min^{-1}).

4. Photochemical properties

The photochemical properties of polymer **I** were studied at 22°C for solutions and thin films using a UV/visible spectrometer Unicam UV2 in the 200–600 nm

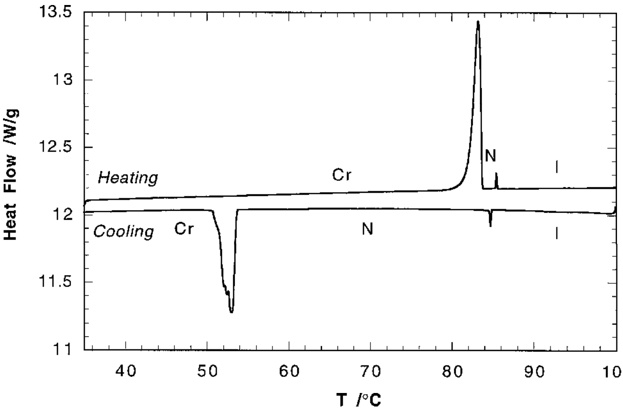

Figure 1. DSC thermograms of monomer **3** on heating and cooling at 1°C min^{-1}.

Table. Transition temperatures (°C) and enthalpies (in brackets) (J g^{-1}) obtained by DSC analysis.

Sample		g	Cr		N		I
Monomer **3** (1°C min^{-1})	Heating	—	•	83.2 (83.3)	•	85.5 (1.06)	•
	Cooling	—	•	53.1 (71.9)	•	84.8 (1.18)	•
Polymer **I** (5°C min^{-1})	Heating	—	•	73.8 (8.12)	•	94.9 (0.23)	•
	Cooling	•	—	57.4	•	90.8 (1.06)	•

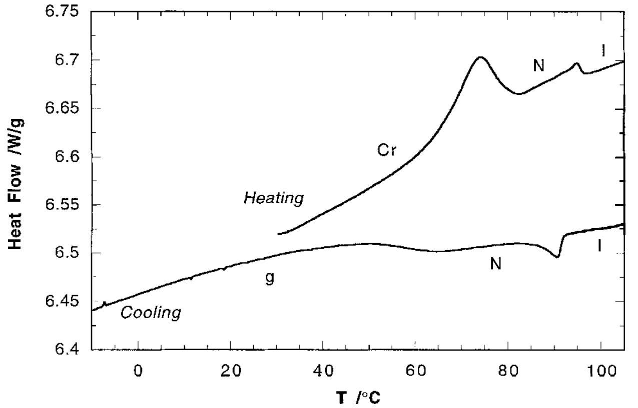

Figure 2. DSC thermograms of polymer **I** on heating and cooling at 5°C min^{-1}.

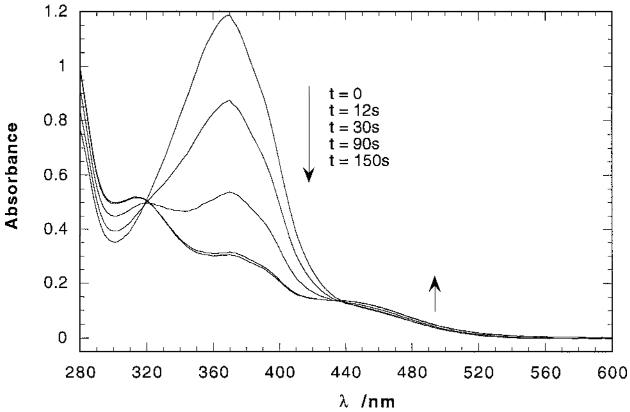

Figure 3. Variation of the UV/visible absorption spectra of polymer **I** in chloroform solution with irradiation time. Irradiation wave length is 365 nm.

spectral region. The solution was prepared using $CHCl_3$ (0.33 g l^{-1}) and kept in the dark overnight before further experiments. The measurements were performed using a 0.1 cm path length quartz cuvette. The thin film sample was prepared by spin-coating the polymer **I** (azopolymer) solution (30 mg ml^{-1} in toluene) on a polyimide treated glass plate. The glass plate coated with polyimide (PI) (the polyimide solution ZLI 2650 was purchased from E. Merck, Darmstadt) was rubbed. This treatment is known to promote a uniaxial planar alignment of mesogens. The azopolymer film was left in a vacuum oven at 88°C for 2 h. The thickness of the azopolymer film was estimated to be approximately 800 Å. Using a Mettler hot stage, the azopolymer film was then heated to 100°C for several minutes, cooled to 90°C for several minutes and allowed to cool to room temperature rapidly by removing it from the hot stage. The glass-forming nematic phase with a uniaxial planar alignment was thus obtained in the thin film sample. The latter treatments were done under yellow/orange light so that the desired uniaxial alignment would not be disturbed by light in the absorption region of the azopolymer. UV irradiation experiments were carried out at 365 nm with a UV lamp (non-polarized source). The lamp power was 30 mW and the intensity at sample level was 2.3 mW cm^{-2}.

The *trans*-azobenzene-containing polymer **I** as well as its monomer **3** show, in chloroform solution, a strong UV absorption band centred around 368 nm and a shoulder around 450 nm. For polymer **I**, the molar extinction coefficient ε was calculated to be 2.17×10^4 l mol^{-1} cm^{-1} at $\lambda = 368$ nm and 2.03×10^3 l mol^{-1} cm^{-1} at $\lambda = 450$ nm. These two bands are attributed to the π-π* and n-π* electronic transitions of the *trans*-azobenzene chromophore, respectively [11]. The polymer in solution undergoes a *trans–cis* photoisomerization of the azobenzene moiety upon irradiation at 365 nm in the π-π* absorption region. Figure 3 shows the absorption spectra of polymer **I** as a function of irradiation time. The intensity of the π-π* absorption band decreases with irradiation time, while that of the n-π* absorption band increases with irradiation time. These phenomena are similar to those observed in classical side group polymers [12].

We also characterized the photochemical behaviour of polymer **I** as a thin film. *Trans–cis* photoisomerization similar to that seen in solution is also observed (see figure 4). After 5.5 min of irradiation (at $\lambda = 365$ nm), the UV/visible absorption spectrum stops changing, which means that an equilibrium has been reached and the *cis*-form predominates in the azobenzene moieties in the polymer film. If the thin film sample is then kept in the dark and its UV/visible absorption spectrum is recorded after 1 day, 2 days, etc., the *cis–trans* thermal return can be clearly observed (figure 4). About 7 days in the dark are needed to restore the initial state, i.e. to recover the initial absorption spectrum.

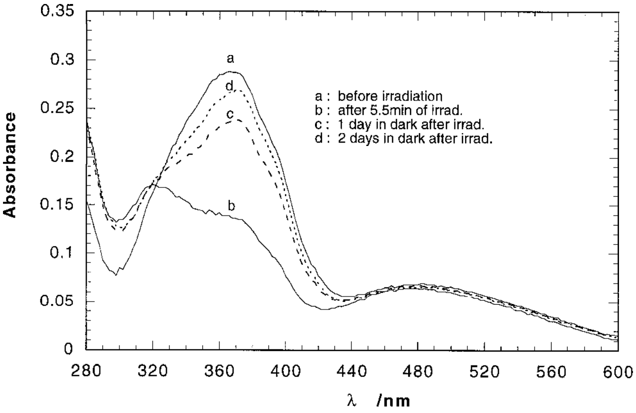

Figure 4. UV/visible absorption spectra of polymer **I** as a thin film before and after irradiation (365 nm) (curves a and b, respectively) and their variation with storage time in the dark (curves c and d).

5. Photochemically induced N–I phase transition

In our LC polymer, the mesogenic side groups contain three phenyl rings and their length-to-width ratio is rather large compared with classical mesogens which contain only an azobenzene moiety [13]. Thus it was important to check whether the kink at the first phenyl ring due to the *trans–cis* photoisomerization could induce the N–I phase transition in the polymer. We used a Reichert–Jung Polyvar Met polarizing microscope for optical observation in reflection mode. The azopolymer sample was prepared by spin-coating a polymer **I** solution ($30\,\mathrm{mg\,ml^{-1}}$ in toluene) on a silicon wafer. The silicon wafer was covered with rubbed PI, similarly to the glass plates in the preceding section. A well aligned glass-forming nematic phase was again obtained. The thickness of the azopolymer film was 805 Å, as measured by ellipsometry. A mask, consisting of several parallel stripes (width: 100 µm; distance between two stripes: 500 µm) was placed on the azopolymer film. The film sample was then exposed to UV light at $\lambda = 365$ nm for 25 min. Figure 5 shows the photomicrograph of the azopolymer film irradiated under these conditions. It demonstrates clearly that the irradiated parts (stripes) are isotropic. They are smooth and without texture. When rotating the sample platform between crossed polarizers, no change was observed in the irradiated stripes, while bright and dark aligned textures were successively observed in the non-irradiated parts.

We can conclude that in our side-on LC azopolymer, the N–I phase transition can be induced by the *trans–cis* photoisomerization of the azobenzene units. The printed stripe pattern is stable and remains unchanged in the dark after at least 40 days (time interval after which the sample was examined), while the thermal return from *cis*- to *trans*-isomers needs only about 7 days as discussed in the preceding section. This means that the polymer remains isotropic even after the thermal *cis–trans* return of the mesogens. When the sample was then heated to 60°C ($> T_g$), the stripes disappeared completely after about 30 min at 60°C and assumed the same texture as the non-irradiated parts, i.e. the aligned texture imposed by PI. These phenomena are similar to those observed in classical end-on LC azopolymers by the group of Ikeda [13]. It was proposed that after the *trans–cis–trans* cycle, the *trans*-form resulting from the thermal return has a random orientation, frozen in the absence of segmental motion of the polymer backbone below T_g. When the temperature of the irradiated sample is raised above T_g, the N phase is restored because of the reorientation process. These properties are useful in optical image storage. Therefore, like classical end-on LC azopolymers, the side-on LC azopolymer discribed here would also be an interesting system for optical image storage.

The N–I phase transition due to the *trans–cis* photoisomerization of the mesogenic units may be accompanied by conformational changes of the polymer chains which can induce, under some conditions, a macroscopic change in the sample dimensions: the material would undergo a reversible contraction/dilation upon irradiation. This photomechanical property has been explored with non-liquid crystalline main-chain azopolymers or polymer networks containing azobenzene moieties [14–16]. In [14], a semi-crystalline film was prepared with a polyimide containing azoaromatic groups in the backbone. The film contracted on heating and irradiation, due, in part, to the *trans–cis* isomerization in the amorphous regions of the film. However, the contraction and dilation yields were not controlled linearly by the isomerization fraction. In [15], a polyamide containing azobenzene

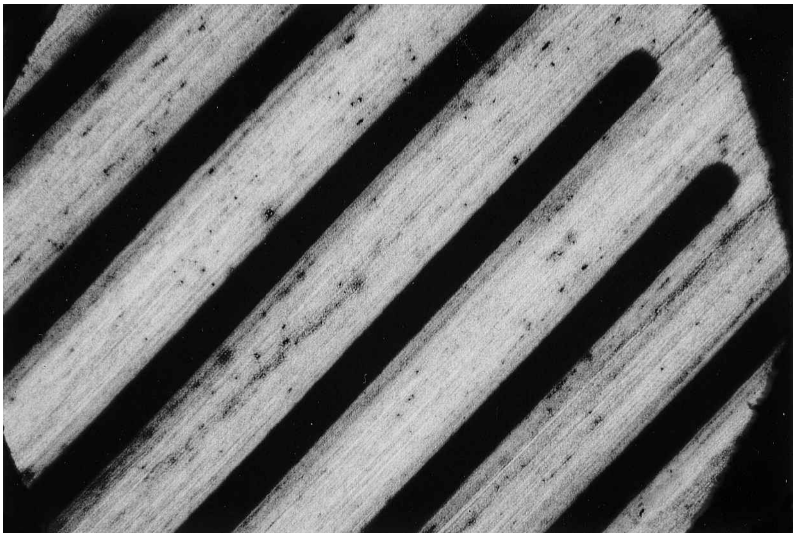

Figure 5. Photomicrograph of the azopolymer film on a PI treated wafer covered by a mask after irradiation (365 nm). The irradiated parts (stripes) are isotropic and the masked parts remain in the nematic phase with a birefringent uniaxial planar alignment.

groups in the backbone was used; the contraction and dilation seemed again to be inhomogeneous. Some poly(ethyl acrylate) networks crosslinked with 4,4-bis(dimethacryloylamino)azobenzene [16] have also been reported to have photomechanical properties. However the observed contraction amounted to only about 0.15–0.25%. Using our side-on liquid crystalline azopolymer, we think that larger and more homogeneous contraction and dilation may be obtained upon irradiation with an appropriate design of the polymer system. This is now under investigation.

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