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Synthesis, spectroscopic characterization and alignment of novel azobenzene-containing monomers

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A series of novel bifunctionalized photochromic monomers were synthesized, focusing on those with polymerizable acrylic/methacrylic groups attached to both ends of an azobenzene core via flexible spacers. The phase behaviour of the monomers was investigated using DSC, polarizing optical microscopy and X-ray diffraction. The change in UV-vis absorbance of the monomers under illumination with non-polarized/polarized UV light was studied for both solutions and thin films; also studied was its relaxation in the dark. On illumination with LPUV light, in-plane reorientation of the molecules normal to the polarization of the exciting UV light, and aggregation of the molecules in the films, were found.

1. Introduction

The most attractive feature of azobenzene-based polymers within LCD technology is their ability to undergo reorientation under irradiation with linearly polarized light, revealing itself macroscopically as, for example, photo-induced birefringence [1–3]. Linearly polarized light can induce the reorientation of azobenzene groups through photochemical *trans–cis–trans* isomerization [4–7].

Azobenzene and its derivatives are characterized by the reversible transformation, from the generally more stable *trans*- to the less stable *cis*-form upon irradiation with UV light. The intense absorption band at 320 nm, due to $\pi \rightarrow \pi^*$ transition of the *trans*-isomer, decreases during such an isomerization, while the absorption maximum at 430 nm relating to the $n \rightarrow \pi^*$ transition increases. The *cis*-isomer thermally relaxes back to the *trans*-isomer [4–12]. Numerous repetitive *trans–cis–trans* isomerization cycles result finally in the reorientation of the azobenzene photochromic groups to a position in which they do not absorb more light quanta, i.e. with the long axis of the aromatic core perpendicular to the electric vector of the illuminating light (in-plane orientation) or along the light propagation direction (out-of-plane orientation) [1, 8–10, 12].

Polymers containing azobenzene moieties in the side chains have recently become the subject of intensive investigation [9–20]. It is noteworthy that the slowest photoisomerization has been observed for monomers which increase the rigidity of the chain. As compared with side chain polymers, photo-orientation in cross-linked azo dye polymer systems has received less study, although such systems are interesting for applications in optical information technologies both as thin films [21] and as spread networks penetrating, for example, a liquid crystal structure (the polymer-stabilized liquid crystals, PSLCs) [10]. We should note here that the photochromism of azo groups in polymers is influenced by the nature of the polymer matrix and by the presence or absence of flexible spacers [8]. The latter should decouple molecular motions of the photochromes from the polymer network, thus making conformational changes of the azobenzene core easier and faster.

In this work, we report the synthesis and photochromism of novel bifunctionalized monomers, in which polymerizable acrylic or methacrylic groups are attached to both ends of an azobenzene core via flexible spacers, each containing six methylene groups. Both ether- and ester-type linkages of the spacers to the central core have been investigated. The monomers synthesized should serve as intermediates for cross-linked polymer thin films. The preparation of such polymer films and the study of their photochromism is in progress and will be published separately.

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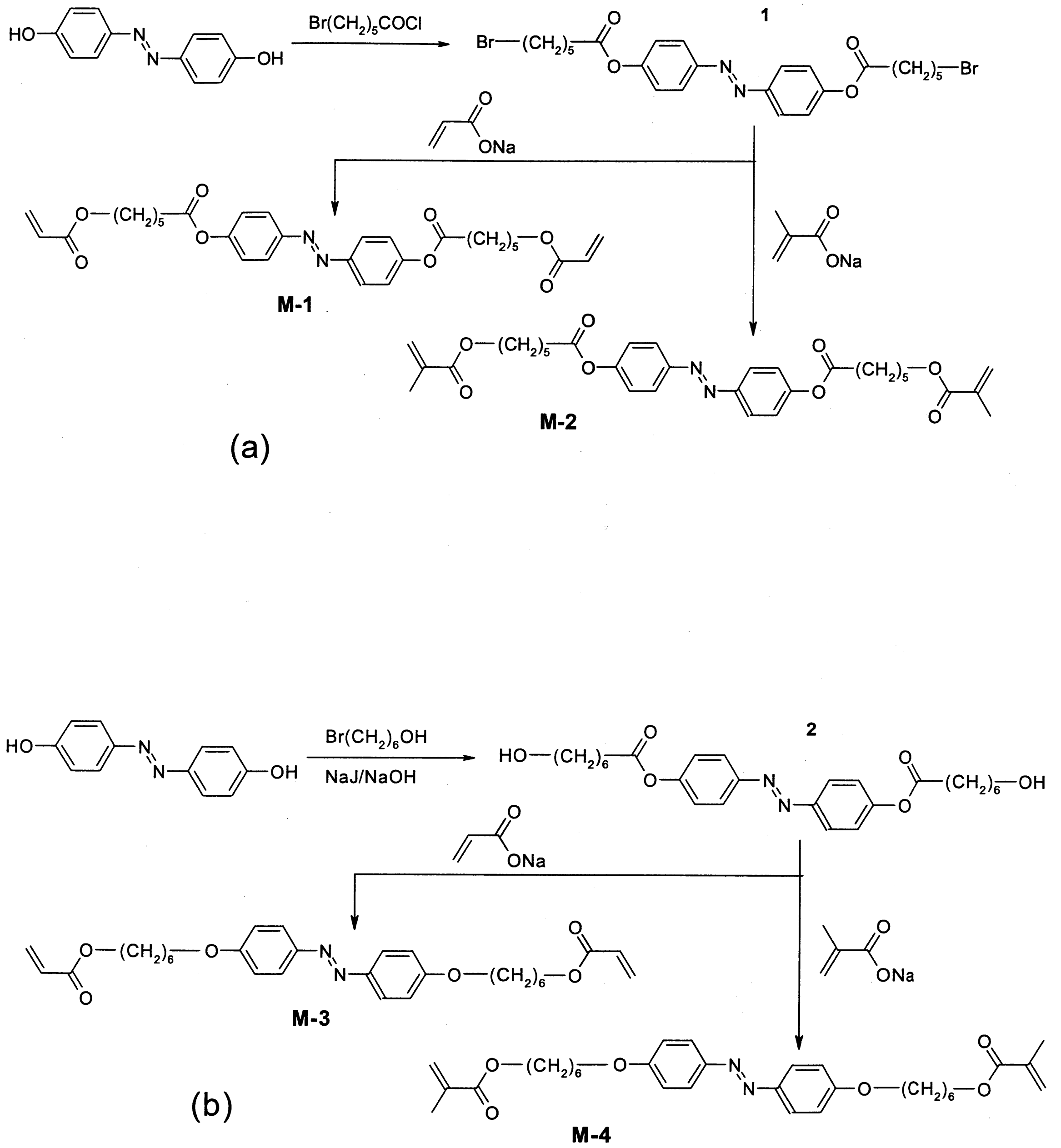


Figure 1. Synthetic route for (*a*) monomers **M-1**, **M-2** and (*b*) monomers **M-3**, **M-4**.

2. Experimental

The synthetic route used to obtain the monomers is shown in figure 1.

2.1. *Materials*

The starting materials including 4-nitrophenol, acryloyl chloride, methacryloyl chloride, sodium acrylate, sodium methacrylate, 6-chlorohexan-1-ol, 6-bromohexanoyl chloride, 1,3-dimethyl-2-imidazolidinone, toluene, triethylamine and THF were purchased from Sigma-Aldrich. 1,3-Dimethyl-2-imidazolidinone was distilled over CaO immediately before using.

2.2. *Preparation of 4- azophenol*

A mixture of KOH (50 g, 760 mmol.), 4-nitrophenol (10 g, 72 mmol) and 10 ml water was heated and held at 120°C for 1 h. The temperature was then raised slowly to 195–200°C, giving a vigorous reaction leading to a brown viscous liquid with a large number of bubbles.

After the reaction was completed, the reaction mixture was dissolved in water, to give a dark red solution, which was then acidified to pH 3 with conc. HCl. The product was extracted with ether, dried over Na_2SO_4 and the solvent removed *in vacuo*. The product was recrystallized from H_2O/ethanol (50/50) [20]; yield 43%, m.p 214°C.

2.3. *Synthesis of 4,4′-azobis-6-bromohexanoyloxybenzene (1)*

Five methylene group spacers were added to each end of 4-azophenol via an esterification process [22]. Compound **1** was obtained by adding a solution of 6-bromohexanoyl chloride (2.4 mol. eq.) dropwise to a solution of 4-azophenol and triethylamine (2.4 mol.eq.) in dry toluene, followed by agitation for 6 h. The solvent was evaporated, and the product dissolved in ether. This solution was washed with dil. H_2SO_4, water, sodium bicarbonate and water, then dried over $MgSO_4$. The solution was filtered through a mixture of silica gel and alumina, the solvent removed, and the product recrystallized from methanol; yield 63%. IR (cm^{-1}): (C=O) 1751, (C=C Ar.) 1600, 1589. H^1 NMR. ($CDCl_3$) δ 7.9 (m, 4H) Ar., 7.2–6.9 (m, 4H) Ar., 3.4 (t, 4H), 2.6 (t 4H), 1.9 (m, 4H), 1.8 (m, 4H), 1.6 (m, 4H). DSC: Cr_1 77 Cr_2 82.I 103.

2.4. *Synthesis of 4,4′-azobis-6-acryloyloxyhexanoylbenzene (M-1) and 4,4′-azobis-6-methacryloyloxyhexanoyloxybenzene (M-2)*

Compound **1** was treated with 4 equiv. of sodium acrylate (for **M-1**) or sodium methylacrylate (for **M-2**) in DMEU for one week at room temperature. The reaction mixture was poured into ice, melted and filtered; the solid was dissolved in ether, dried over $MgSO_4$ and chromatographed on silica, using 5% ethyl acetate in toluene as eluant; yield 75% for **M-1** and 85% for **M-2**. **M-1**. IR (cm^{-1}): (C=O) 1752, 1712, (H_2–C=CH–) 1634, (C=C Ar.) 1600, 1589, (N=N) 1493. H^1 NMR ($CDCl_3$) δ: 7.9 (m, 4H), 7.2 (m, 4H), 6.4 (d, 2H), 6.2 (q, 2H), 5.85 (d, 2H), 4.2 (t, 4H), 2.6 (t, 4 H), 1.8–1.5 (12H). **M-2**. IR (cm^{-1}): (C=O)1747, 1710; (H_2–C=CH–) 1639; (C=C Ar.) 1589. H^1 NMR ($CDCl_3$) δ: 7.9 (m, 4H), 7.25 (m, 4H), 6.1 (d, 2H), 5.6 (d, 2H), 4.2 (t, 4H), 2.6 (t, 4 H), 1.8–1.5 (18 H).

2.5. *Synthesis of 4,4′-azobis-6-hydroxyhexyloxybenzene (2)*

Six methylene group spacers were added to each end of 4-azophenol via an etherification process [23]. Compound **2** was obtained by first dissolving 1.76 g (0.04 mol) of sodium hydroxide in 2-butanone (105 ml). Then 4.75 g (0.02 mol) of 4-azophenol, 6.59 g (0.04 mol) of sodium iodide, and 6.0 g (0.04 mol) of 6-chlorohexanol were added, and the mixture was heated at 60°C for 10 h. The solvent was removed *in vacuo*; the residue was washed with NaOH (300ml, 0.4M), several times with water, and recrystallized from ethanol; yield 70%, m.p 151°C (150°C lit. [24]).

2.6. *Synthesis of 4,4′-azobis-6-acryloyloxyhexyloxybenzene (M-3) and 4,4′-azobis-6-methacryloyloxyhexyloxybenzene (M-4)*

Compound **2** (5 mmol) was added to a solution of 12 mmol *N*, *N*-dimethylaniline in 40 ml dry dioxane. Then 12 mmol acroyl chloride (for **M-3**) or methacroyl chloride (for **M-4**) was added slowly over for about 30 min. The reaction mixture stirred for 2 h at 50°C to give a homogeneous solution. The reaction mixture was then poured into a vigorously stirred mixture of water (50 ml), ice (30.0 g), and conc. HCl (0.3 ml). The yellow precipitate was filtered, washed with 200 ml water, and recrystallized from acetone /methanol. **M-3**. IR (cm^{-1}): (C=O) 1717, (H_2–C=CH–) 1634, (C=C Ar.) 1601, 1589. H^1 NMR ($CDCl_3$) δ: 7.9 (m, 4H), 7.0 (m, 4H), 6.4 (d, 2H), 6.1 (q, 2H), 5.8 (d, 2 H) 4.2 (t, 4H), 4.1 (t, 4H) 1.9–1.5 (16 H). M.p. 106°C. **M-4**. IR (cm^{-1}): (C=O) 1716, (H_2–C=CH–) 1637, (C=C Ar.) 1601, 1589. H^1 NMR ($CDCl_3$) δ: 7.9 (m, 4H), 7.0 (m, 4H), 6.1 (q 2H), 5.55 (d 2 H), 4.2 (t 4H), 4.0 (t 4H), 0.93–1.9 (22 H). M.p. 65°C.

2.7. *Characterization and measurements*

H^1 NMR spectra were obtained with a JEOL 400 MHz NMR spectrophotometer; IR spectra were obtained with a Perkin-Elmer One Fourier transform spectrophotometer; UV-vis spectra for solutions and films were recorded using a Perkin-Elmer Lambda 900 spectrophotometer. A USH-250BY UV-lamp with a 350 nm filter was used for LPUV-light illumination. Thermal properties were studied using a Perkin-Elmer DSC Pyris Diamond at a heating rate of 10°C min^{-1}. X-ray scattering curves were measured from Ø2 mm capillary samples by a modified STOE STADI 2 diffractometer using CuK_α radiation and a PSD linear position scanning detector.

2.8. *Thin film preparation*

Compound **M-4** was dissolved in toluene at concentration of 3 wt%. For spin-coating, the substrate was spun at 1500 rpm for 6 s, then at 3000 rpm for 60 s; it was dried in a vacuum oven at 50°C for 24 h to give a film of thickness 30–40 nm estimated by a $Dektak^3$ ST surface profile measuring system. Solutions for isomerization investigations were prepared in THF at concentrations 6.45×10^{-5}M (**M-1**), 9.6×10^{-5}M (**M-2**), 5.51×10^{-5}M (**M-3**) and 7.91×10^{-5}M (**M-4**).

3. Results and discussion

3.1. *Phase behaviour of the monomers*

The monomers **M-3** and **M-4**, with ether linking groups between the azobenzene core and spacers, show no polymorphism, melting from the crystal to isotropic liquid at 105 and 65°C, respectively. **M-3** has already been reported, but neither its synthesis nor phase transitions were given [25]. In contrast, the monomers **M-1** and **M-2**, with spacers attached to the photochromic core via ester groups, show more complicated phase behaviour. Thus, for the methacrylic monomer **M-2**, a phase transition to another crystalline phase was detected at 70°C prior to melting at 87°C. The most interesting mesomorphic behaviour was observed, however, for the acrylic monomer **M-1**; this compound shows the following phase transition upon heating, Cr~95°C I; and on cooling, I (between 75 and 70°C) SmX. In the next heating, from the SmX at about 75°C to I; a phase transition between two crystalline modifications may occur below 68.5°C. Figures 2 and 3 show the X-ray patterns obtained for **M-1** on cooling from the I phase and reheating from the SmX phase, respectively. The SmX phase of **M-1** was characterized by an orthogonal monolayer packing of the molecules in smectic layers, but with a complicated (non-hexagonal) intralayer packing of the molecules along the layer plane. A single small angle X-ray scattering peak corresponding to the calculated length of the molecule supports the smectic structure, while the intralayer packing gives rise to several wide angle X-ray scattering peaks. In any case, the SmX is not a crystalline phase because no peaks in the intermediate range of the scattering angle, $4°<2\Theta<18°$, are present. In general, the X-ray pattern corresponds to a highly ordered orthogonal 'crystal smectic' phase. The molecular model of monomer **M-1** (figure 4) gives a calculated length of 35.5 Å, corresponding to the distance between two edge vinyl hydrogens, and it is not surprising that the interlayer distance in the smectic phase at 70°C is somewhat shorter, d=33.5 Å. There is reasonable agreement between the molecular length and layer spacing.

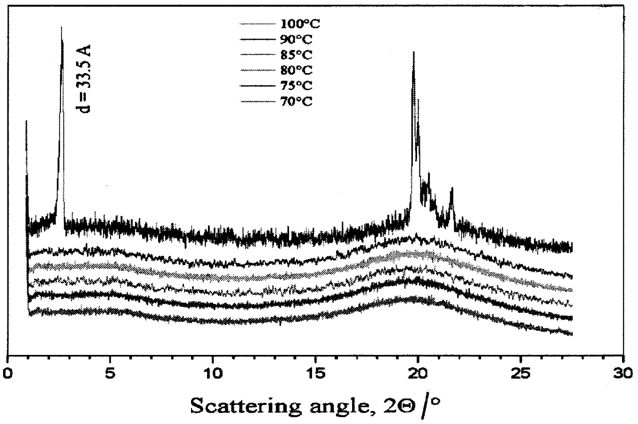


Figure 2. X-ray patterns for **M-1** on cooling from the isotropic phase.

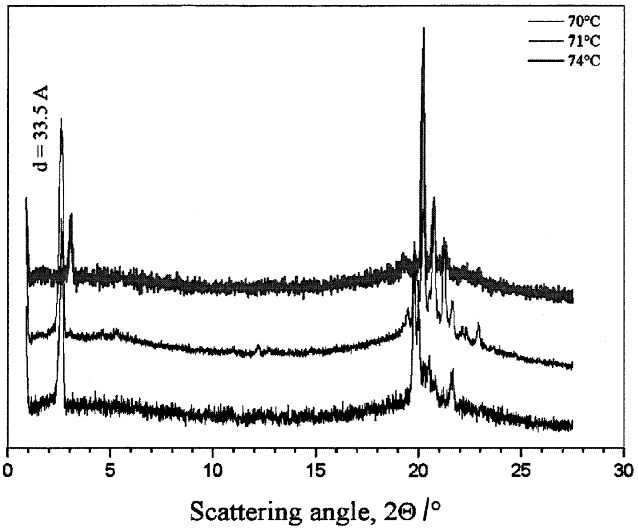


Figure 3. X-ray patterns for **M-1** on heating from the smectic phase.

The texture observations of the intermediate phases under polarizing optical microscopy, associated with the transitions on heating at 70 and 77°C which correspond to those observed at 69 and 75°C in the DSC, in

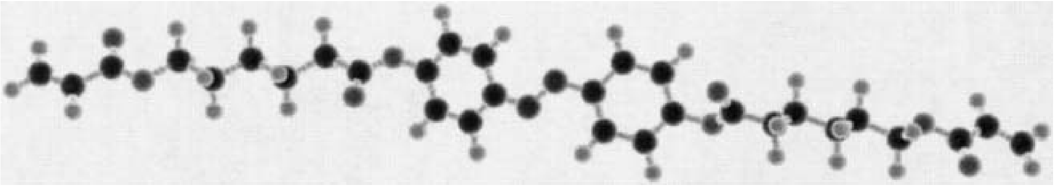


Figure 4. The molecular model of monomer **M-1**.

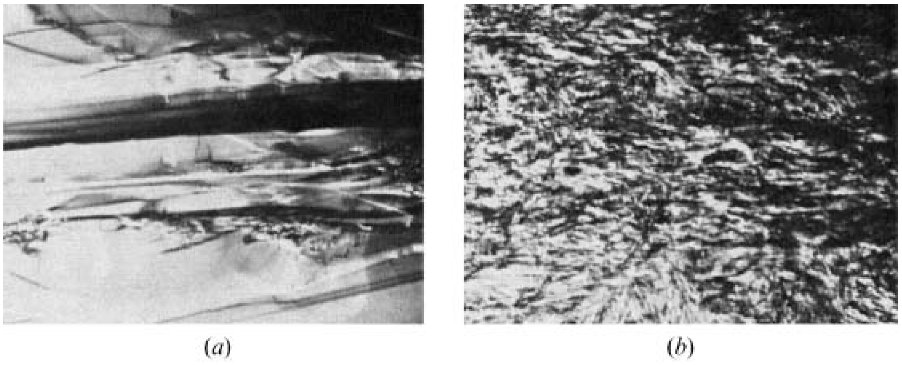


Figure 5. Textures observed for **M-1** on cooling: (*a*) at 70°C, (*b*) at 68°C.

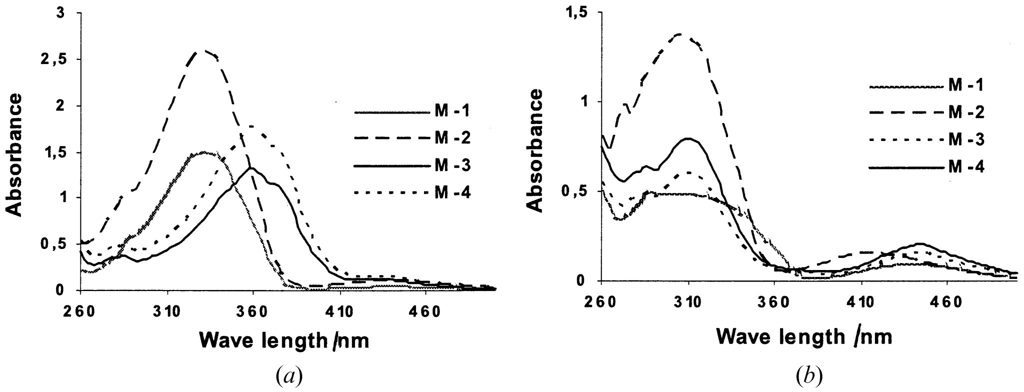


Figure 6. UV-vis spectra of the monomers in THF solution (*a*) before illumination and (*b*) after UV illumination.

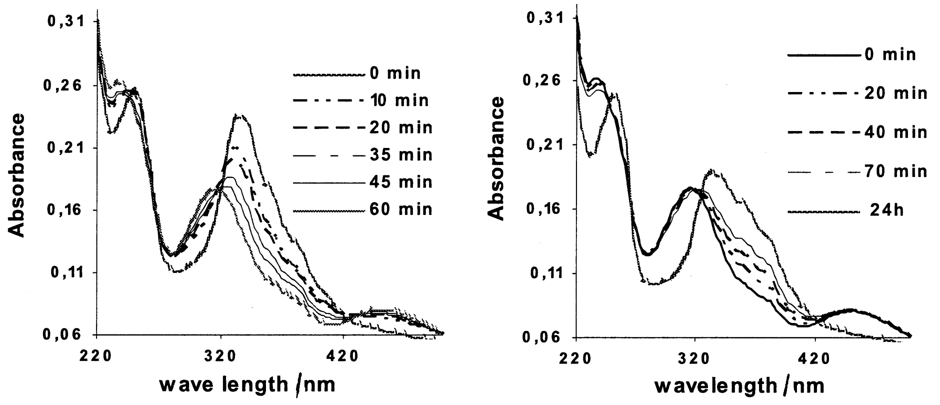
combination with the results from X-ray diffraction which reveal the crystalline modification in this temperature range, confirm the transition between crystalline modifications. The isotropic phase is obtained at 90°C and persists to 70°C when the phase transition to the highly ordered smectic X phase occurs, followed by a fast transition to the ordered crystalline phase at 68°C corresponding to the transition at 67°C in the DSC. The former clears on reheating at 73°C, while the latter becomes isotropic at 90°C. Slow transitions occur at 50 and 38°C, which appear also to be crystalline modifications corresponding to the fine structure in the DSC curves. Figure 5 shows representative optical textures for **M-1**.

To summarize, ester linkages of the spacers to the azobenzene core favour an enhanced polymorphism in bifunctionalized azo dye monomers (**M-1**, **M-2**), as compared with ether linkages (**M-3**, **M-4**).

3.2. *Photochromism of the monomers in solution*

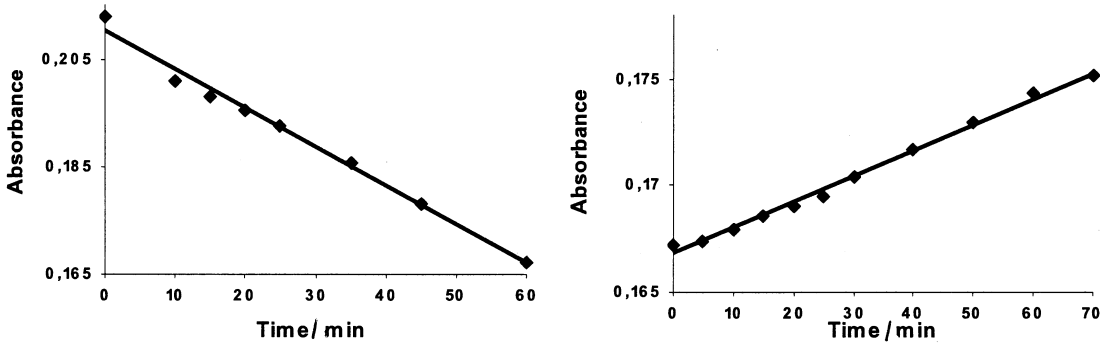
The photo-induced *cis-trans* isomerization of single monomer molecules in solution was undertaken, and the change in UV-vis absorption monitored. The UV-vis spectra of the four monomers are shown in figure 6; intense absorption maxima corresponding to the π→π* transition (*trans*-isomer) are observed at 332 nm for **M-1** and **M-2**, but at 359 nm for **M-3** and **M-4**. Such a shift towards longer wavelength can be explained by the change in the *para*-substituents on both sides of the azobenzene core, from the electron-withdrawing carboxylic groups, *R*–COO– (**M-1**, **M-2**) to the electron-donating ether groups, *R*–O– (**M-3**, **M-4**). The effect is much less pronounced in the absorption of the corresponding *cis*-isomers, the maxima being at 440 nm for **M-1** and **M-2**, but at 450 nm for **M-3** and **M-4**.

The absorption relating to the π→π* transition in the *trans*-isomer decreases after illumination under 365 nm UV light (45 s), and undergoes a blue shift (303 nm non-symmetric band for **M-1** and **M-2**, 311 nm for **M-3** and **M-4**). Conversely, the weak absorption band due to the n→π* transition in the *cis*-isomer (at 440 nm for **M-1** and **M-2**, 450 nm for both **M-3** and **M-4**) increases. Similarly, the intensity of the shoulder π→π* transition (*cis*-isomer) increased with a small blue shift (294 to 288 nm for **M-1** and 290 to 274 nm for **M-2**). The



(*a*) (*b*)

Figure 7. Changes of the UV-vis spectra of an **M-4** film (*a*) under UV illumination and (*b*) during the dark relaxation.



(*a*) (*b*)

Figure 8. Change in the absorbance (maximum value) for the π→π* transition band (*a*) on UV illumination, (*b*) during dark relaxation.

corresponding absorption appeared as a separate maximum at 286 nm, its intensity increasing under UV illumination. This indicates a *cis-trans* isomerization induced by the UV light.

Finally, we should note that the *cis*-isomers of the monomers in solution show remarkable stability: no change was observed in the spectra for over one hour in the dark.

3.3. *Photochromism of the monomer M-4 in thin films*

The acrylic monomer **M-4** was selected for detailed investigation of the photo-induced reorientation in thin films because of its superior reorientation. UV-vis spectra of the spin-coated monomer films are presented in figure 7. As seen in figure 7 (*a*), the absorption of a virgin film is qualitatively similar to that of the monomer solution, figure 6 (*a*), with the π→π* transition peak of the *trans*-isomer shifted slightly towards shorter wavelengths (332 nm in the thin film, as compared with 359 nm in solution). Some 'steps' can be observed, however, on the long wavelength side of the peak, and may suggest the formation of molecular aggregates [18].

In a similar fashion to other azobenzene-based chromophores, the excitation of the π–π* band with non-polarized UV light results in *trans-cis* isomerization, so that the π–π* band absorption maximum decreases and shifts towards shorter wavelengths, reading 317 nm after 1 h of illumination (365 nm, 6 W). In turn, the n–π* band absorption at 450 nm grows substantially, indicating the formation of the *cis*-isomer, figure 7 (*a*). The isobestic points at ~322 and ~424 nm give evidence that only one photoisomerization process is involved.

Switching off the UV illumination stops the photo-induced *trans-cis* isomerization and allows the molecular relaxation to the stable *trans*-isomer to occur. The change in the UV-vis absorption during the dark relaxation, as shown in figure 7 (*b*), indicates a complete reversal to that originally seen, figure 7 (*a*), with an increased maximum of the π–π* band absorption being shifted back to longer wavelengths (from 317 to 332 nm), and with a decreasing or even vanishing n–π* band absorption at ~448 nm. However, some additional features appear again at 360 and 383 nm, in contrast to the spectra of the pure *cis*-isomer, and no isobestic point can be clearly observed. These observations provide strong evidence for aggregate formation in the thin film, in contrast to the behaviour of the monomer solution.

Both a reduction of the absorbance at the π–π* band maximum under UV illumination and its backward growth during dark relaxation, as shown in figure 8 (*a*) and 8 (*b*), respectively, can be fitted with a straight line, thus indicating that the *cis-trans* isomerization in the monomer is far from complete. This is confirmed also by the data shown in figures 7 (*a*) and 7(*b*), which reveal that complete isomerization/relaxation takes 24 h or more. We should note here that the *cis-trans* relaxation can be efficiently accelerated by illumination within the n–π* band, as, for example, by daylight insulation.

Light absorption in azobenzene dyes is angularly dependent and therefore can be affected by the light polarization. Before studying the photo-orientation with polarized light, we had to distinguish first between the in-plane and out-of-plane orientation. The latter can be induced using non-polarized UV light, since the photochromic molecules should rotate to the position with their long axes along the propagating light direction. The film illuminated with oblique non-polarized light at the incident angle of 45° for 15 min shows no photo-induced dichroism orthogonal to the film, and the polarized UV-vis spectra show optical isotropy. This allows us to exclude the possibility of any photo-induced out-of-plane orientation.

To study the photo-induced in-plane orientation of the **M-4** film, it was exposed to linearly polarized UV light (20 mW cm^{-2}). The polarized UV-vis spectrum was recorded both parallel and perpendicularly to the polarization of the pumping LP light. The anisotropy of the films was checked before and after each irradiation. The film showed no anisotropy before irradiation with LPUV light. After irradiation, a remarkable change in the absorbance of the π→π* transition at 320 nm was observed, and the film exhibited UV-vis dichroism. The absorbance in the direction parallel to the pumping light, $A_{\|}$, showed a decrease relative to the virgin film, while the absorbance in the perpendicular direction, $A_{\perp}$, increased: see figure 9. This gives conclusive proof for the reorientation of the molecules normal to the polarization of the exciting UV light. It is noteworthy that if we compare the parallel and perpendicular spectra with the isotropic one, the increase of the perpendicular absorbance ($\Delta A_{\perp}$) is approximately equal to the decrease of the parallel absorbance ($\Delta A_{\|}$) at any irradiation dose: $\Delta A = A(t) - A(0\,\text{min})$. Thus, the average value of absorbance, $A_a = (\Delta A_{\|} + \Delta A_{\perp}) \approx 0$ remains constant over time.

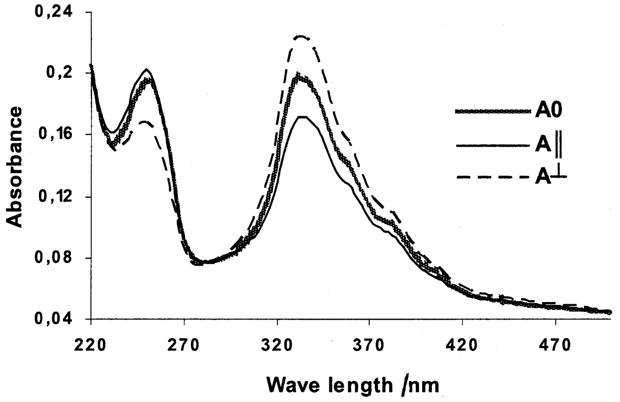


Figure 9. UV-vis spectra for **M-4** film irradiated for 20 min.

One can conclude from the data shown in figure 10 that the concentration of the chromophores oriented perpendicularly increases insofar as the concentration of those oriented in parallel decreases. This provides evidence supporting the regular reorientation from the parallel direction to the perpendicular within the film plane. This conclusion could be related to the initial order of the film characterized by a preferred in-plane orientation of the azobenzene groups, whereas the long axes are randomly distributed in this plane. In combination with the LPUV light it produces an in-plane ordering [26]. This conclusion virtually coincides with the absence of out-of-plane reorientation, when the film is illuminated with oblique non-polarized light.

To investigate the dichroic behaviour of the film, the *DR* (dichroic ratio) was calculated from the equation, $DR = (A_{\perp} - A_{\|})/(A_{\|} + A_{\perp})$ [27], and evaluated versus the exposure time. As shown in figure 11, the *DR* increased with increasing illumination time. Although the relative rate of change in the DR values decreased, no definite saturation point of *DR* was observed during 1 h.

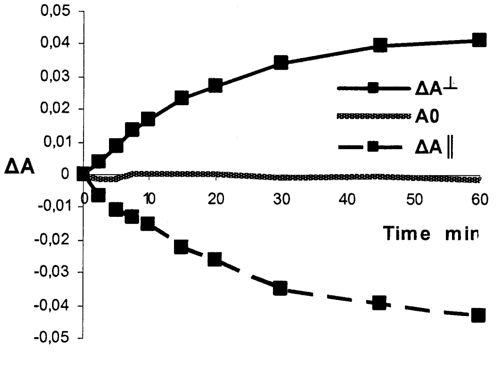


Figure 10. Change of the average absorbance of the film, A_0, and those parallel ($\Delta A_{\|}$) and perpendicular ($\Delta A_{\perp}$) to the polarization of the pumping light.

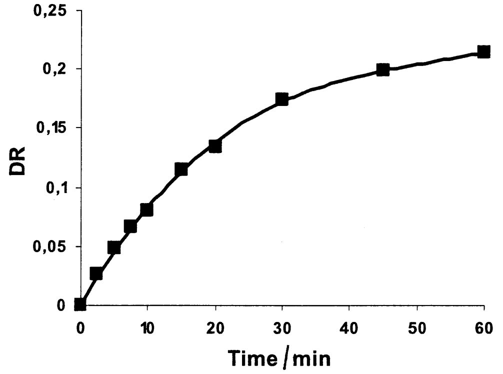


Figure 11. Dichroic ratio of the film, as a function of irradiation time.

4. Conclusions

Ester linkages of the spacers to the azobenzene core favours an enhanced polymorphism in bifunctionalized azo dye monomers (**M-1**, **M-2**), as compared with ether linkages (**M-3**, **M-4**). A monotropic LC phase (smectic X) was characterized by X-ray analysis on cooling at 70°C, with an interlayer distance in the smectic phase $d=33.5$ Å; this corresponds to slightly less than the calculated molecular length of **M-1**. *Cis*-*trans* isomerization can be induced in solutions of monomers using UV light, and the *cis*-isomers of the monomers in solution are remarkably stable.

A virgin thin film of monomer shows optical isotropy. On illumination using LPUV light an induced in-plane photo-reorientation occurs perpendicular to the *E*-vector of the activating light. The out of plane reorientation was excluded in this typical experiment. No definite saturation point of the dichroic ratio, *DR*, was achieved during 1 h.

The synthesized monomers are interesting materials for the preparation of crosslinked polymer films for application as photo-orienting layers, and as polymer stabilizers in LCD technology.

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