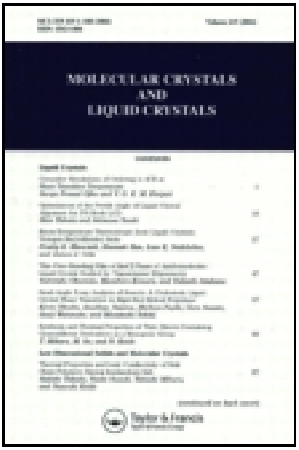

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Photochemically Induced Modification of Polymer Dispersed Liquid Crystals with Photochromic Stilbene. Photoreactions in Liquid Crystals (Part 8)

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Photochemically Induced Modification of Polymer Dispersed Liquid Crystals with Photochromic Stilbene. Photoreactions in Liquid Crystals (Part 8)

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Photosensitive polymer dispersed liquid crystals (PDLC) were prepared using the nematic mixture E-5 doped with 2 wt-% photochromic stilbene dye in a gelatin binder. The stilbene undergoes E-Z photoisomerization on irradiation. The change of the configuration of dopants perturbs the liquid-crystalline order and the clearing point of the mixture is lowered slightly. Irradiating the stilbene-doped gelatin PDLC, the preferred director orientation of the dopants is destroyed. Therefore, the optical properties as well as the Volta potential ΔV of stilbene-doped PDLC are changed. Differences have been observed between hot- and cold-dried PDLC films.

Keywords: E-Z photoisomerization, gelatin binder, PDLC, stilbene, Volta potential

INTRODUCTION

In recent years systems of low molecular weight liquid crystals dispersed in polymer binders (polymer dispersed liquid crystals, PDLC, or nematic droplet films) have met with growing interest.[1–4] PDLC combine the advantages of low molecular weight liquid crystals, such as good orientational behaviour and fast response, with typical properties of polymeric materials, as e.g. providing self-supported layers. This opens up a variety of different applications, e.g. light shutters, displays, optical nonlinear materials and special membranes.[5–8] Electric fields influence the orientation of liquid crystals in the droplets. Thus, the optical properties of PDLC can be switched electrically between an opaque and a transparent state.

Several polymers, such as epoxies, polyurethanes, polycarbonates or gelatin have been used as the polymer matrix of PDLC. The use of gelatin binders offers the interesting opportunity to obtain PDLC either with or without preferred orientation of the liquid crystal droplets in the film. This behaviour depends on different thermal preparation methods of the PDLC-gelatin films.[9] It is known that in cold–dried gelatin layer the mesogenic molecules in the separate LC phase are preferably arranged in a homogeneous orientation.[10]

Mesogenic properties of liquid crystalline materials are highly sensitive to added substances. Incorporation of a solute into a liquid crystalline matrix leads to a change of the order in the surrounding of the solute and to the orientation of the guest molecules. Both processes depend on the form anisotropy and the differences in shape between the host and guest molecules. It has been shown recently that the liquid crystalline order may influence the photoreactivity of solutes[11-13] and that the liquid crystalline order may be modified photochemically.[11] Thus, the light-induced change of the geometrical shape of a small amount of guest molecules causes a photochemically triggered phase transition[14-17] or local disruption of order. Such phase transitions or variations of supramolecular structure cause a drastic alteration of the optical properties of the whole sample.

Upon irradiation, stilbene derivatives undergo E-Z photoisomerization in nematic guest-host mixtures,[16] as well as azobenzene derivatives or cinnamates.[18,19] Thus, the rod-like shape of the E-isomer of stilbene is switched into the more crooked Z-isomer with modified geometrical shape, planarity as well as polarity.

The light-induced modification of the photochromic moiety as well as the order of the mesophase can be determined by absorbance spectroscopy and by measuring the Volta potential differences.[20] The measurement of Volta potentials and their differences ΔV is a very sensitive method to determine spatial reorientation processes within a sample, since ΔV only depends on the resulting dipole moment μ in an electrically neutral sample [$\Delta V = f(\mu)$].[21-25] Thus, by measuring $\Delta V/T$, phase transitions can be detected in films of low molecular weight liquid crystals,[21-23] liquid crystal polymers,[24] and even in polymer dispersed liquid crystals.

In this paper we describe the photochemically induced effects on the optical properties of the liquid crystalline guest-host mixture of a stilbene derivative in a nematic liquid crystal as well as in PDLC films containing the same mixture in gelatin.

EXPERIMENTAL

The E-4-N,N-dimethylamino-4′-methoxystilbene 1, m.p. 176°C, has been recrystallized twice from a small amount of ethanol. The guest-host mixture consisting of 2 wt-% of stilbene 1 in the liquid crystalline mixture E-5 (Merck) is nematic at room temperature.

For the preparation of the gelatin-PDLC an alkaline-digested gelatin was diluted to give a 10% solution as described in References 9 and 26. 5 ml of this solution were heated to 50°C and 0.5 ml of E-5 or 0.5 ml of the mixture E-5/stilbene 1 added dropwise and mixed in a high-speed mixer to give a highly dispersed emulsion.

This emulsion was applied to a glass support to form a thin layer and dried under hot or cold conditions. The layer was allowed to solidify in the cold drying regime at 4°C and was dried in an air current at the same temperature afterwards. In the hot drying method of preparation the layers were dried at 45–50°C under a heating lamp without cooling and setting. The thickness of the layers was about 60 μm.

Irradiations were carried out by using a mercury high pressure lamp HBO-100 (Narva). An IR-filter, quartz lenses and a monochromator for selecting the wavelength of 365 nm (metal interference filter, Schott & Gen. Jena) were arranged on an optical bench between lamp and sample.

UV/VIS absorption spectra were recorded on a Specord M-40, VEB Carl-Zeiss-Jena.

The Volta potential differences (ΔV) were determined by means of the ionization method. In our case we used ^{241}Am as probe (sond) and an annealed brass plate as counter electrode.[20]

RESULTS AND DISCUSSION

The phase behaviour of the nematic mixture E-5 is changed when E-4-N,N-dimethylamino-4′-methoxystilbene 1 is added. Thus the clearing point of the pure mixture is increased from 50.5°C to 52°C at a content of 2 wt-% of 1.[27] Both thermal microscopy and the measurement of the Volta potential differences ΔV unanimously indicate this increase in phase transition temperature of doped E-5. It seems to be unusual to stabilize a mesophase by doping a liquid crystalline mixture with nonmesogenic compounds. However, it has been shown recently that the degree of order of the cyanobiophenyls is increased on adding polar substances.[28,29]

Isotropic Solution

The E-4-N,N-dimethylamino-4′-methoxystilbene 1 represents the photoreactive component in the guest-host mixture. On irradiation the stilbene 1 undergoes E-Z photoisomerization to give the Z-isomer 2 (as illustrated in Figure 1).

The E-Z photoisomerization is the dominant process in the beginning of the photolysis of stilbene. This transformation takes place until a photostationary state is reached (Figure 2).

The optical absorbance spectra of the photolysis of 1 in ethanol are characterized by a decrease in absorbance at 369 nm, a hypsochromic shift of the maximum as well as an isosbestic point at 296 nm. Further irradiation causes the disappearance of the photostationary equilibrium between the two isomers.

Irreversible photochemical side reactions such as the [2 + 2] photocycloaddition or the cyclization of Z-stilbene to give dihydrophenanthrene, are of minor importance and may be neglected in these investigations.

The E-Z isomerization is thermally reversible, with the E-stilbene representing the thermodynamically more stable isomer form.

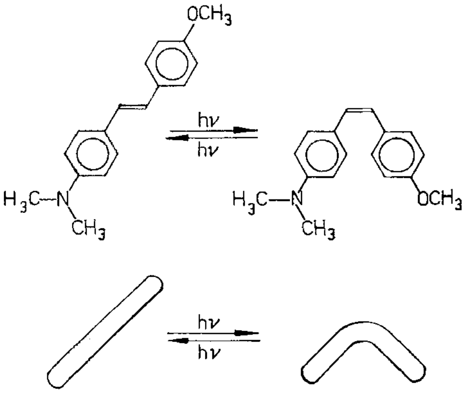

FIGURE 1 Scheme of E-Z photoisomerization of 4-N,N-dimethylamino-4'-methoxystilbene 1 and idealized illustration of the change in shape of the molecule.

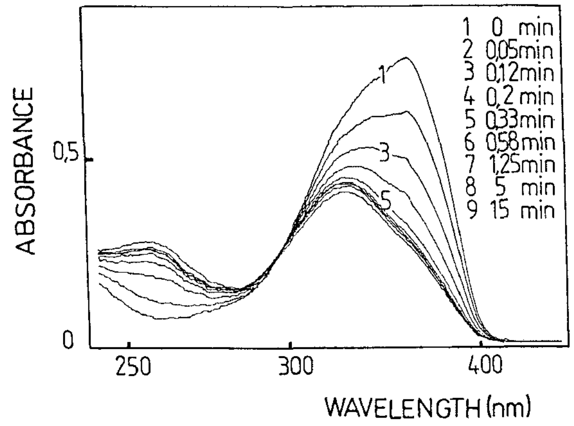

FIGURE 2 E-4-N,N-dimethylamino-4'methoxystilbene 1 in ethanol, irradiation at λ = 365 nm, UV/VIS absorption spectra at different irradiation times.

Nematic Mesophase

Irradiation of the stilbene 1 in the nematic mixture E-5 causes the change in UV/VIS absorbance illustrated in Figure 3.

The photoreaction of the stilbene derivative can be observed spectroscopically only at wavelengths longer than 350 nm due to the predominant absorption of the liquid crystalline cyanobiphenyl matrix. Irradiating and recording the spectra in the nematic state at room temperature, the UV/VIS absorbance shows only a comparably small difference before and after irradiation. A significant decrease of absorbance, however, has been observed, when the sample was irradiated in the mesophase and the absorption measured in the isotropic melt, as you see in Figure 3. This comparison indicates, that the optical behaviour of the stilbene is not only influenced by the photoreaction, but also by orientational effects of the dichroic molecules in the mesophase.

The dominance of photoisomerization is indicated by the spectroscopic behaviour

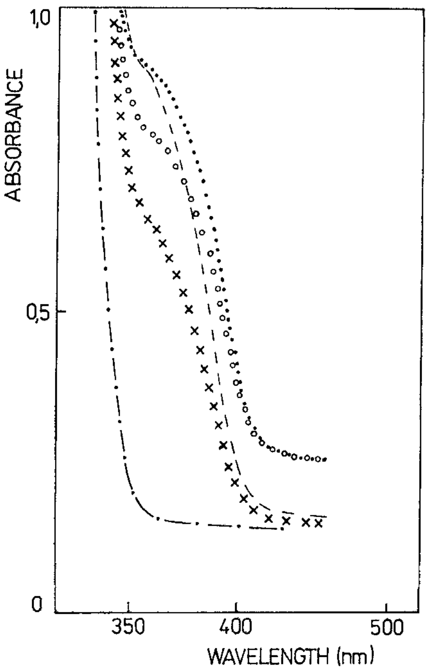

FIGURE 3 E-4-N,N-dimethylamino-4'methoxystilbene 1, 2 wt-% in nematic mixture E-5, irradiation at λ = 365 nm, UV/VIS absorption spectra: . . . ., nematic phase (r.t.), before irradiation; O O O O O, nematic phase (r.t.), after irradiation; - - - - -, isotropic phase (65°C), before irradiation; X X X X X, isotropic phase (65°C), after irradiation; - . - .-, pure E-5 mixture, nematic phase (r.t.).

under these conditions as well as by the reversibility of the spectroscopic and thermal properties of the photochromic guest-host mixture. This reversibility is a typical result of the backreaction towards the thermodynamically more stable E-stilbene. On irradiation the clearing temperature decreases from 52 to 49°C containing 2 wt-% stilbene 1 in the mixture. The initial state was restored again after leaving the sample at room temperature for ten days.

Figure 4 demonstrates that the temperature dependence of Volta potential differences has also been changed by the photoreaction of stilbene. Generally, a drastic change in the Volta potential is caused by modifying the orientational sites of dipole moments of liquid crystals, especially as a result of the transition from an ordered nematic sample to a disordered isotropic melt. Plotting ΔV versus temperature, the potential jumps indicate the decrease of phase transition temperatures.

Moreover, the altitude of the potential change indicates the extent of the molecular reorientation process in the sample throughout the phase transition. As shown in Figure 4, the altitude of ΔV is about 9 mV for the irradiated sample and $\Delta V = 16$ mV for the nonirradiated sample.

The comparison of the curves between irradiated and nonirradiated mixtures in Figure 4 shows that Volta potentials in the liquid crystalline state of the irradiated mixture are smaller at lower temperatures. The photochemically produced Z-isomer of stilbene decreases the liquid crystalline order and the mesophase stability, and, thus, a physical reorientation of the dipoles occurs already at 30°C.

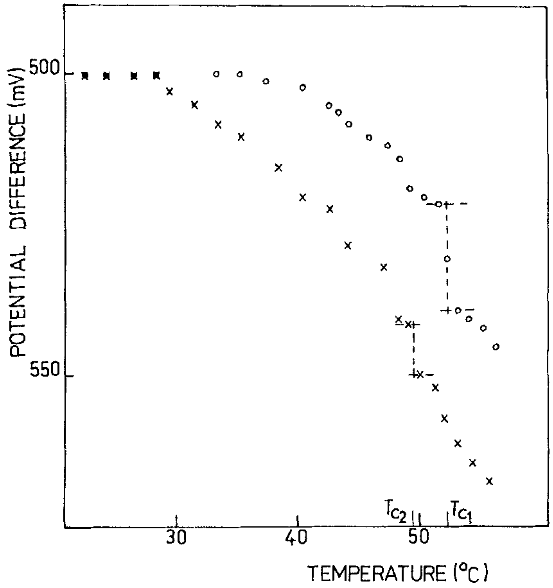

FIGURE 4 E-4-N,N-dimethylamino-4′-methoxystilbene 1, 2 wt-% in nematic mixture E-5, ΔV-T plot: O, before irradiation; X, after irradiation.

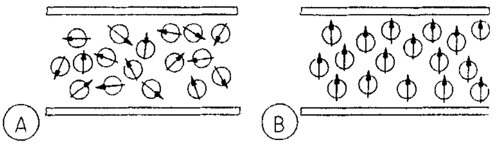

FIGURE 5 PDLC, idealized illustration: a) random droplet director orientation; b) preferred droplet director orientation.

Photoisomerization of the stilbene causes a modification of the form anisotropy and, in this way, a physical reorientation of the liquid crystalline matrix.

Dye-Doped PDLC

The directors of separate LC droplets[30] are arranged in the PDLC with random orientation unless an uniform orientation is caused by external fields or any boundary surface interactions. A random director orientation is obtained with a hot-dried gelatin matrix, as outlined in Figure 5.

However, a preferred orientation of LC droplets induced by the supramolecular structure of the gelatin matrix is obtained using PDLC based on cold-dried gelatin films.

From microscopical investigations under crossed polarizers it can be seen that the cold-dried gelatin PDLC exhibits a very regular wide refraction pattern differing from hot-dried layers which provide irregular images.

Photochromic PDLC containing stilbene 1 as guest component in E-5 droplets which are dispersed in gelatin undergo modification on irradiation. The result of irradiation, however, significantly depends on the thermal method of layer preparation. A significant change in UV/VIS absorption could not be observed after irradiating a hot-dried PDLC layer with random orientation of the droplet directors, as shown in Figure 6a. Figure 6b shows completely different curves for the cold-dried gelatin PDLC. The absorption increases in the region of longer wavelengths ($\lambda > 400$ nm) where neither stilbene 1 nor its photoproducts absorb. This increase in background absorbance is caused by increasing light scattering within the sample. The absorbance of stilbene 1 is decreased simultaneously at 362 nm.

Microscopic investigation of cold-dried PDLC doped with stilbene 1 shows that the regular pattern has been destroyed upon irradiation. The resulting image is

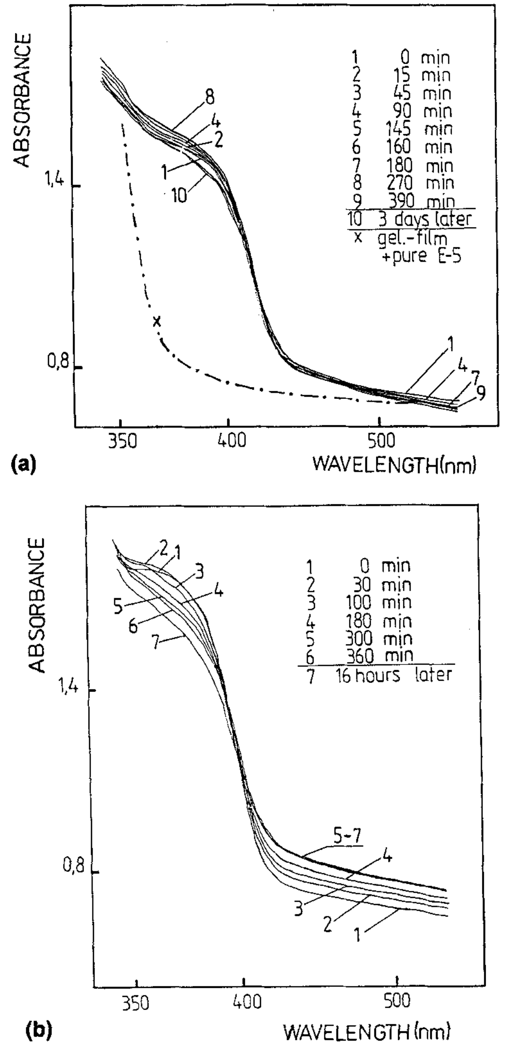

FIGURE 6 PDLC layer (E-4-N,N-dimethylamino-4′-methoxystilbene 1, 2 wt-% in E-5, dispersed in a gelatin matrix), irradiation at $\lambda = 365$ nm, UV/VIS absorption spectra: a) hot-dried layer (random director orientation); b) cold-dried layer (preferred director orientation).

rather similar to that of hot-dried gelatin PDLC. The microscopic image is not altered, however, if an analogous cold-dried PDLC layer without stilbene 1 is irradiated under the same conditions.

Modification of gelatin PDLC has also been confirmed by Volta potential measurements. Potential differences have been determined between irradiated and nonirradiated areas of the same PDLC layer, in both cases of hot-dried and cold-dried gelatin PDLC. This difference has been determined to be $\Delta V = 86$ mV for hot-dried PDLC layers (without director orientation). Consequently, irradiation produced a change of the resulting dipol orientation in these PDLC's. In cold-dried gelatin PDLC the potential difference is $\Delta V = 157$ mV, i.e. approximately twice the amount measured for the hot-dried sample. This much higher potential difference resulting from the modification of the layer is caused by the significantly higher degree of order of the droplets in the cold-dried PDLC before irradiation.

Upon irradiation, the preferred director orientation of LC droplets in the cold-dried gelatin PDLC has been destroyed and the degree of order has dropped. The director orientation of the LC droplets in the layer has been converted into a more irregular order, which causes the loss of the macroscopic optical anisotropy.

Since the liquid crystals exhibit optical anisotropy, a change in director orientation of LC droplets brings about different optical properties of the layer when light is passing through. This might be caused by a modified situation inside the liquid crystalline droplets and/or at the phase boundary surface between the LC droplets and the surrounding gelatin matrix. This results in increasing scattering, refraction and reflection effecting losses in light transmission through the PDLC layer.

The absorption of stilbene 1 is decisive for the optically induced modification of gelatin PDLC layers. This has been examined by investigating the behaviour of PDLC which did not contain the chromophore. PDLC without photochromic guest molecules did not show any optical modification upon irradiation.

The molecular mechanisms causing the breakdown of the preferred director orientation of LC droplets in cold-dried PDLC are under further investigation. Two principle ways appear to be possible. On the one hand, E-Z photoisomerization of stilbene 1 induces a decreasing stability of the nematic phase due to a modified form anisotropy of the chromophores which might effect a drastic decrease in the degree of order in the PDLC layer.

On the other hand, another thermal mechanism should be discussed. The radiation energy absorbed by the stilbene 1 could possibly be transformed into thermal energy by an efficient internal conversion process. This heat would destroy the thermally unstable supramolecular structure of the gelatin matrix thus changing the orientation of the LC droplets.

Consequently, the system stilbene 1/E-5 dispersed in a gelatin matrix represents a class of PDLC which changes its optical properties not only in an electric field but which can also be modified by light.

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