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# Photochromism of side-chain liquid crystal polymers containing spironaphthoxazines

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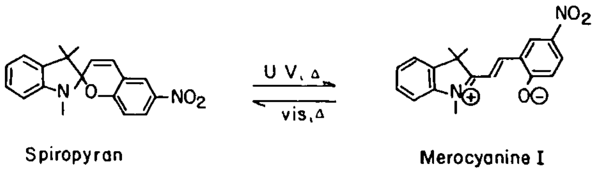
Side-chain liquid crystal polyacrylates and polysiloxanes containing different photochromic spironaphthoxazine side groups were synthesized. Thermodynamic, spectral and kinetic properties of the polymers were investigated. The structure of the mesophase is discussed.

## 1. Introduction

Side-chain liquid crystal polymers containing dye side groups have attracted much attention in the past few years (see [1] and references therein). The liquid crystal polymers with photochromic azobenzene derivatives in side chains were synthesized and used for reversible optical data storage [2–6].

Recently thermochromic and photochromic properties of polyacrylic and polysiloxane macromolecules containing mesogenic and spiropyran side groups were reported [7–11]. Films of these mesomorphic copolymers change colour on heating or irradiation as a result of the reversible reaction shown in Scheme I.



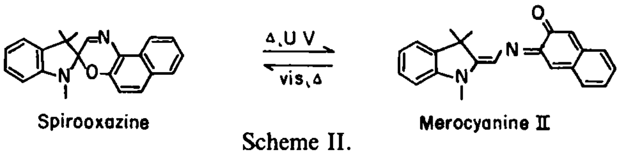
Scheme I.

Aggregation of the merocyanine dye moieties gives rise to physical cross-linking of the polymers and to formation of a network which in turn changes mechanical and optical properties of the polymers [7–10].

The visible absorption bands with $\lambda_{max} \leqslant 560\,nm$ have been ascribed to dimers and higher merocyanine aggregates, while the bands with $\lambda_{max} \geqslant 570\,nm$ belong apparently to non-aggregated merocyanines.

Usually UV irradiation of the polymer films below the glass transition temperature ($T_g$) leads to formation of the isolated merocyanine dye molecule. Above $T_g$ the merocyanine dimers and higher aggregates appear. The spiropyran form of the photochrome can be restored by irradiation of a coloured film with visible light.

The main factor which controls the rate of the thermal decoloration reaction of UV irradiation polymers is the rigidity and polarity of the polymer matrix. For example cyano-substituted mesogenic groups stabilize the merocyanine form of the photochrome due to the solvatochromic effect more than methoxy substituted



Scheme II.

mesogenic groups and retard the spontaneous decoloration reaction much more than factors such as the steric hindrance caused by the mesomorphic structure.

In the present communication we report the photochromic properties of liquid crystal polymers containing spironaphthoxazine side groups of various structures (Scheme II).

Spirooxazine is substantially less prone to photochemical fatigue than spiropyran [12]. This may open a new possibility for use of these photochromic polymers as photo- and electrosensitive materials.

## 2. Experimental section

### 2.1. *Materials*

The schemes of the synthesis of the spirooxazine monomers and polymers are given in figure 1 (*a*), (*b*). The monomers were synthesized as described in [7–13]. The polymers P(I), P(II), P(III) and P(IV) were synthesized by free radical copolymerization of monomers I, II, III and IV with the cyanophenylbenzoate monomer in 20 per cent toulene and THF solution as described in [7]. The polymers were precipitated by methanol, purified by reprecipitation and freeze dried from benzene. The yield of the polymers was about 50 per cent.

Polysiloxanes, P(V) were synthesized by polymer analogues reaction in two steps. First the active ester–mesogen copolymers (figure 1 (*b*)) were prepared by addition of the olefines via a hydrosilylation reaction to Si–H containing polymers as described in [9]. The spirooxazine was incorporated in the copolymers by reaction of the active ester copolymers with 5-aminospirooxazine [9]. The copolymers P(V) were isolated by repeated precipitation with methanol and freeze dried from benzene. The yield of the polymers was about 60 per cent. The composition of the polymers was determined by spectroscopic measurements [7].

### 2.2. *Characterization of the polymers*

Transition temperatures of the polymer were investigated by polarization microscopy and differential scanning calorimetry (DSC). A Wild M8 polarizing microscope with an Ernst Leitz Wetzlar hot stage were used. The DSC measurements were performed with a Mettler TA 3000 instrument. Optical absorption measurements were performed on a Varian 2200 spectrophotometer with a heating–cooling attachment. For the polysiloxane films the spectra were taken at low temperatures. Flash photolysis was conducted as described in [14], using a thin ($\sim 1\ \mu$m) polysiloxane film placed at 45° toward the flash lamp.

### 2.3. *Phase behaviour*

The phase diagrams of the copolymers (P(II)–P(V)) are given in figure 2. For the P(I) copolymer the phase transitions were examined for only one composition, 12 mol % of the photochrome: $T_g = 56°$ and $T_c = 90°$C. The diagrams show that mesophase still exists when the photochrome content in the polyacrylic copolymers reaches almost 50 per cent although the temperature range becomes rather narrow.

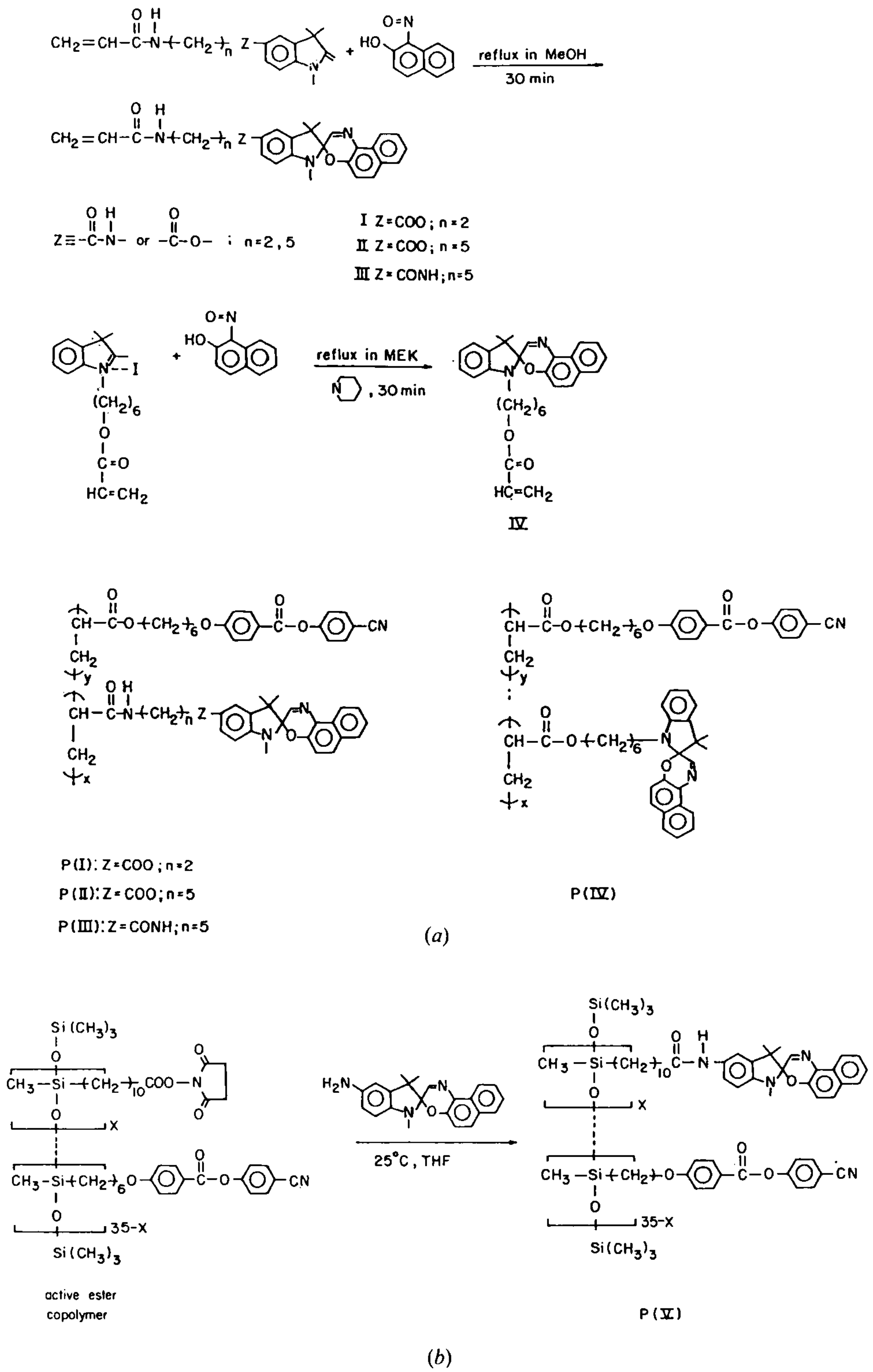
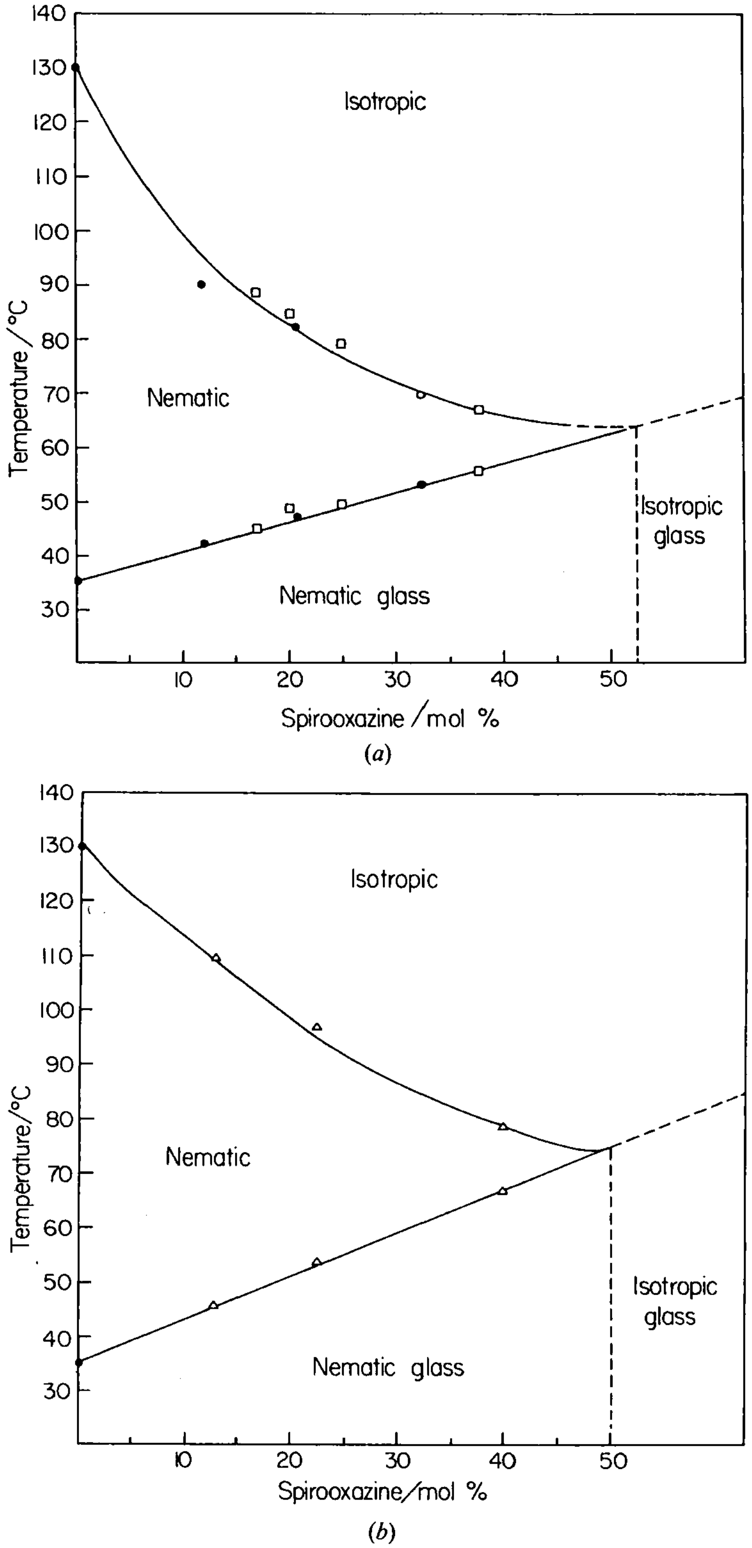


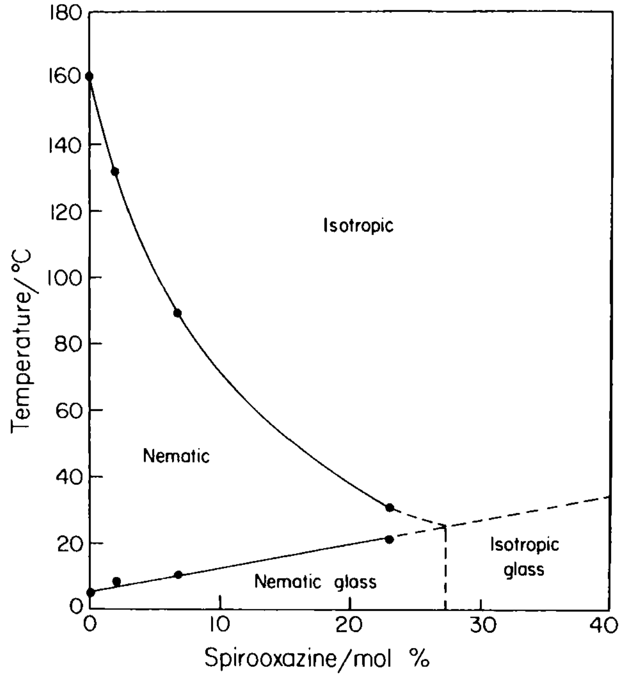
Figure 1. (*a*) Reaction scheme for the synthesis of acrylic monomers and liquid crystal polymers containing spironaphthoxazine. (*b*) Reaction scheme for the synthesis of polysiloxane liquid crystal polymers containing spironaphthoxazine.



(a)

(b)

Figure 2. Phase diagrams of photochromic liquid crystal polymers: (a) (●) P(II), and (□) P(III); (b) (△) P(IV); (c) P(V).



(*c*)

Figure 2 (*continued*).

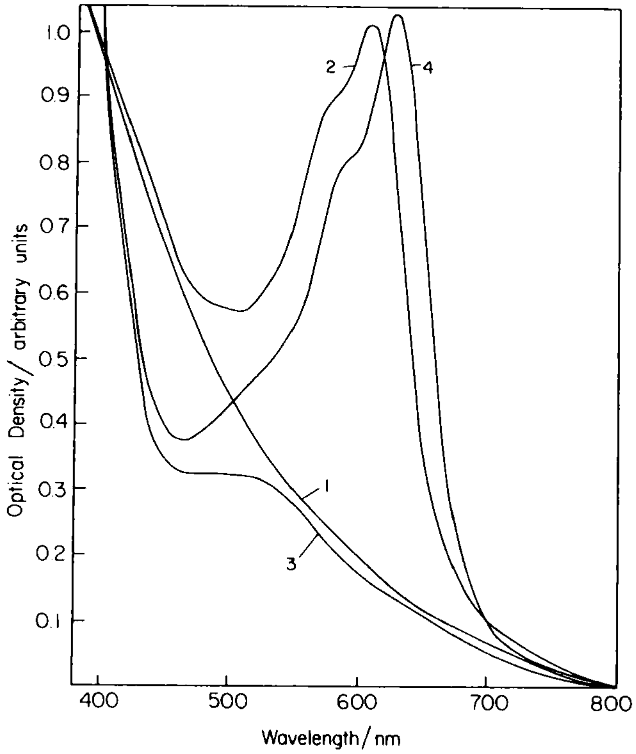
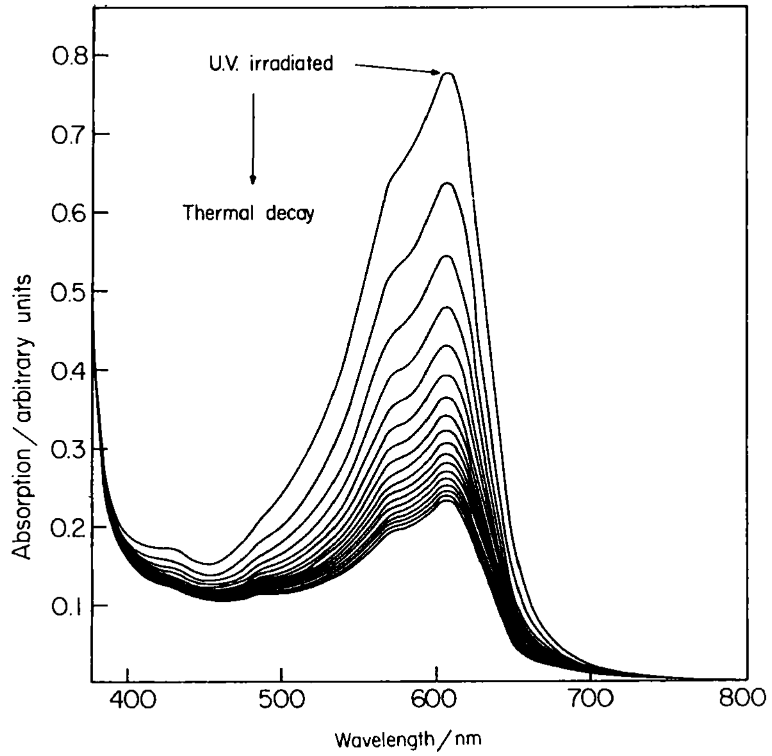


Figure 3. Absorption spectra of glassy nematic films at room temperature: (1) P(II) before UV irradiation, (2) P(II) after UV irradiation, (3) p(III) before UV irradiation, (4) P(III) after UV irradiation.

There is no substantial difference between mesophase polyacrylic copolymers with linear or lateral attachment of spirooxazine groups. The effect of the spacer length is not pronounced. The polysiloxane polymers lose the mesomorphic properties at a substantially lower content of the spirooxazine groups than the polyacrylic polymers.

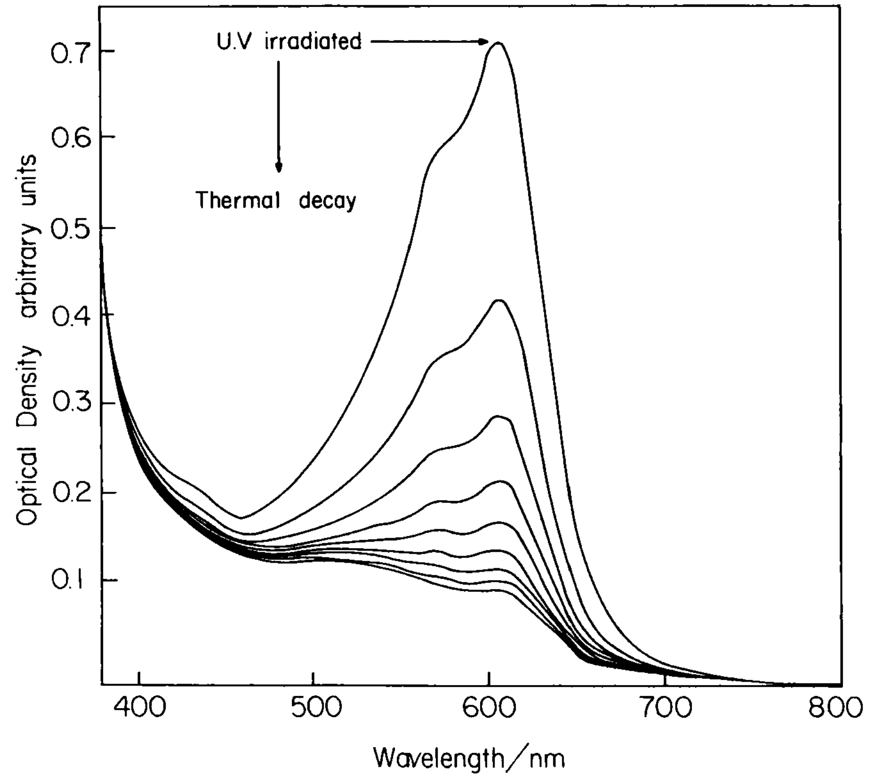
### 2.4. *Spectra and colour decay kinetics*

The absorption spectra resulting from the UV irradiation of P(I), P(II), and P(IV) polymers in the mesophase, amorphous phase and in tetrahydrofuran solution are similar (an example is given in figures 3 and 4) and remained unchanged when the temperature (from +25 to −20°C) or the concentration of the photochromic side groups is changed. Similar spectra were observed for photochromic low molar mass liquid crystals containing spirooxazine units [13]. The absorption maximum at 610 nm and a pronounced shoulder around 580 nm indicate two overlapping bands that were ascribed to two merocyanine isomers which are in thermal equilibrium with each other. The bathochromic shift of the visual spectrum ($\lambda_{max}$ 630 nm) for P(III) (figure 3) can be ascribed to the conjugation of the $\pi$ orbitals of the amide bond with the merocyanine part of the side group. The shape of the spectra remains unchanged during the thermal colour decay of the irradiated mesogenic glass (figure 4) which is in agreement with the two-isomer assumption. Unlike polymers containing spiropyran photochromic side groups [7–11], we found no spectral indication of aggregation of merocyanine formed from spironaphthoxazine.



(*a*)

Figure 4. Change of absorption spectra of copolymer (*a*) P(I) (12 mol % spirooxazine, and (*b*) P(IV) (17 mol % spirooxazine) during the thermal colour decay. Spectra (*a*) were recorded at 20 min and (*b*) at 10 min intervals after UV irradiation.



(*b*)

Figure 4 (*continued*).

Typical kinetics of decolouration processes of an UV irradiated glassy mesomorphic film are shown in figure 5. The colour decay does not obey first order kinetics and its rate decreases with increasing concentration of photochromic groups in the copolymer. The slowest decay was observed in the homopolymer containing only the spirooxazine side groups. The mesomorphic structure of a glassy film has no marked effect on the decay kinetics.

The spectrum of the polysiloxane polymers P(V) has $\lambda_{max}$ at 630 nm and a shoulder at 590 nm, which may also be ascribed to the amide conjugation effect (figure 6). The colour decay in the UV irradiated polysiloxane copolymers is more than one order of magnitude faster than in the polyacrylic polymers (figure 7) and does not depend on concentration.

The retardation of the colour decay caused by increasing photochrome concentration in polyacrylic copolymers can be attributed to steric hindrance of thermal ring closure by surrounding bulky photochromic groups. In the more flexible polysiloxane polymers this effect seems to be insignificant, at least at temperature much above $T_g$.

### 2.5. *Film alignment in an electric field and order parameter*

Films of the copolymers aligned by an electrostatic field of ~ 1 kV/mm between parallel aluminium thin-film electrodes deposited on a glass slide [5] produced dichroic absorption after irradiation with UV light. This enabled us to estimate an order

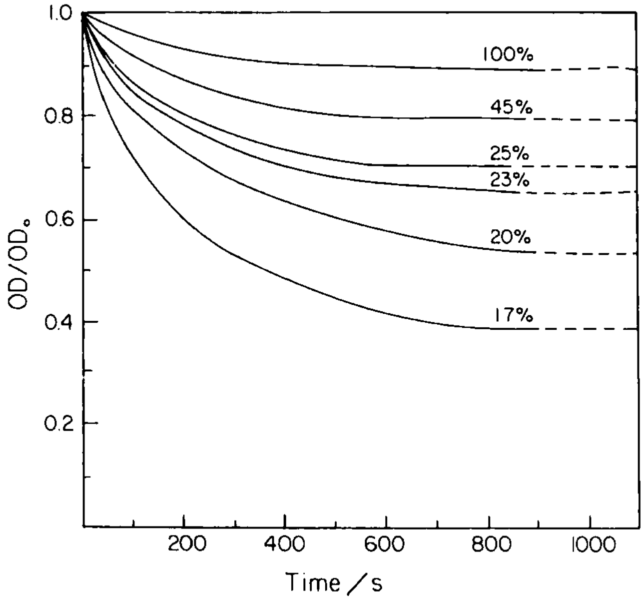


Figure 5. Thermal colour decay of copolymer P(IV) with different spirooxazine content (indicated in the figure). The two upper curves relate to glassy amorphous films.

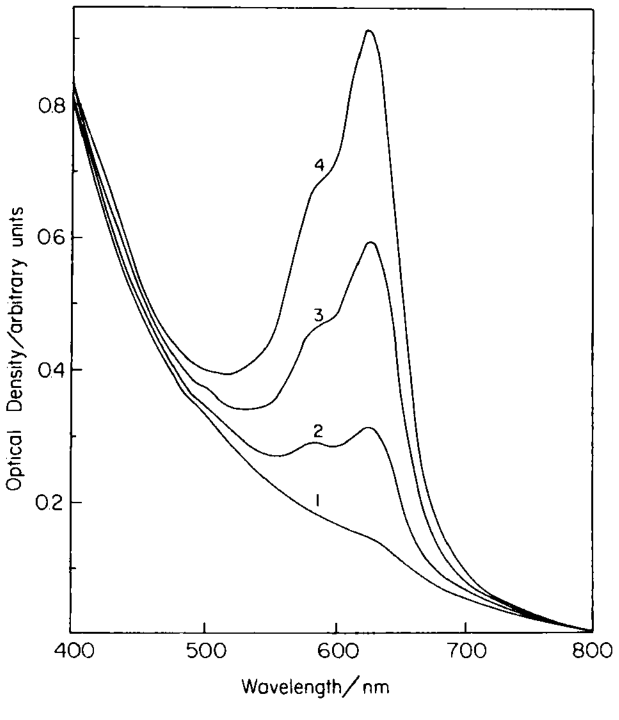


Figure 6. Absorption spectra of copolymer P(V) (6·5 mol % spirooxazine) at $-12$°C: (1) before irradiation, (2–4) successive exposures to UV light ($\lambda$ = 365 nm) for 5, 10 and 20 min.

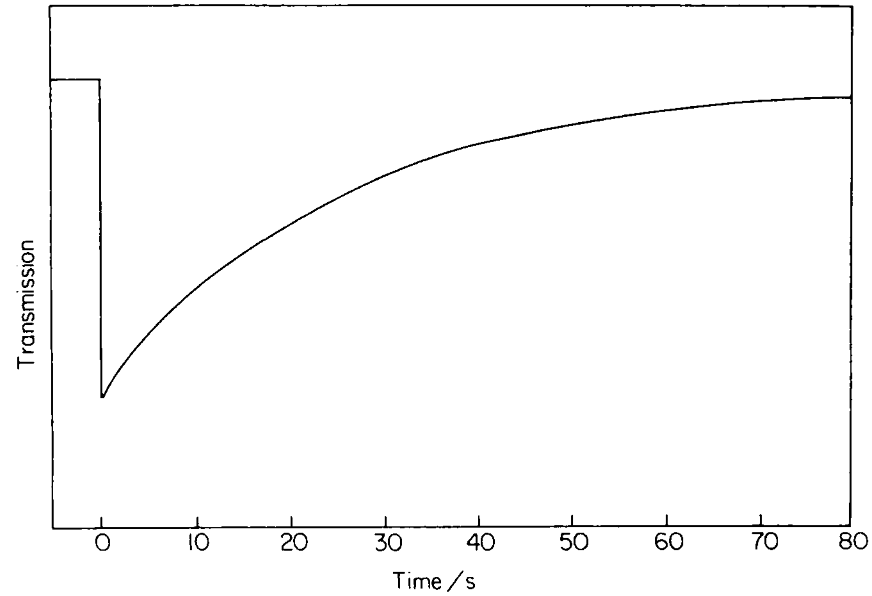


Figure 7. Flash photolysis of copolymer P(V) (2·1 mol % spirooxazine). Change of film transmission with time at 26°C, measured at 625 nm.

parameter of the merocyanine dye

$$S = (D_{\parallel} - D_{\perp})/(D_{\parallel} + 2D_{\perp}),$$

where $D_{\parallel}$ and $D_{\perp}$ are, respectively, the absorptions parallel and perpendicular to the liquid crystal director.

For polyacrylic copolymers the order parameter was very low ($S \leqslant 0{\cdot}2$). Earlier we also reported [11] approximately the same order parameter for the merocyanine dyes formed on irradiation of spiropyran side groups. Such a low order parameter and the absence of influence of the mesophase on the decolouration kinetics were explained by a hypothesis assuming separation of photochromic and mesomorphic sites due to structural incompatibility of photochromic and mesogenic groups. The photochromic transformations therefore seem to have little impact on the mesogenic domain structure, especially taking into account the absence of appreciable aggregation of the merocynine groups formed from spirooxazine. In turn the mesophase has no effect on the photochromic properties of spirooxazines.

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