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Photochromic chiral liquid crystalline systems containing spiro-oxazine with a chiral substituent

II. Photoinduced behaviour

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The photoinduced behaviour of low molecular mass liquid crystalline (LC) systems doped with the chiral photochromic spiro-oxazine, 9′-{5-(−)-menthoxyacetoxy-1,3-dihydro-1,3,3-trimethyl-spiro[2H-indole-2,3′-[3H]naphth-[2,1-*b*][1,4]oxazine]} 4-[11-(tetrahydro-2-pyranyloxy)-undecyloxy]biphenyl-4′-carboxylate (THP11SOM) was observed by means of transmittance measurements at 21°C. The experimental results revealed that the ring-opened merocyanine form of THP11SOM resulting from the photochromism first disturbed the helical planar orientation of the LC molecules and then induced a new helical pitch. The magnitudes of both the disturbance in orientation of the LC molecules and the shift in the helical pitch were significantly influenced by the concentration of THP11SOM. The photoinduced behaviour was reversible due to the photochemical and thermal back reaction of the THP11SOM. In addition, the effect of UV light on the nematic–isotropic transition temperatures of the mixtures with or without a hindered amine light stabilizer was studied.

1. Introduction

Spiro-oxazine has long been known as a promising photochromic compound with good photo-fatigue resistance [1]. Because the spiro-carbon of a spiro-oxazine molecule has potential as a chiral centre, spiro-oxazines could be utilized as chiro-optical molecular switches [2]. However, spiro-oxazines are usually racemic mixtures [3, 4]. Therefore, if spiro-oxazines are to be utilized as chiro-optical molecules in a chiral nematic liquid crystalline (LC) system, modification of the spiro-oxazine with a chiral group is required (see the scheme). We have recently reported the synthesis of spiro-oxazines with a chiral substituent [5]. In this paper, we describe the photo-induced behaviour of low molecular mass LC systems containing 9′-{5-(−)-menthoxyacetoxy-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H]naphth-[2,1-*b*][1,4]oxazine]} 4-[11-(tetrahydro-2-pyranyloxy)-undecyloxy]biphenyl-4′-carboxylate (THP11SOM) as a right-handed photochromic chiral dopant. In addition, we report the effect of a hindered amine light stabilizer, bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (LS-770) on the nematic–isotropic transition temperatures of the photochromic chiral LC mixtures when irradiated with UV light.

2. Experimental

The synthetic method for THP11SOM has been previously described in detail [5, 6]. The nematic host mixture (ZLI-3103) and the right-handed chiral dopant (ZLI-3786) were purchased from Merck (Japan). The LS-770 was a gift from Sankyo Co., Ltd. (Japan). Chemical structures of the THP11SOM, ZLI-3786, and LS-770 are shown in figure 1. The photochromic chiral LC mixtures were filled into parallel rubbed polyimide-coated cells (cell gap 9 μm, EHC Co., Ltd., Japan). The compositions of the mixtures are given in the table. Mixture D was prepared by addition of LS-770 to mixture C. Phase transition temperatures of the LC mixtures were measured using an optical polarizing microscope (Olympus BH-2) equipped with a hot stage (Mettler FP84) and a temperature programmer (Mettler

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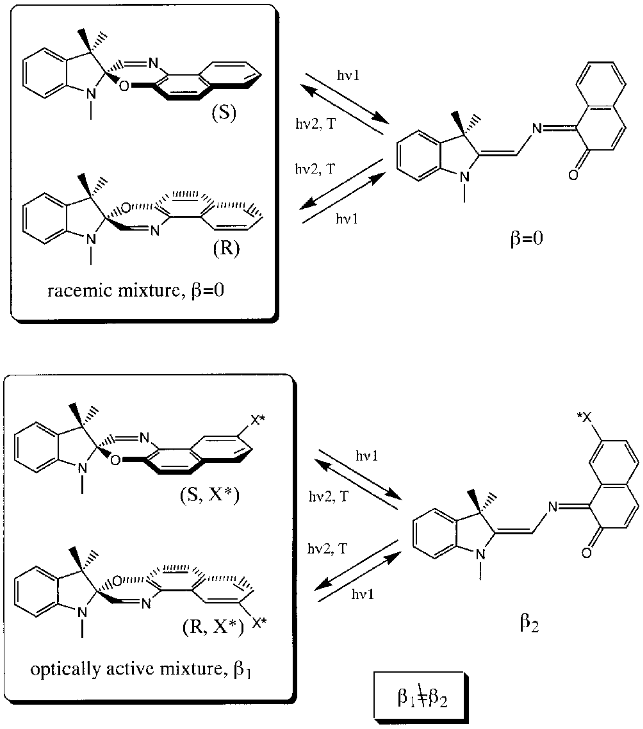
Table Compositions and transition temperatures of photochromic chiral liquid crystalline mixtures studied. T_{NI} = nematic to isotropic transition temperature.

	Composition/wt %				
Mixture	THP11SOM	ZLI-3786	ZLI-3103	LS-770	T_{NI}/°C[a]
A	9.7	25.9	64.4	0	59.8
B	25.0	21.2	53.8	0	44.2
C	34.3	12.1	53.6	0	47.6
D	33.5	11.8	52.4	2.3	41.7
E	36.9	14.2	48.9	0	44.4

[a] Determined by optical polarizing microscopy.



Scheme. Conceptual representation of the chiroptical system in this study. β = helical twisting power.

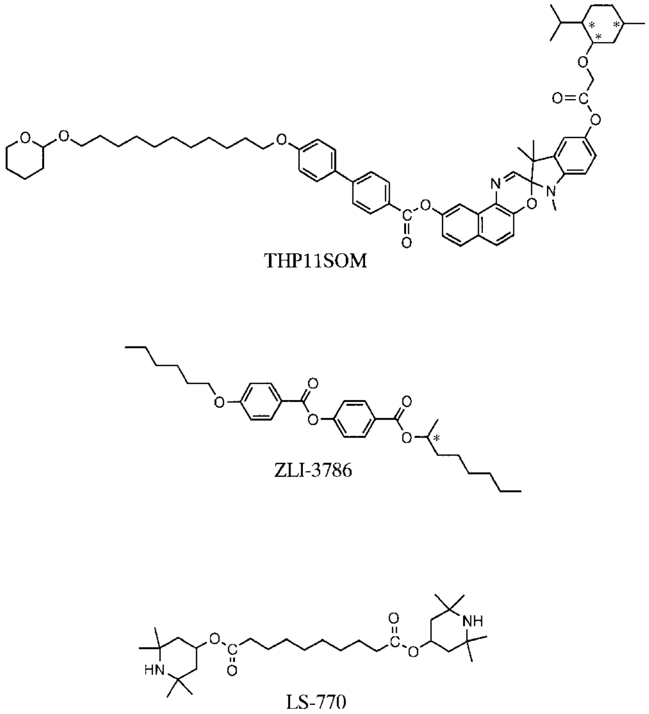


Figure 1. Structures of the compounds in this study.

FP80). Transmittance measurements were carried out using a Shimadzu UV-3100 spectrophotometer equipped with a 365 nm UV irradiation system [6] at 21°C. The intensity of UV light was 2.2 mW cm^{-2}. The angles of incidence of the UV light and the spectroscopic light on the sample were, respectively, 0° (normal incidence) and 45°.

3. Results and discussion

Figures 2(*c*–*e*) indicate that the photochemical reaction of the THP11SOM influenced the helical orientation of the LC molecules and the influence was strongly dependent on the concentration of the THP11SOM. Because each reflection peak in figures 2(*a*) and 2(*b*) did not shift even on UV irradiation for 15 min, each shift in the reflection peak in figures 2(*c*–*e*) is apparently due not to the thermal effect of the UV light, but to the photoreaction of THP11SOM. It is noted that the absorption peak around 604 nm in figure 2 is due to the ring-opened form of THP11SOM and that there is no unfavourable absorption of the incident UV light by the light stabilizer, LS-770, as shown in the case of figure 2(*d*) (for mixture D).

To discuss the behaviours of the reflection peaks more precisely, transmission spectra around the reflection peaks of mixtures C–E during and after UV irradiation are shown in figure 3. According to the spectra of figures

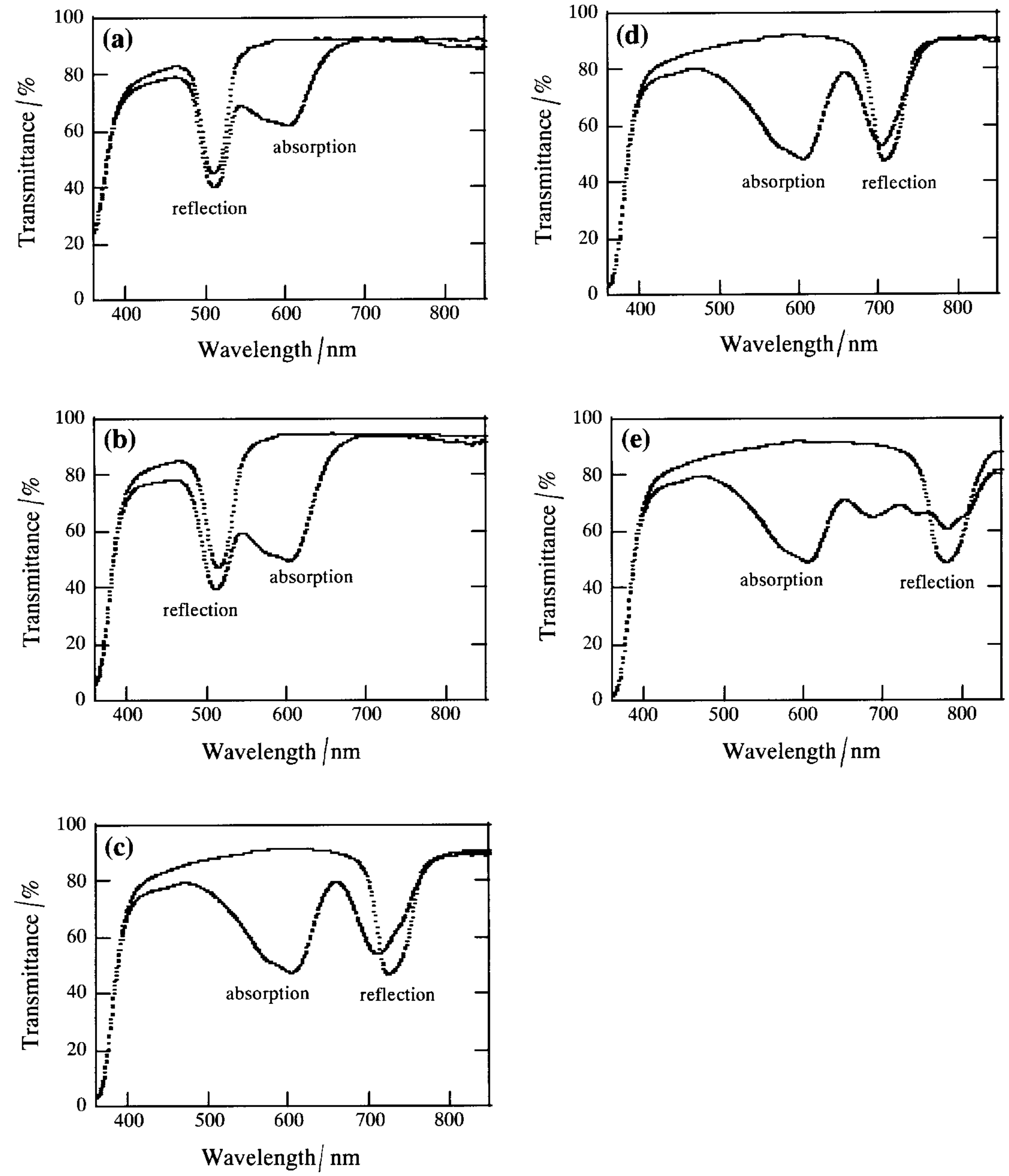


Figure 2. Full transmission spectra before and after UV irradiation for 5 min at 21°C: (*a*) mixture A, (*b*) mixture B, (*c*) mixture C, (*d*) mixture D, (*e*) mixture E.

3(*a–c*), during UV irradiation the reflection peaks first deformed, i.e. their heights became less and the peaks became wider on each side, and then the peaks began shifting to shorter wavelength. These results suggest that the photoinduced behaviour occurred first and gave scattering of the spectroscopic light whose range was around the reflection peak. It is interesting that there was a considerable difference in the magnitude of scattering between figures 3(*a*) and 3(*c*), although the difference in composition between mixtures C and E was small, as shown in the table.

It is noted that the reaction of THP11SOM reached a photostationary state; i.e. the proportion of the ring-opened to the ring-closed form of THP11SOM reached an equilibrium state, within 10–20 s in this study. On the other hand, the decrease in the scattering loss on the longer wavelength side of the reflection peaks, and the shift of the reflection peaks to shorter wavelength, mainly occurred upon irradiation over 30 s as shown in figures 3(*a–c*). Therefore, the second photoinduced behaviour mentioned in this section occurred mainly under the photostationary state of the THP11SOM. This result

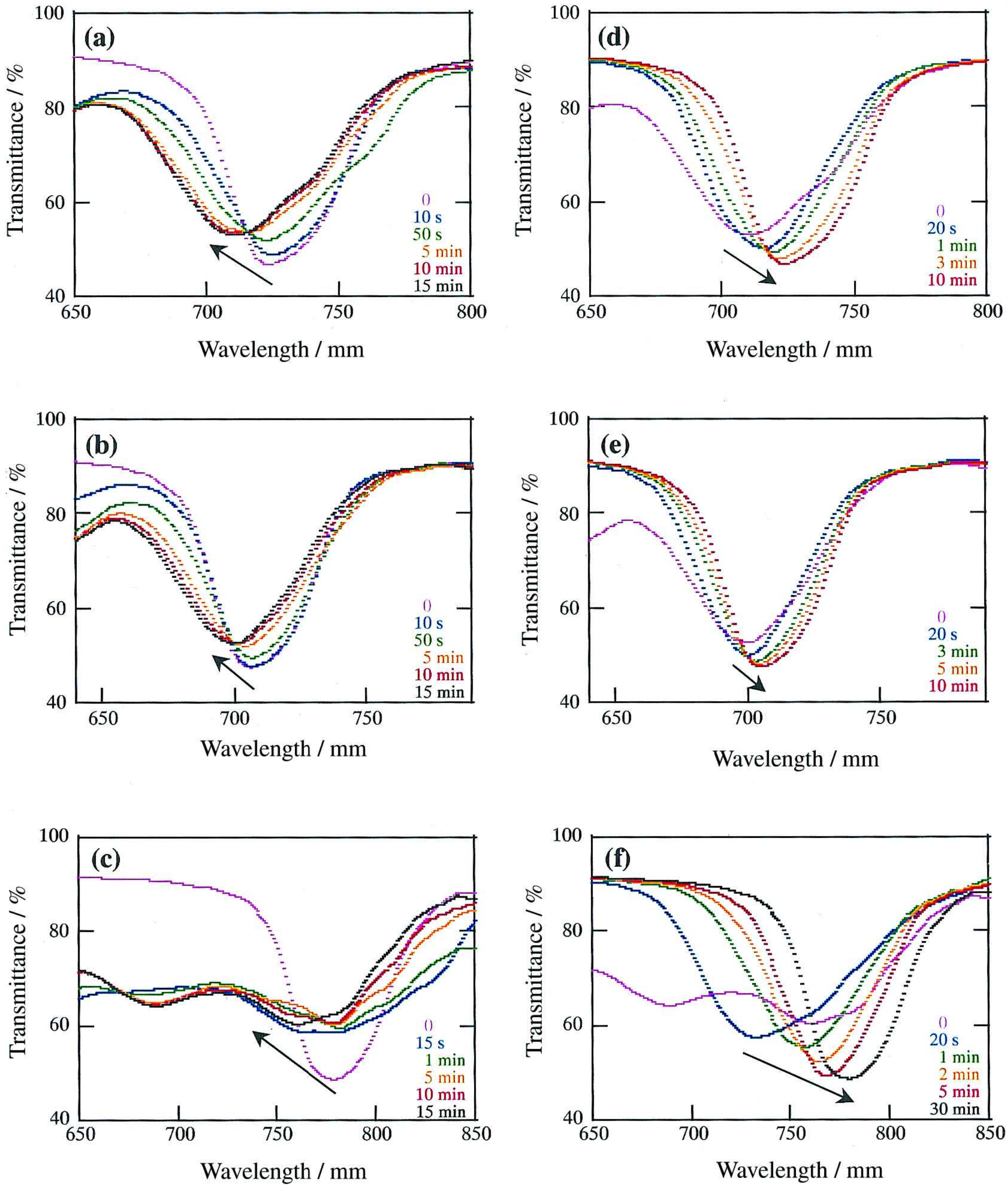


Figure 3. Transmission spectra around the reflection peak during (*a*–*c*) and after (*d*–*f*) UV irradiation at 21°C. Mixture C (*a*, *d*); mixture D (*b*, *e*); mixture E (*c*, *f*). Recording order: violet, blue, green, orange, red, and black.

strongly suggests that the helical twisting capabilities of the ring-closed and ring-opened forms of THP11SOM are different. Because the reflection peaks shifted to shorter wavelength, the helical twisting capability of the ring-opened form of THP11SOM seems to be larger than that of the ring-closed form. It is noted that the chiral dopants mutually correlate in our systems because of their high concentrations. In these cases, the helical twisting powers (HTP) [7, 8] of the chiral dopants cannot be determined.

The spectra after UV irradiation in figures 3(*d*–*f*) show that the scattering disappeared immediately on turning the UV light off, and then the reflection peaks became sharper. The decay time to the initial state seems to depend on the extent of shift of the reflection peak.

Monitoring of the transmittance of mixture D at 604, 706, and 743 nm, as shown in figure 4, offered further information on the behaviour of the peak. Upon UV irradiation, each transmittance at 706 and 743 nm began increasing and decreasing, respectively, due to the

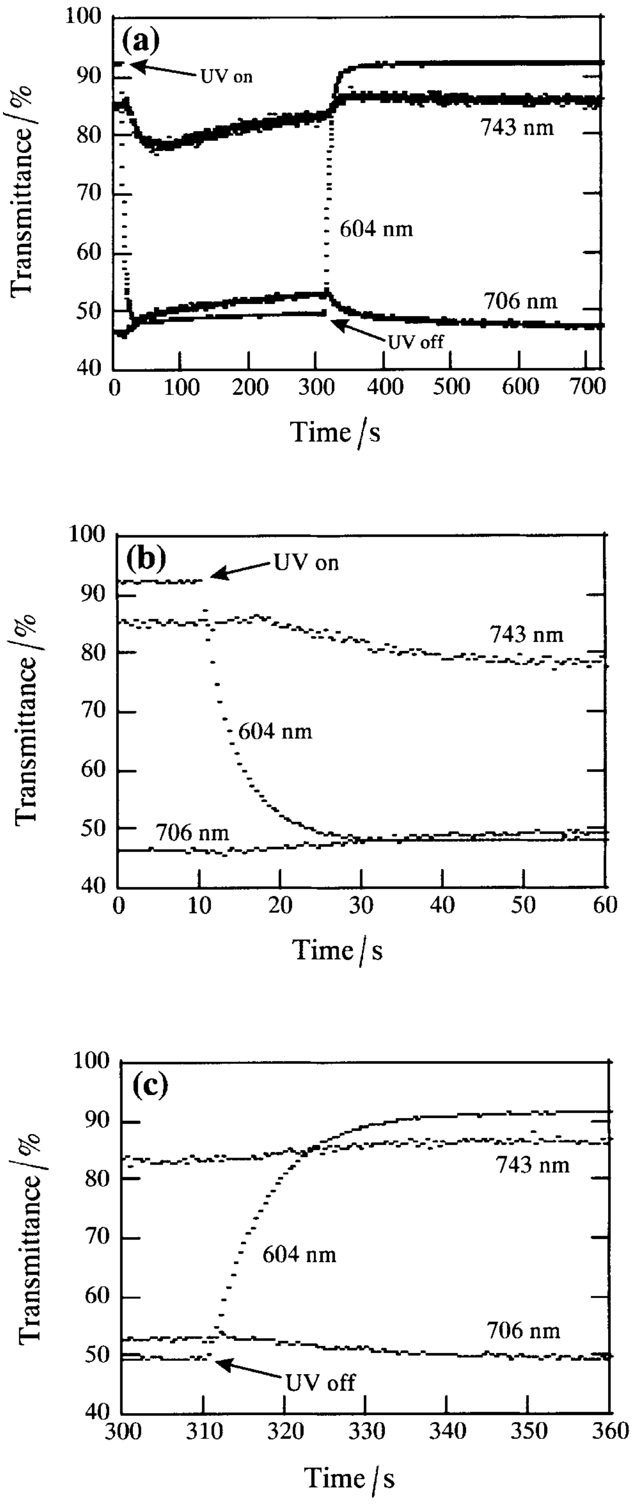


Figure 4. Real-time transmission measurements of mixture D at 604, 706, and 743 nm at 21°C: (*a*) full data, (*b*) data for first 60 s, (*c*) data for last 60 s.

deformation of the planar orientation to give a light-scattering polydomain structure with a decrease in the transmittance at 604 nm due to the absorption of the ring-opened form of THP11SOM. According to figure 4 (*b*), there was an induction period of about 5–10 s in the transmittance behaviours at 706 and 743 nm. However, as shown in figure 4 (*a*), the transmittances at 706 and 743 nm began increasing slightly after the THP11SOM reached the photostationary state, because a planar orientation of the LC molecules was restored with induction of a new helical pitch. By turning the UV lamp off, the transmittances at 706 and 743 nm immediately began reverting to each of the initial values. The decay process of the transmittance at 706 nm seems to consist of fast and slow processes. According to figures 4 (*a*) and 4 (*c*), the fast decay process almost synchronized with the thermally induced back reaction of the THP11SOM.

As shown in figure 5, LS-770 contributed to the photodurability of THP11SOM. In the case of a UV intensity of 2.2 mW cm^{-2}, which is the same intensity as that in the transmittance measurements in this study, the nematic to isotropic transition temperatures of mixtures C and D were decreased by 0.6°C and 0.4°C, respectively, by irradiation for 30 min. On the other hand, in the case of an intensity of 20 mW cm^{-2}, the transition temperatures of mixtures C and D decreased by 2.9°C and 1.0°C, respectively. We assume that the photoinduced behaviours of the photochromic chiral LC systems used in this study were little affected by the photoinduced decomposition of the THP11SOM.

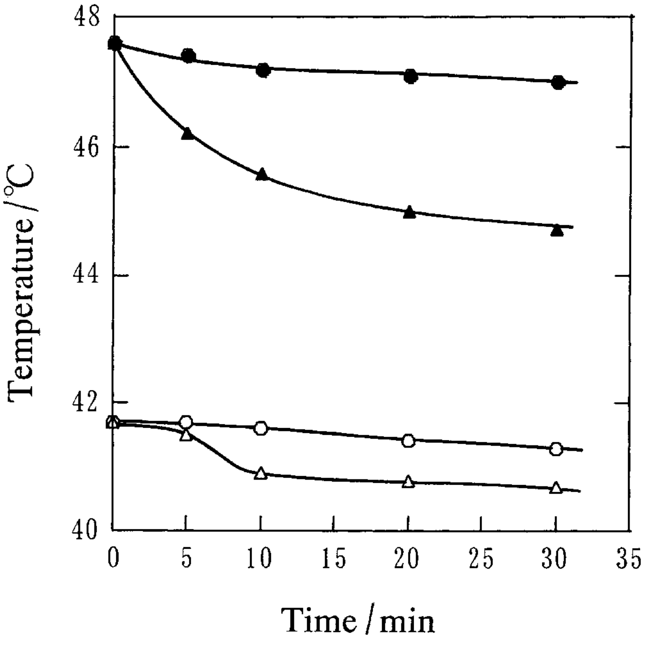


Figure 5. Nematic–isotropic transition temperatures of mixture C (filled symbols) and mixture D (open symbols) irradiated with 365 nm UV light at 21°C. UV intensity (mW cm^{-2}): 2.2 (filled and open circles), 20 (filled and open triangles).

4. Conclusions

We have studied the photoinduced effect due to photochemical reaction of a spiro-oxazine with a chiral substituent (THP11SOM). The experimental results suggest that the orientation of the LC molecules was disturbed first and then a pitch shift occurred. The photoinduced behaviours were strongly dependent on the concentration of THP11SOM. By turning the UV lamp off, the reflection peak immediately started to revert to the initial state. It seems that the decay process consists of fast and slow processes, and the former synchronizes with the thermal back reaction of THP11SOM. In addition, the hindered amine light stabilizer, LS-770, improved the light fatigue resistance of the THP11SOM.

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