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Liquid Crystals

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Photoreactivity and emission properties of liquid-crystalline twin dimers containing cinnamic acid moieties at both ends of ethylene glycol spacers

I. Synthesis, thermotropic properties and photoreactivity

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Twin dimers containing 4-methoxycinnamic acid moieties at both ends of various lengths of ethylene glycol spacers (*n*EGMC) were found to exhibit liquid-crystalline phase behaviour, while those with cinnamic acid moieties (*n*EGC) at both ends did not show the liquid-crystalline phase behaviour. The liquid-crystalline phase behaviour of *n*EGMC depended on the length of the ethylene glycol spacers, *n*. Photoirradiation of *n*EGMC at > 300 nm resulted in the formation of photodimers through cyclobutane ring formation at the C=C part of the 4-methoxycinnamic acid moieties. The photoreaction was explored by following a decrease in ν C=C (FTIR), formation of the photodimers (GPC) and structural analysis of the photoproducts (NMR). It was found that the morphology of the systems strongly affected the photoreactivity and the head-to-head photodimer was predominantly formed. The photoreactivity of *n*EGMC is discussed in relation to the morphology of the systems.

1. Introduction

It is well known that cinnamic acid derivatives undergo photodimerization through cyclobutane formation at the C=C part of the cinnamic acid moieties on photoirradiation at > 300 nm. Schmidt *et al.* [1] found that the photoreactivity and the structure of the photoproducts are determined predominantly by spatial orientation of the relevant two chromophores in crystals and termed this sort of photoreaction as a topochemical reaction. For example, *trans* cinnamic acid possesses two types of crystals, an α form and a β form, in which the α type crystal is associated with a head-to-tail configuration of molecules and similarly the β form also has a head-to-head configuration. Photoirradiation of these two forms of crystals resulted in α-truxillic acid from the α form and β-truxinic acid from the β form.

The topochemical photoreaction was extended to bifunctional molecules by Hasegawa *et al.* [2] who showed in an elegant way that photopolymerization takes place in these bifunctional molecules in such a way that the crystalline structure of the resulting polymers retains its original crystalline structure. Later, they found a number of bifunctional monomers capable of the topochemical polymerization.

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It seems to be a reasonable extension to explore the topochemical photoreaction in liquid-crystalline systems, since the liquid crystals possess the ordered structure of mesogens, though the order is somewhat lower than those of crystals. Because of the different ordering of mesogens in liquid crystals from those in crystals, it may be expected that we can observe different types of topochemical photoreactions in these systems [3].

Photochemical reactions in polymer liquid crystals have recently been investigated intensively in relation to the photon-mode optical image storage systems. Griffin *et al.* [4] reported that photoirradiation of a liquid-crystalline polyester composed of the cinnamic acid moieties and methyl siloxane spacers resulted in photodimerization at the cinnamic acid parts, leading to interchain cross-linking. This cross-linking is an irreversible process which can be used as a write-in process in write-once-read-only recording systems.

We demonstrated that polyesters composed of *p*-phenylene diacrylic acid moieties and ethylene glycol spacers exhibited liquid-crystalline phase behaviour and photoirradiation caused the interchain cross-linking through cyclobutane ring formation [5]. The photocross-linking induced the isotropic phase effectively at the irradiation sites and the photoreaction proceeded faster in the liquid-crystalline state than in the isotropic phase or below the glass transition temperature (T_g) of the polyesters. Further, the photoreactivity was found to depend strongly on the ethylene glycol spacer length.

In the present study, we prepared various ethylene glycol derivatives which possess cinnamate groups at both ends of the molecules and examined the liquid-crystalline behaviour in relation to the length of the ethylene glycol spacers. We have further explored the photoreactivity of the compounds by following a decrease in νC=C (FTIR), formation of the photodimers (GPC) and structural analysis of the photoproducts (NMR). Advantages of twin dimer liquid crystals over polymer liquid crystals are (1) facility of product analysis since the photodimers of the twin dimers are easily soluble in common solvents while in the polymer liquid crystals the photoproducts are insoluble due to cross-linking; (2) effect of flexible spacers on the liquid crystal phase behaviour is greatly enhanced in the twin dimers in comparison with that in polymer liquid crystals [6].

2. Experimental

The structures of two series of twin dimers (*n*EGMC and *n*EGC) used in this study and their abbreviations are shown in figure 1.

2.1. *Materials*

2.1.1. *Synthesis of nEGMC*

4-Methoxycinnamic acid (5·0 g; 28 mmol) was dissolved in purified tetrahydrofuran (THF; 20 ml) and oxalyl chloride (3·0 ml; 35 mmol) was added dropwise with stirring at room temperature. After evolution of carbon dioxide and hydrochloric acid gas, THF and the excess oxalyl chloride were removed, giving 4-methoxycinnamoyl chloride. The 4-methoxycinnamoyl chloride was used throughout for the preparation of *n*EGMC and a detailed procedure is shown by the synthesis of 2EGMC as an example.

4-Methoxycinnamoyl chloride was dissolved in a mixture of THF (20 ml) and pyridine (1 ml) and to this solution diethylene glycol (1·0 g; 94 mmol) dissolved in purified THF (20 ml) was added dropwise with stirring at room temperature. After the addition was finished, the resulting mixture was refluxed for several hours. The mixture was then poured into an aqueous solution of $NaHCO_3$ (5 per cent) and the product was extracted with benzene. The crude product in benzene was washed with 5 per cent aqueous $NaHCO_3$ several times, then with water, and was isolated by evaporation of the solvent. 2EGMC was purified by column chromatography on silica gel using 1 : 1 benzene/chloroform as eluent, followed by recrystallization from methanol.

Yield, 43 per cent. ^1H NMR ($CDCl_3$), δ 3·83 (m, 10 H), 4·37 (t, 4 H), 6·37 (d, 2 H), 6·8–7·5 (m, 8 H), 7·66 (d, 2 H). IR (KBr) 1701, 1635 cm^{-1}. Elemental analysis $C_{24}H_{26}O_7$ (FW 426·45), calc. C 67·59 per cent, H 6·15, per cent, found C 67·01 per cent, H 5·87 per cent.

*n*EGMCs with $n=3$, 4 and 5 were prepared similarly (for $n=3$, 4-methoxycinnamoyl chloride and triethylene glycol (3EGMC); $n=4$, tetraethylene glycol (4EGMC); and for $n=5$, pentaethylene glycol (5EGMC)). Yields and analytical data are:

3EGMC. Yield, 55 per cent. ^1H NMR ($CDCl_3$), δ 3·7–3·9 (m, 14 H), 4·37 (t, 4 H), 6·34 (d, 2 H), 6·8–7·5 (m, 8 H), 7·66 (d, 2 H). IR (KBr) 1701, 1635 cm^{-1}. Elemental analysis $C_{26}H_{30}O_8$ (FW 470·52), calc. C 66·37 per cent, H 6·43 per cent; found C 66·27 per cent, H 6·30 per cent.

4EGMC. Yield, 34 per cent. ^1H NMR ($CDCl_3$), δ 1·9 (m, 8 H), 3·5–3·9 (m, 10 H), 4·23 (t, 4 H), 6·31 (d, 2 H), 6·7–7·6 (m, 8 H), 7·69 (d, 2 H). IR (KBr) 1709, 1635 cm^{-1}. Elemental analysis $C_{28}H_{34}O_9$ (FW 514·57), calc. C 65·35 per cent, H 6·66 per cent; found C 65·09 per cent, H 6·19 per cent.

5EGMC. Yield, 33 per cent. ^1H NMR ($CDCl_3$). δ 1·9 (m, 10 H), 3·6 (t, 4 H), 4·23 (t, 4 H), 6·31 (d, 2 H), 6·7–7·6 (m, 8 H), 7·69 (d, 2 H). IR (KBr) 1709, 1635 cm^{-1}. Elemental analysis $C_{30}H_{38}O_{10}$ (FW 558·62), calc. C 64·50 per cent, H 6·86 per cent; found C 63·95 per cent, H 6·34 per cent.

2.1.2. *Synthesis of nEGMC*

As a typical example, the synthetic procedure for 2EGC is described here. Cinnamoyl chloride (5·0 g; 30 mmol) dissolved in purified THF (20 ml) was added dropwise with stirring to a solution of diethylene glycol (0·50 g; 5 mmol) in THF (20 ml) at room temperature. After addition, the mixture was refluxed for several hours. After cooling to room temperature, the reaction mixture was poured into an aqueous $NaHCO_3$ solution and the precipitate was extracted with chloroform. The product was then washed with an aqueous $NaHCO_3$ solution and water, several times successively, and purified by column chromatography on silica gel using 1 : 1 hexane/benzene as eluent. 2EGC was finally purified by recrystallization from hexane.

Yield, 30 per cent. ^1H NMR ($CDCl_3$), δ 3·83 (t, 4 H), 4·43 (t, 4 H), 6·51 (d, 2 H), 7·3–7·7 (m, 10 H), 7·77 (d, 2 H). IR (KBr) 1700, 1625 cm^{-1}. Elemental analysis $C_{22}H_{22}O_5$ (FW 366·41), calc. C 72·12 per cent, H 6·05 per cent; found C 71·95 per cent, H 6·01 per cent.

*n*EGCs with $n=3$, 4 and 5 were prepared similarly (for $n=3$, cinnamoyl chloride and triethylene glycol (3EGC); $n=4$, tetraethylene glycol (4EGC); and $n=5$ pentaethylene glycol (5EGC)). Yields and analytical data are:

3EGC. Yield, 44 per cent. ^1H NMR ($CDCl_3$), δ 3·8 (m, 8 H), 4·37 (t, 4 H), 6·49 (d, 2 H), 7·3–7·7 (m, 10 H), 7·74 (d, 2 H). IR (KBr) 1705, 1625 cm^{-1}. Elemental analysis $C_{24}H_{26}O_6$ (FW 410·47), calc. C 70·23 per cent, H 6·38 per cent; found C 69·89 per cent, H 6·19 per cent.

4EGC. Yield, 35 per cent. ^{1}H NMR ($CDCl_3$), δ 3·8 (m, 8 H), 4·40, (t, 4 H), 6·51 (d, 2H), 7·3–7·7 (m, 10 H), 7·74 (d, 2 H). IR (KBr) 1700, 1620 cm^{-1}. Elemental analysis $C_{26}H_{30}O_7$ (FW 454·52), calc. C 68·74 per cent, H 6·65 per cent; found C 68·09 per cent, H 6·24 per cent.

5EGC. Yield, 30 per cent. ^{1}H NMR ($CDCl_3$), δ 1·9 (m, 12 H), 3·6 (t, 4 H), 4·27 (t, 4 H), 6·46 (d, 2 H), 7·3–7·7 (m, 10 H), 7·91 (d, 2 H). IR (KBr) 1695, 1635 cm^{-1}. Elemental analysis $C_{28}H_{34}O_8$ (FW 498·57), calc. C 67·45 per cent, H 6·87 per cent; found C 66·84 per cent, H 6·27 per cent.

2.2. *Thermotropic properties*

Liquid-crystalline behaviour and phase transition behaviour were examined on an Olympus model BHSP polarizing microscope equipped with a Mettler hot stage, model FP 80 and FP 82 respectively. Thermodynamic properties were determined with a differential scanning calorimeter (DSC; SEIKO I&E SSC-5000) at a heating rate of 2°C min^{-1}. At least four scans were performed for each sample to check reproducibility. Before each scan, the samples were annealed in a thermostat at the reduced temperature of $\approx$0·98.

2.3. *Photochemical reactions*

Samples for photoreactions were prepared by injecting an isotropic melt of *n*EGMC into a liquid crystal cell with a 12 μm gap and by gradually cooling to an appropriate temperature. The sample thus prepared was placed in a thermostatted block and irradiated with a 300 W high pressure mercury lamp through a glass filter (> 300 nm).

After irradiation, the sample was removed from the liquid crystal cell and was subjected to various measurements: FTIR (JEOL JIR-3505), GPC (JASCO 880-PU; column, Shodex KF800P + FF80M + KF8025; eluent, chloroform) and NMR (JEOL FT90Q; solvent, $CDCl_3$ and $(CD_3)_2CO$).

3. Results and discussion

3.1. *Liquid-crystalline phase behaviour*

Examination of the liquid-crystalline phase behaviour of *n*EGMC and *n*EGC with the polarizing microscope revealed that *n*EGC exhibited no liquid-crystalline phase regardless of the ethylene glycol spacer length while *n*EGMC showed liquid-crystalline phase behaviour in every compound. Figure 2 shows the textures observed for *n*EGMC in the polarizing microscope. All samples were annealed at temperatures where the

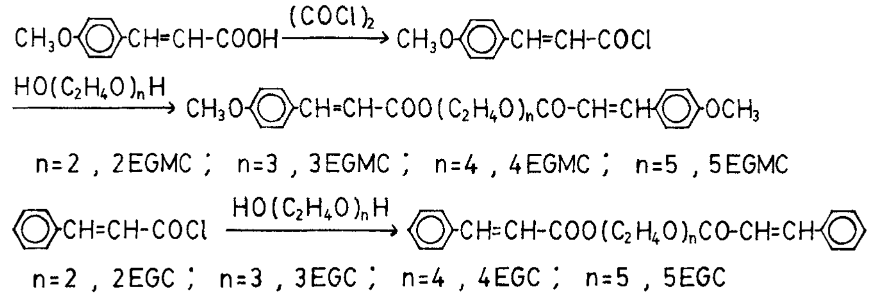

Figure 1. The structures of *n*EGMC and *n*EGC used in this study and their synthetic route.

samples showed the liquid-crystalline phase. The texture observed for 5EGMC is similar to that of the smectic B phase [7], however, the liquid-crystalline phase exhibited by *n*EGMC cannot be determined conclusively at the present stage.

Figure 3 shows the DSC thermograms obtained for *n*EGMC. These thermograms were only observable after prolonged annealing of the samples at temperatures where they showed the liquid-crystalline phase. Once the samples were heated above the liquid-crystalline phase to the isotropic phase transition temperature (T_C), the liquid-crystalline phase appeared only after prolonged annealing at the liquid-crystalline temperatures. The thermograms shown in figure 3 are, therefore, those observed on heating. The table lists the crystal to liquid crystal phase transition temperature (T_M), (T_C), the enthalpy change associated with the crystal to liquid crystal phase transition (ΔH_M) and with the liquid crystal to isotropic phase transition (ΔH_C) and the entropy change for the crystal to liquid crystal phase transition (ΔS_M) and for the liquid crystal to isotropic phase transition (ΔS_C). Of note are the high values of ΔH_C and ΔS_C observed for 2EGMC and 3EGMC in comparison with those of ΔH_M and ΔS_M. It is generally observed that ΔH_C and ΔS_C are smaller than ΔH_M and ΔS_M for liquid-crystalline compounds [8]. From this point of view, 4EGMC and 5EGMC have shown quite an ordinary liquid-crystalline phase behaviour, since in these compounds $\Delta H_M \gg \Delta H_C$ and $\Delta S_M \gg \Delta S_C$. At first, we considered that the large endothermic peaks observed for 2EGMC and 3EGMC at higher temperatures corresponded to a crystal–isotropic phase transition and the small peaks observed at lower temperatures were due to the phase transition from one crystalline phase to another crystalline phase. However, we recognized the mobility of 2EGMC and 3EGMC when flushed, even though very low, in the temperature range between the two endothermic peaks observed in the DSC. Therefore, we assigned the phase between the two endothermic peaks in these compounds as a liquid-crystalline phase.

3.2. *Photochemical reactions*

Figure 4 shows FTIR spectra of 3EGMC before and after photoirradiation at the reduced temperature ($T_{red} = T/T_C$) of 0·98. It is clearly seen that on photoirradiation a peak at 1635 cm^{-1} due to stretching of the C=C bond adjacent to the carbonyl group decreased and concomitantly a peak at 1710 cm^{-1} due to stretching of the C=O bond was shifted towards the high frequency region. Further, a peak at 980 cm^{-1} due to out of plane bending of C=C–H also decreased. These results indicate that photoreaction takes place at the C=C bonds in 3EGMC. The same change in the IR spectra were observed in the other twin dimers.

It is worth mentioning here the change in the texture observed in *n*EGMC in the course of photoirradiation. Figure 5 shows the textures observed in the polarizing microscope at various irradiation times, where 3EGMC in a liquid crystal cell was irradiated at $T_{red} = 0·90$ (75°C). In this experiment, a left half of the sample was covered with a mask to prevent exposure to light. It is seen that with irradiation time the liquid-crystalline texture faded out and finally disappeared completely, indicating that the liquid-crystalline phase is disorganized and transformed to the isotropic phase isothermally on photoirradiation. The liquid-crystalline–isotropic phase transition can be induced in this way by photochemical reaction of the systems.

In order to explore the photochemical reaction quantitatively, the photochemical reactivity was evaluated by measuring the decrease in absorbance at 1635 cm^{-1} (A_{1635}) relative to the absorbance at 2950 cm^{-1} (A_{2950}) which remained unchanged in intensity

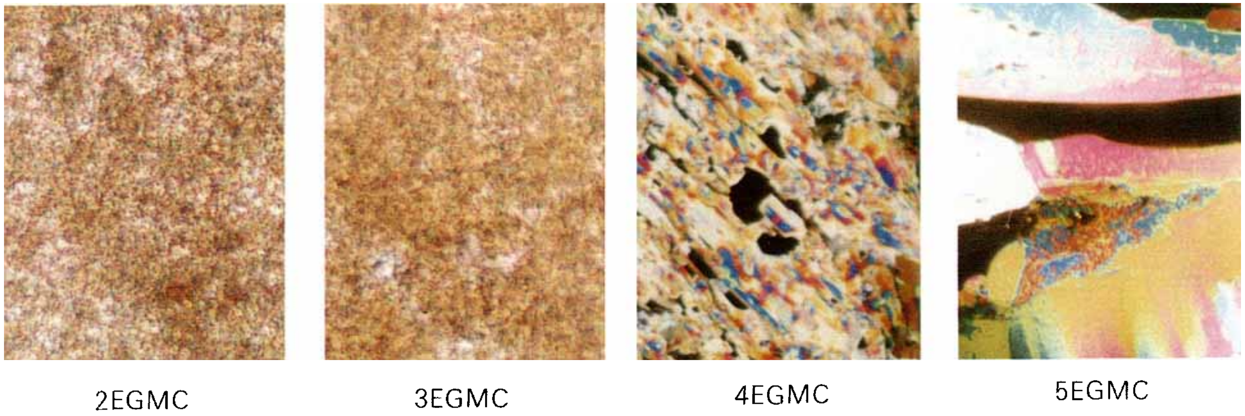

Figure 2. Photographs of textures observed for *n*EGMC. Magnification ×100. Temperature, 65°C (2EGMC); 76°C (3EGMC); 26°C (4EGMC); 20°C (5EGMC).

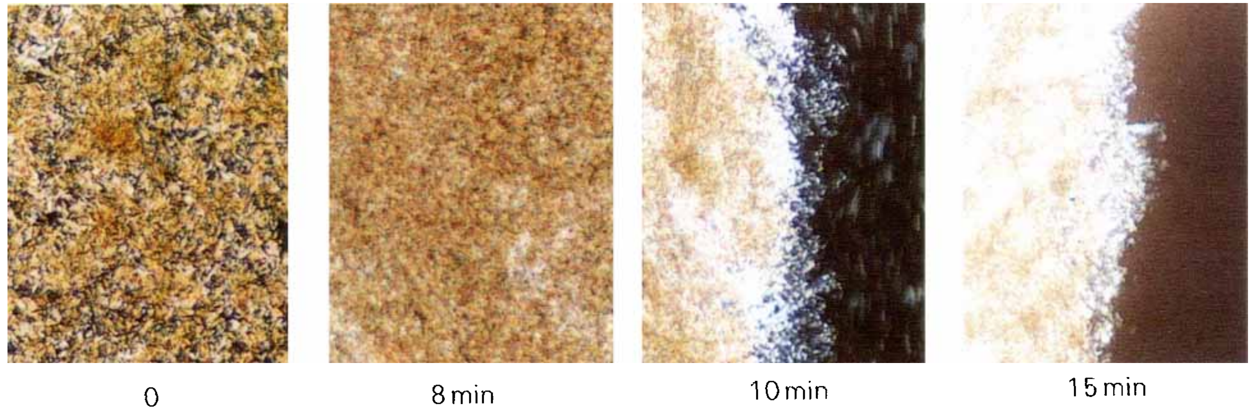

Figure 5. Change in texture of 3EGMC on photoirradiation. Left half was covered with a mask to prevent exposure to light and the photoirradiation was performed in the liquid crystalline state.

Thermodynamic properties of *n*EGMC.

	T_M/°C	ΔH_M/kJ mol^{-1}	ΔS_M/J K^{-1} mol^{-1}	T_C/°C	ΔH_C/kJ mol^{-1}	ΔS_C/J K^{-1} mol^{-1}
2EGMC	56	2·8	45·1	72	27·2	78·8
3EGMC	72	17·1	49·6	83	37·8	106·3
4EGMC	24	22·1	74·3	29	4·6	15·2
5EGMC	16	27·9	95·3	26	3·5	11·7

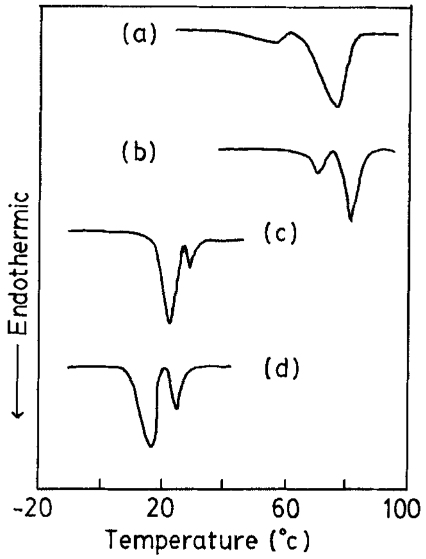

Figure 3. DSC thermograms observed for *n*EGMC. (*a*), 2EGMC; (*b*), 3EGMC; (*c*), 4EGMC; (*d*), 5EGMC. The thermograms are those of heating at a rate of 2°C min^{-1}.

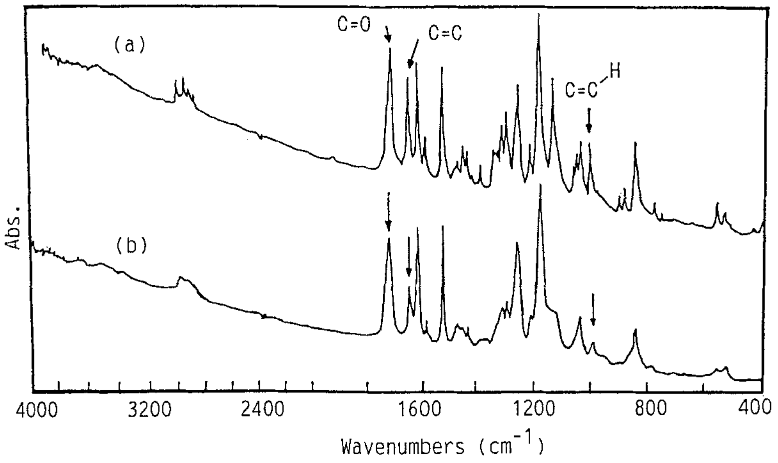

Figure 4. Change in IR spectra of 3EGMC on photoirradiation at >300 nm. (*a*) before photoirradiation; (*b*) after 30 min photoirradiation in the liquid crystalline phase.

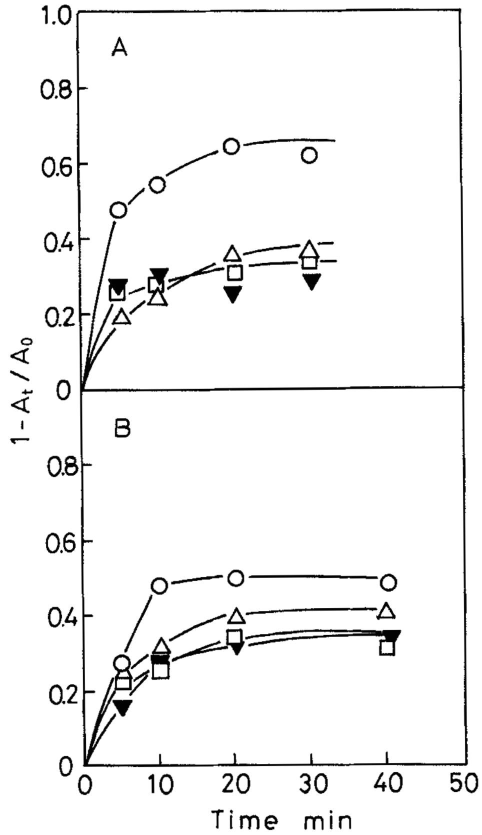

Figure 6. Change in absorbance due to C=C bonds as a function of irradiation time. (A), Isotropic phase; (B), liquid-crystalline phase. ○, 2EGMC; △, 3EGMC; □, 4EGMC; ▼, 5EGMC.

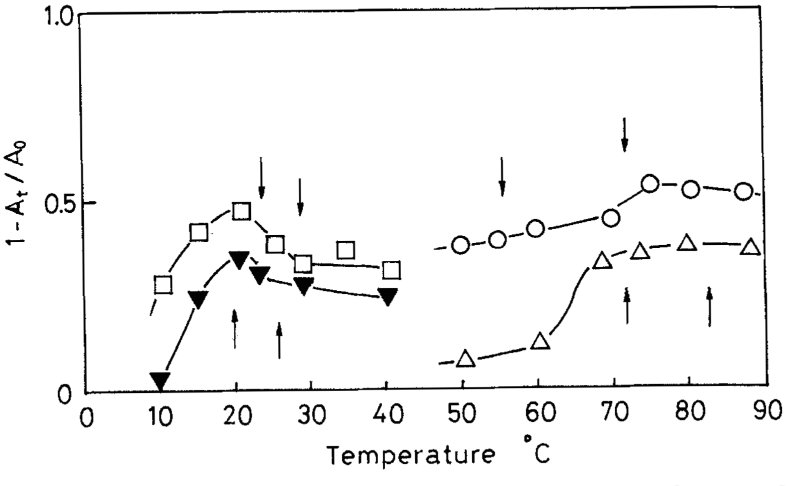

Figure 7. Temperature dependence of photoreactivity in *n*EGMC. ○, 2EGMC; △, 3EGMC; □, 4EGMC; ▼, 5EGMC. Photoirradiation was performed for 20 min. Arrows in the figure indicate the phase transition temperatures (T_M and T_C; $T_M < T_C$) of each sample.

on photoreaction. In figure 6 the relative photochemical reactivity, $1-(A_t/A_0)$, is plotted as a function of the irradiation time in two phases: liquid-crystalline ($T_{red}=0{\cdot}99$) and isotropic ($T_{red}=1{\cdot}01$) phases. Here, A_t indicates the ratio of A_{1635}/A_{2950} at time t and A_0 is A_t at $t=0$. The photochemical reactivity of 2EGMC was found to be higher in both phases than those of the other homologues and after 20 min irradiation no further decrease in absorbance was detected in all samples under present experimental conditions. Owing to lower light intensity used in this experiment than that employed in figure 5, the liquid-crystalline phase still remained after 20 min of irradiation. Figure 7 shows the photochemical reactivity of *n*EGMC as a function of the irradiation temperature, where the reactivity was evaluated at $t=20$ min. This figure reveals an interesting feature in the photochemical reactivity of *n*EGMC: 2EGMC and 4EGMC showed higher reactivity than 3EGMC and 5EGMC in the whole temperature range and *n*EGMC with $n=2$ and 3 and those with $n=4$ and 5 exhibited a similar temperature profile for the photochemical reactivity, respectively. Below T_M, the reactivity was more or less depressed and in a family with $n=4$ and 5 it was again depressed above T_C. In this family, the maximum reactivity was observed at a temperature where the crystalline phase and the liquid-crystalline phases coexist. Depression of the photoreactivity below T_M may be reasonably interpreted in terms of suppressed mobility and unfavourable orientation for the photoreaction of relevant chromophores in the crystalline phase. The lower reactivity observed above T_C in the family of $n=4$ and 5 may be a consequence of random orientation of chromophores in the isotropic phase, although the cinnamic acid derivatives are known to have strong tendency to associate as a pair in the ground state [9].

It is worth mentioning here that the decrease in νC=C reflects the overall reactivity of the cinnamate chromophores; it is a consequence of all photochemical reactions associated with the excited cinnamate such as photodimerization, the photo-Fries reaction and so on. It is, therefore, not directly correlated to the photodimerization. The photodimerization behaviour can be quantitatively discussed only after the product analysis is conducted.

The time course of the photodimerization behaviour was followed by GPC. Figure 8 shows the GPC chromatograms of irradiated samples of 3EGMC. 3EGMC was irradiated in the liquid-crystalline phase at 75°C. Before irradiation, we observed only a single peak, but after irradiation the peaks were detected which corresponded to photoproducts of dimer, trimer and oligomers with higher molecular weight. This result clearly indicates that photodimers and photooligomers were produced on photoirradiation. Figure 9 shows the time course of the formation of the photodimer and the photooligomers with a degree of polymerization of more than 2 at three different phases (crystal, liquid crystal ($T_{red}=0{\cdot}98$) and isotropic ($T_{red}=1{\cdot}03$) phases). In 2EGMC and 3EGMC, the photoreactivity for the dimer formation increased in the order of crystal < liquid crystal < isotropic whereas in 4EGMC and 5EGMC it increased in the order of isotropic < liquid crystal < crystal. Coupled with the thermodynamic data obtained for the twin dimers (see the table), these results seem to indicate that the spatial orientation of the relevant mesogenic chromophores is different between the two families and the temperature dependence of the mutual orientation of the two 4-methoxycinnamate moieties is also different between the two families. Of note is the specifically high reactivity of 4EGMC in the crystalline phase. In the other compounds, the photoreactivity for the dimer formation was less than 20 per cent conversion, however, in 4EGMC the conversion in the crystalline phase was nearly 40 per cent.

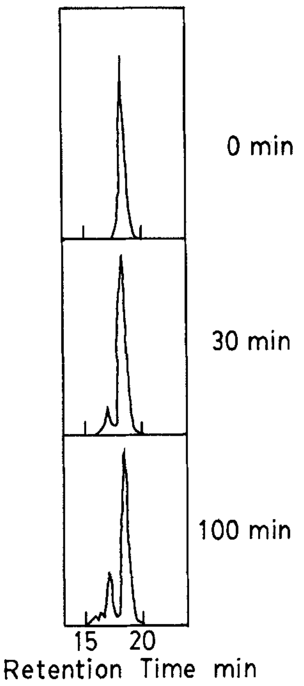

Figure 8. Gel permeation chromatograms of irradiated 3EGMC.

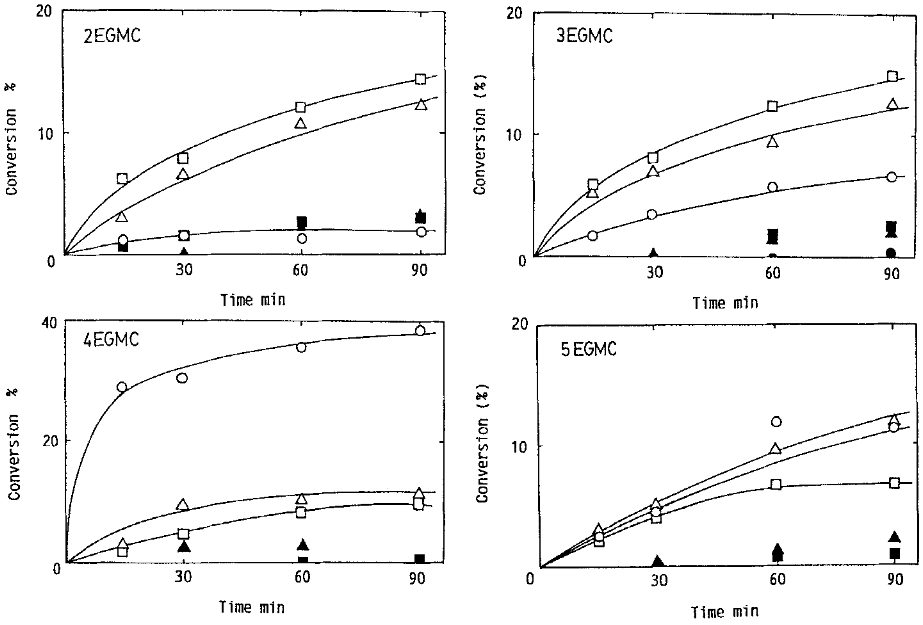

Figure 9. Formation of photodimers and photooligomers on photoirradiation as a function of time. Photodimers: ○, crystal; △, liquid crystal; □, isotropic phases. Photooligomers: ●, crystal; ▲, liquid crystal; ■, isotropic phases.

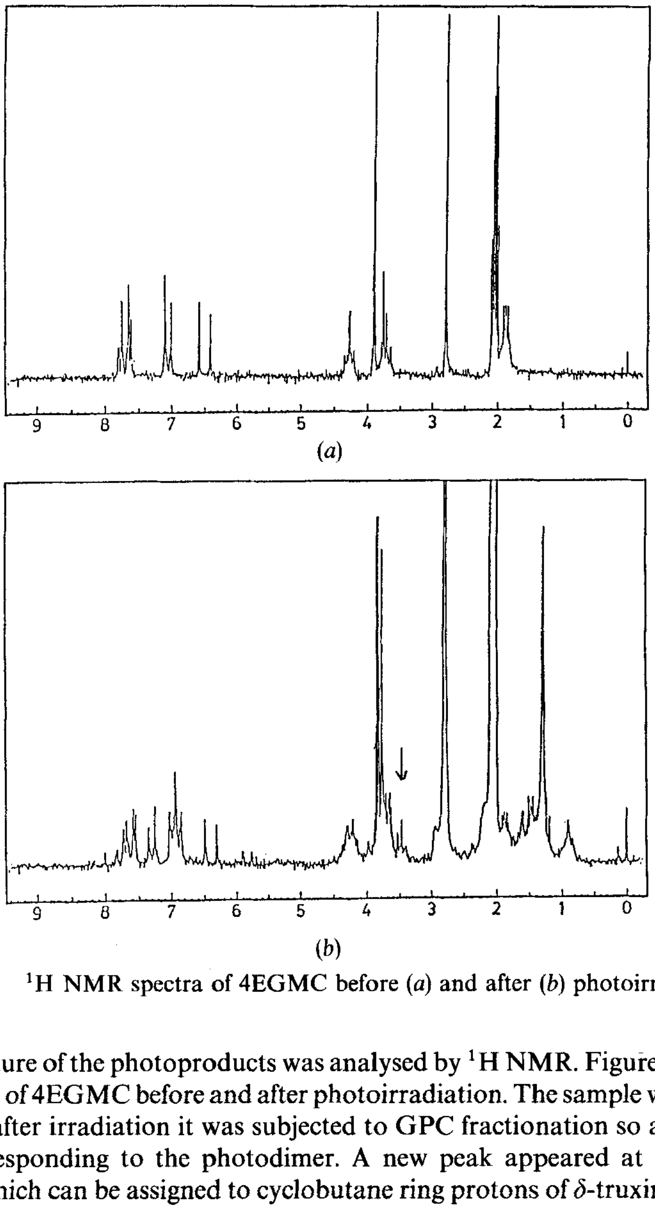

Figure 10. ^{1}H NMR spectra of 4EGMC before (*a*) and after (*b*) photoirradiation.

The structure of the photoproducts was analysed by ^{1}H NMR. Figure 10 shows the NMR spectra of 4EGMC before and after photoirradiation. The sample was irradiated at 15°C and after irradiation it was subjected to GPC fractionation so as to obtain a fraction corresponding to the photodimer. A new peak appeared at 3·4 ppm after irradiation which can be assigned to cyclobutane ring protons of δ-truxinic acid esters according to Green *et al.* [10], indicating that the photoproduct has head-to-head configuration at the methoxycinnamic parts. Although the NMR spectra of various photodimers have been reported (α-truxillic acid, β-truxinic acid, δ-troxinic acid, μ-truxinic acid and so on) [10], the NMR spectra we observed experimentally showed only cyclobutane ring proton signals in agreement with those of δ-truxinic acid ester among those photodimers, but inconsistant with those of possible head-to-tail photodimers, α-truxillic acid ester.

4. Conclusion

In the present study, twin dimers containing 4-methoxycinnamic acid groups at both ends of various lengths of ethylene glycol spacers (*n*EGMC) have been treated.

The liquid-crystalline behaviour, the photoreactivity and the structure of the photoproducts in relation to the morphology of the systems have been examined. It has been demonstrated that the photodimerization takes place quite effectively in 4EGMC so as to keep the head-to-head configuration of the cinnamate moieties, indicating that the 4-methoxycinnamate moieties are in close proximity to each other in the crystalline phase of 4EGMC. The photoreactivity was dependent on the phases as demonstrated by the temperature profile of the photoreactivity.

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