

The photo-Fries rearrangement in a side-chain liquid-crystalline polymer

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The photo-Fries reaction of aryl esters provides a mechanism for the stimulation of a selective photoinduced structural rearrangement. We demonstrate that, in a side-chain liquid-crystal polymer containing 20% 4-methoxyphenyl cinnamate and 80% 4-cyanophenyl benzoate mesogens, photoinduced phase depressions may be achieved by selective irradiation of the cinnamate esters. When only the photo-Fries process is activated, by irradiation in dilute solution, subsequent phase depressions as high as 60–70°C are observed. In the liquid-crystalline state, other photoprocesses, including crosslinking, tend to predominate over the photo-Fries reaction and inhibit large-scale rearrangement, and hence rather limited phase transition shifts are observed.

(Keywords: liquid-crystalline polymer; photoactive; crosslinking; photo-Fries rearrangement; aryl esters; optical data storage)

INTRODUCTION

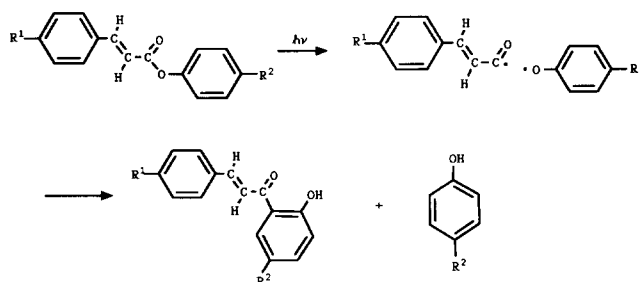
The photo-Fries rearrangement of aryl esters¹ is so named because the starting materials and principal products are the same as those formed in the Lewis-acid-catalysed Fries rearrangement. The mechanism involves homolysis of the carbonyl–oxygen bond and the products are those derived from the recombination of the radical pair (Scheme 1). The formation of some free phenol is confirmation of the dissociative nature of the reaction pathway.

We have been interested in studying the effect of photoinduced structural changes of a chromophoric guest on a host liquid-crystal phase in polymers with mesogens in the side chain. We have chosen to investigate the photochemical reactions of cinnamate esters and their analogues in this context. The materials we have prepared were generally methacrylate polymers prepared by free-radical polymerization^{2–4}, although acrylate polymers can be prepared by an alternative route². The cinnamate esters have been incorporated into the polymers in the form of mesogenic side chains and, in the case of bulky analogues of cinnamate esters, as non-mesogenic side chains. The liquid-crystalline matrix consisted of cyanophenyl benzoate esters, although homopolymers of the mesogenic cinnamate monomers were also prepared.

Aryl esters of cinnamic acids are good candidates for the photo-Fries reaction; indeed, in one class of cinnamate ester mesogen that we prepared, the photo-Fries reaction is the main photolysis pathway seen in dilute solution⁴. Since the rearrangement process destroys the linear configuration of the mesogen, this process is expected to affect profoundly the stability of any liquid-crystal phases exhibited by the material. This rearrangement can be compared with the *trans*–*cis* photoisomerization of azobenzenes, which has been shown to induce phase transitions in low-molar-mass⁵ and polymeric liquid crystals^{6,7}. *Trans*–*cis* photoisomerization can also occur in cinnamate

esters and their analogues⁸ and this may result in modification of the phase behaviour of polymeric liquid crystals⁹. In all these materials changes in the liquid-crystal properties of the system are brought about by a photoinduced shift in the composition of the molecular ensemble, changing some of the molecular entities to new structures that pack less well into the anisotropic array. It ought therefore to be possible to induce isothermal phase transitions of this type by means of the photo-Fries rearrangement, or indeed by any other molecular rearrangement that brings about a transformation to a molecular configuration that is less favourable for the formation of liquid-crystal phases than the initial unit. The main distinction between molecular rearrangements such as the photo-Fries reaction and photoisomerization processes is that the former is irreversible, whereas the latter has the potential for reversibility and consequent cycling of the effect. Aryl cinnamate esters may be selectively irradiated in the presence of aryl benzoate mesogens because the cinnamate ester u.v. absorption maximum occurs at a longer wavelength owing to its more highly conjugated nature⁴.

Most of the work on the photo-Fries rearrangement in polymer science has been concerned with glassy polymers. Examples include the generation of non-random chromophore distributions in a low-molar-mass



Scheme 1 Photo-Fries rearrangement of an aryl cinnamate ester

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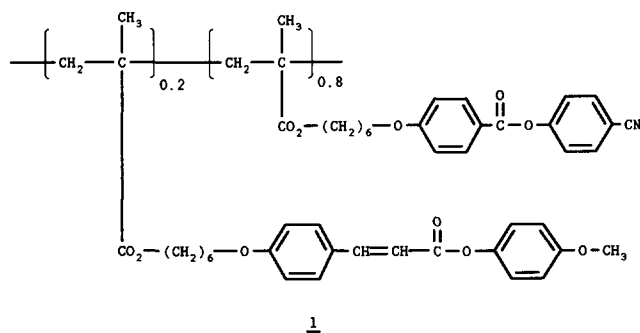
guest-polymeric host system¹⁰ and the design of an experimental photoresist¹¹. In the latter material the photolysis of pendant ester groups to phenolic fragments results in sufficient modification in the solubility characteristics of a polymer for the material to be exploited as both a negative- and positive-working resist, depending on the choice of developing solvent.

Photo-Fries rearrangement has been observed in liquid-crystalline polymers as one of the processes occurring in the photolysis of a main-chain polymer containing aryl cinnamate mesogens¹². A homologous material has been used as the basis of a laser-writing technique¹³ where optical contrast results from the yellow colouration due to the photo-Fries process, which can be viewed using unpolarized light, and from a birefringent image, observable between crossed polarizers, due to a thermo-optic mechanism. The effect of liquid-crystalline environments on the rates and quantum yields of the photo-Fries rearrangement of aryl benzoates has been reported¹⁴. No mention has been made, however, of the potential of the photo-Fries rearrangement as a means of influencing the phase stability of a liquid-crystal system.

In this work we have set out to exploit the liquid-crystal matrix as a means of amplifying the result of photo-induced molecular rearrangements; in this report we focus our attention on the photo-Fries rearrangement as the photochemical trigger.

MATERIALS

The syntheses of monomers and polymer are described elsewhere⁴. The liquid-crystal polymer used in this study is the copolymer 1. The phase transition temperatures (determined by differential scanning calorimetry) and



molar-mass data (from gel permeation chromatography, solvent *N,N*-dimethylformamide, calibrated using poly(ethylene oxide)/(poly(ethylene glycol) standards and corrected for the monomer molar masses) are given in Table 1.

EXPERIMENTAL

Polymer samples were irradiated using a 150 W Xe-Hg arc lamp (Photon Technology) or in the experimental set-up illustrated in Figure 1 and described below. U.v. spectra were recorded on a Perkin-Elmer 330 spectrophotometer coupled to a microcomputer data station. Thermal phase transitions were determined by polarizing optical microscopy using a Zeiss Jenalab optical microscope equipped with a Linkam TH 600 hot stage and a photodiode detector recording system.

Table 1 Molar-mass and phase transition data for polymer 1

Polymer	\bar{M}_n (g mol ⁻¹)	\bar{M}_w (g mol ⁻¹)	\bar{M}_w/\bar{M}_n	T_g (°C)	T_1 (°C)	T_2 (°C)
1	3.77×10^5	6.10×10^5	1.62	41	125	132.5

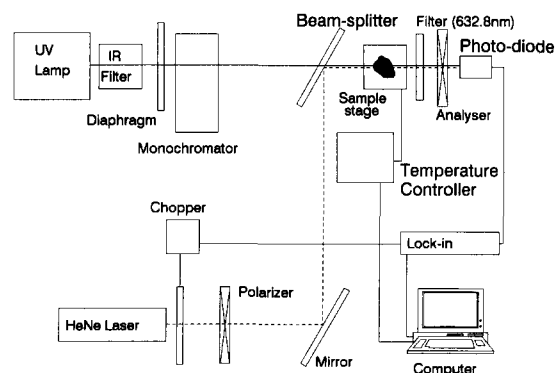


Figure 1 Experimental set-up for the irradiation of liquid-crystalline polymer samples

Solution irradiation

The 20% copolymer, polymer 1 (5.2 mg), was dissolved in dichloromethane (25 ml). Portions of this solution were irradiated in a 1 cm path-length quartz cell placed in front of the exit slit to a monochromator passing a 16 nm wide band centred on 315 nm. Solutions were irradiated for 5, 10, 30 and 60 min and the initial and final u.v. spectra recorded. Samples of each solution were then allowed to evaporate and the clearing transition temperatures of the cast films determined in the polarizing microscope by recording the thermo-optic curves. In such a procedure the intensity of the transmitted light, through an optical microscope arranged with crossed polarizer and analyser, is recorded as a function of the temperature of the sample. At the liquid-crystal-isotropic phase transition the intensity falls to zero.

Irradiation of polymer films in the glassy, liquid-crystalline and isotropic states

Thin films of copolymer 1 on quartz were prepared by casting a dilute solution of the polymer (in dichloromethane) onto the quartz surface and allowing the solvent to evaporate. Films prepared in this way had good optical clarity but uneven surfaces. The thickness of films (not measured) was such that the absorbance of the peak at ~ 320 nm had a value of between 0.3 and 1.2. The film prepared for irradiation in the isotropic state was cast onto the face of a 0.1 cm path-length quartz u.v. cell.

Polymer films prepared in this way were mounted for irradiation in the apparatus illustrated in Figure 1, at room temperature (glassy state), at 120°C (liquid-crystalline state) and at 160°C (isotropic state). Irradiation was carried out using a 40 nm wide band centred on 320 nm. The spectra of the films were recorded by removing the quartz disc, cooling rapidly to room temperature and remounting it in the u.v. spectrometer after each irradiation step. In the case of the film irradiated at 160°C, the quartz cell was mounted in a slot in a heating block similar to that shown in the set-up

of Figure 1, but which could be mounted both in the u.v. spectrophotometer and in the path of the beam from the xenon arc lamp. In this way the polymer film was in the isotropic state during the irradiations and whilst recording the spectra. Light scattering in the film, caused by cooling from the isotropic state through the liquid-crystalline state to the glass, was thereby avoided.

Isothermal phase transitions

Samples of the copolymer **1** were prepared by melting a small amount of the polymer between two glass coverslips. These were introduced into the heating block of the apparatus depicted in Figure 1 and held for 60 min at a temperature of $T_{N-1} - 1^\circ\text{C}$ in order to anneal the liquid-crystal texture. The light from the He-Ne laser, modulated by the optical chopper and transmitted through the polarizer-sample-analyser system, is detected using a photodiode and lock-in amplifier and the signals recorded in a microcomputer system. The transmitted light intensity was initially very low owing to the intensely scattering nature of the polymer liquid-crystal phase but rose to a detectable level after the annealing period. The temperature was then adjusted to some new value, ΔT degrees below the clearing transition, and the sample annealed again at this new temperature for up to 20 min to establish a detectable level of transmitted light intensity. The diaphragm was then opened to allow u.v. light of 350 nm to fall on the polymer sample. The transmitted light intensity was recorded by the computer system as a function of irradiation time, and by this method photoinduced isothermal phase transitions could be identified and the kinetics measured. A fresh sample of polymer was used for each run.

RESULTS AND DISCUSSION

Solution irradiation

The results of irradiation on polymer **1** can be seen from the u.v. spectra, shown in Figure 2. The spectra are typical of those seen for cinnamate esters undergoing the photo-Fries rearrangement, with the development of a new absorption band tailing into the visible region and the loss of the band at 316 nm due to the cinnamate ester. Extending the irradiation time beyond 60 min in a

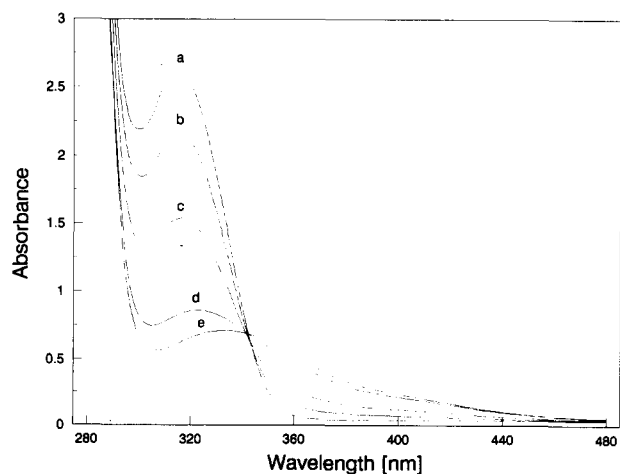


Figure 2 U.v. overlay spectra of polymer **1**, irradiated in solution (0.208 g l^{-1} in dichloromethane). Irradiation times: a, 0 min; b, 5 min; c, 10 min; d, 30 min; e, 60 min

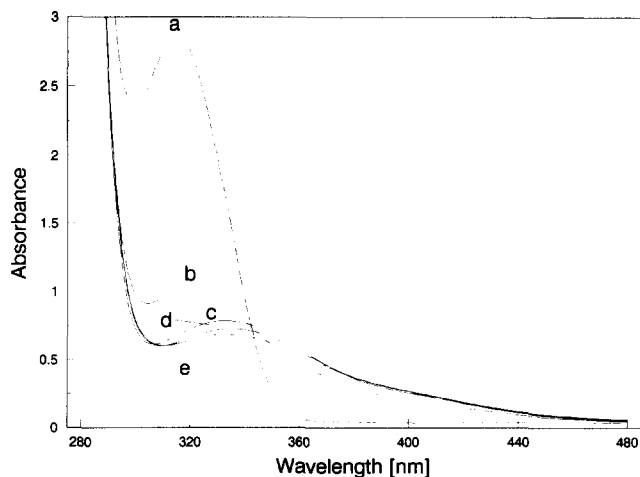


Figure 3 U.v. overlay spectra of polymer **1**, irradiated in solution (0.196 g l^{-1} in dichloromethane). Irradiation times: a, 0 min; b, 30 min; c, 60 min; d, 120 min; e, 180 min

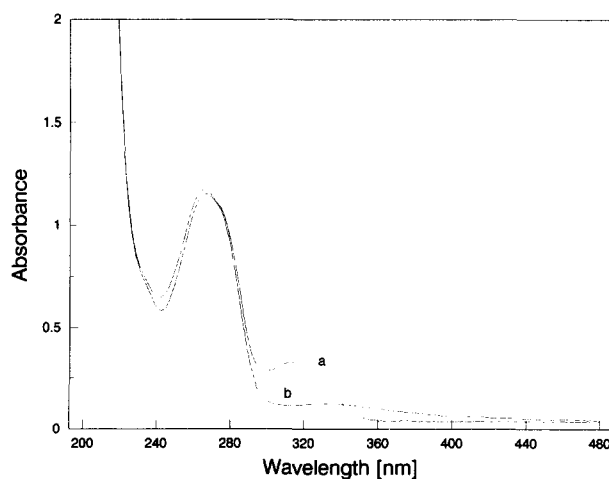


Figure 4 U.v. overlay spectra of polymer **1**, irradiated in solution (0.196 g l^{-1} in dichloromethane). Irradiation times: a, 0 min; b, 60 min

separate experiment (Figure 3) shows no further increase in the long-wavelength tail, but there is a drop in intensity of the new maximum seen at 333 nm. This is due to a secondary photoprocess, presumably $[2\pi + 2\pi]$ photocycloaddition, involving the initial photoproduct, but which occurs at a much slower rate. Figure 4 shows the spectra of the 0 and 60 min irradiated solutions of Figure 3, but recorded in a 0.1 cm path-length quartz cell. From these curves it can be seen that there has been no loss of the cyanophenyl benzoate mesogen, as the intensity of the peak at 267 nm is not reduced.

Kinetics of the photo-Fries rearrangement

If the photo-Fries rearrangement is considered to be complete after 60 min irradiation (which is a reasonable assumption given the data of Figures 2 and 3), the percentage of cinnamate units remaining at each irradiation time can be calculated from an analysis of the u.v. spectra. This allows the time dependence of the photo-Fries rearrangement to be investigated. While not conducted under rigorous kinetic experimental conditions, the available data give very good agreement with the expected first-order kinetics, being an exponential

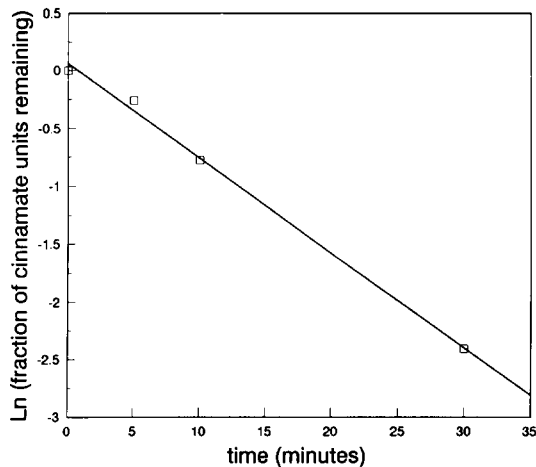


Figure 5 Kinetic data for the photo-Fries rearrangement of polymer 1, plotted on a logarithmic scale (correlation coefficient 0.997)

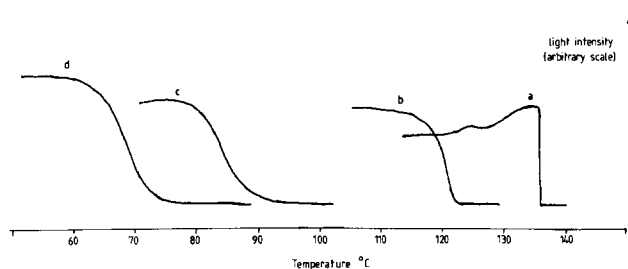


Figure 6 Thermo-optic curves for polymer 1, cast from solution irradiated samples. Irradiation times: a, 0 min; b, 5 min; c, 10 min; d, 60 min

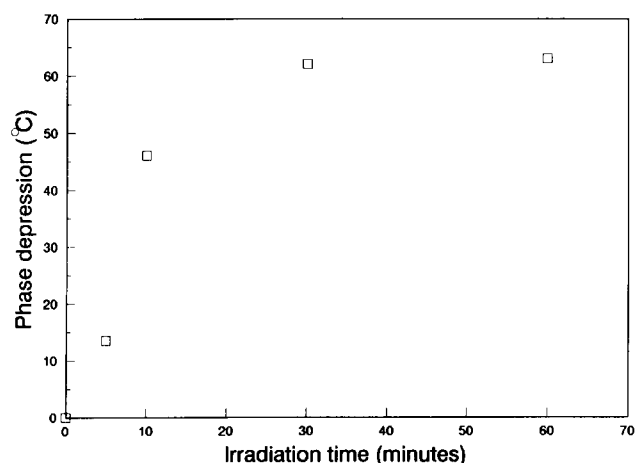


Figure 7 Depression of the clearing transition temperature with irradiation time for polymer 1 irradiated in solution

function, consistent with a unimolecular photoinduced process. These data are presented in logarithmic form in Figure 5.

Depression of phase transition temperature

The phase transition temperatures of the solution-cast films were determined by polarizing optical microscopy, recording the transmitted light intensity as a function of temperature. The clearing behaviour of the irradiated samples showed a broadening of the transition and large depressions of the transition temperature. This is illustrated by the thermo-optic curves shown in Figure

6. In the case of broad transitions the temperature at which the optical transmission has dropped by 90% towards the final value was taken as the transition temperature. Figure 7 shows the depression in the transition temperature, ΔT , plotted against irradiation time. Initially there is a linear relationship between this depression and the fraction of cinnamate units undergoing rearrangement, as shown in Figure 8, although there is some saturation at high fractions of the photo-Fries product. Such a linear dependence in the phase depression is expected from molecular theories⁵.

The observed drop in phase transition temperature is due to the change brought about in the side-chain mesogens. In the unirradiated polymer 100% of the side chains are mesogenic; progressive irradiation converts up to one in five of those units to disruptive non-mesogenic structures with a consequent reduction in the liquid-crystal phase stability. The change in the shape of the side chains brought about by photo-Fries rearrangement is illustrated in Figure 9, the rearranged hydroxychalcone groups having much less linear character than the initial cinnamate esters. Similar effects are reported in liquid-crystalline polymers bearing reversibly photoisomerizable azobenzene substituents, which can safely be irradiated in the bulk without fear of crosslinking. The magnitudes of observed phase

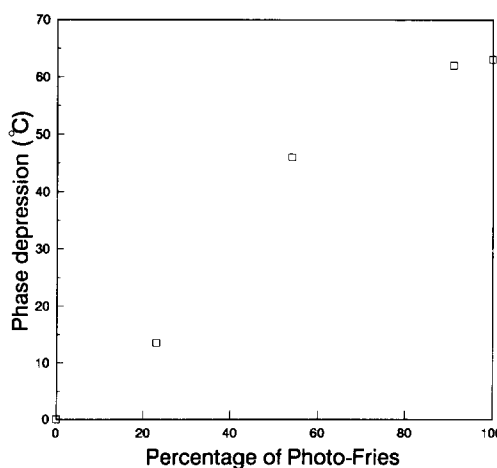


Figure 8 Depression of the clearing transition temperature against percentage of cinnamate groups undergoing rearrangement

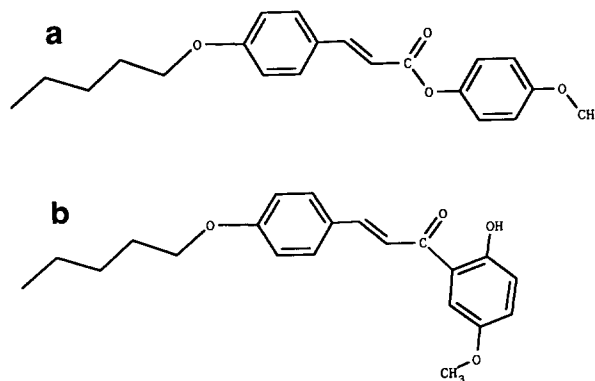


Figure 9 (a) 4-Methoxyphenyl cinnamate mesogen and alkyl spacer chain in its initial state. The spacer chain is shown in the extended conformation, although a number of configurations are possible. (b) *Ortho* photo-Fries product of the irradiated cinnamate ester showing departure from the linear mesogen-like shape

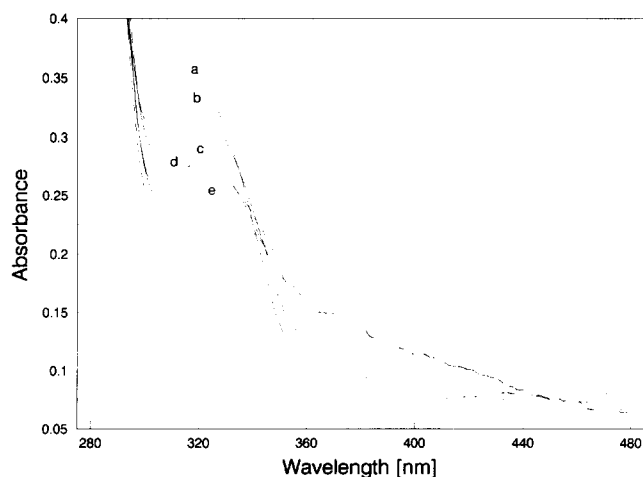


Figure 10 U.v. overlay spectra of polymer 1 irradiated in the glassy state (room temperature). Irradiation times: a, 0 min; b, 20 min; c, 58 min; d, 88 min; e, 118 min

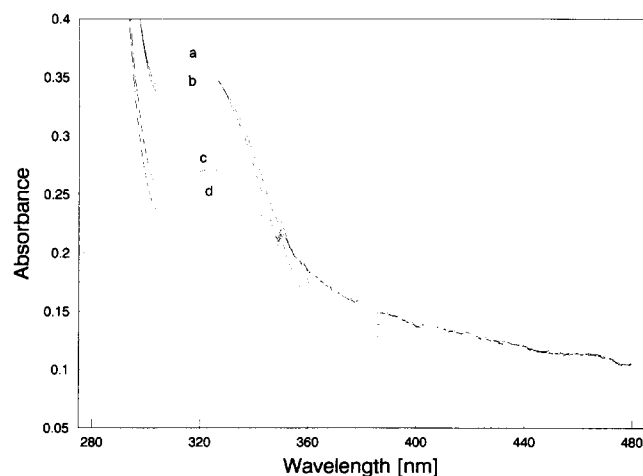


Figure 11 U.v. overlay spectra of polymer 1 irradiated in the liquid-crystalline state (120°C). Irradiation times: a, 0 min; b, 10 min; c, 30 min; d, 60 min

depressions in polymeric liquid crystals are often not reported⁷, the response time for the induction of an isothermal phase transition at a particular reduced temperature being regarded by some authors as the most important experimental parameter. Preliminary studies with an azobenzene-based polymer system suggest that the phase depression may be small⁶, especially in high-molar-mass polymers. Phase depressions of the magnitude shown by the photo-Fries rearrangement are more typical of those seen in low-molar-mass liquid-crystal-azobenzene mixtures⁵, which can be explained in terms of theories of mesogen/non-mesogen mixtures. This is despite the high-molar-mass nature of the polymer. Extrapolation of the results shown in *Figure 8* to a system with 100% photoactive units suggests a liquid-crystal ordering temperature of the photo-Fries product close to -273°C , indicating that such units are essentially non-mesogenic⁵. The broadening of the observed clearing transition in the current materials may be an effect of the increased viscosity of the polymer as the clearing transition approaches the glass transition temperature in addition to any inhomogeneities in the photoinduced rearrangements.

Irradiation in the glassy, liquid-crystal and isotropic states

The u.v. spectra of *Figures 10, 11* and *12* show the result of irradiating films of polymer 1 in the glassy, liquid-crystalline and isotropic states. In the bulk state $[2\pi + 2\pi]$ photocycloaddition, leading to crosslinking via the formation of cyclobutane adducts, is a possible competing process for both the starting cinnamate ester and the product chalcone derivative. This is in contrast to the photolysis of dilute solutions where the unimolecular photo-Fries rearrangement is seen to dominate (*Figure 2*).

Irradiation of the polymer in the glassy state (*Figure 10*) gives results that are still fairly typical of photo-Fries product formation over the period of irradiation studied. *Figure 11*, however, shows little increase (approximately one-third of the increase shown by the curves of *Figure 10*) in the intensity of the long-wavelength absorbance while still showing loss of intensity of the cinnamate ester peak. This would be consistent with cyclobutane formation competing with photo-Fries rearrangement in the liquid-crystalline state. In the isotropic state the situation again resembles the photolysis of the glassy polymer (*Figure 12*) with photo-Fries product formation predominating, although at a much faster rate. The increased rate of reaction in this case is partly due to the modified geometry of the irradiation set-up and the lack of light scattering in the film giving a higher incident light intensity.

These results suggest that when there is an isotropic arrangement of mesogenic cinnamate esters, as is the case above T_{N-I} , irradiation initially induces photo-Fries rearrangement to occur. In the ordered liquid-crystalline state, however, a favourable alignment of side chains increases the likelihood of cycloaddition processes, which compete effectively with rearrangement. In the glassy film the lack of mobility of the polymer chain acts to inhibit bimolecular processes occurring between side chains. A recent study of the photo-Fries rearrangement of a series of mesogenic phenyl benzoates and phenyl-*trans*-cyclohexane carboxylates in host liquid-crystal solvents¹⁴ also reported lower quantum yields for *ortho* photo-Fries product formation in the more ordered liquid-crystal phases due to the reduced mobility of the intermediate radicals. Keller has reported the utilization of poly-

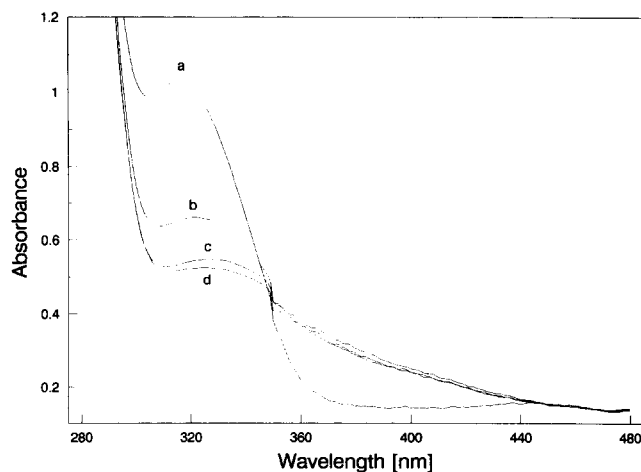


Figure 12 U.v. overlay spectra of polymer 1 irradiated in the isotropic state (140°C). Irradiation times: a, 0 min; b, 10 min; c, 20 min; d, 30 min

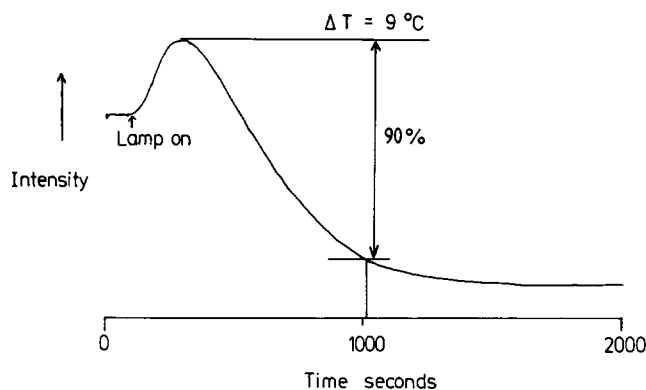


Figure 13 Transmitted light intensity through a sample of polymer 1 between crossed polarizers, plotted against irradiation time. $\Delta T = 9^\circ\text{C}$

siloxanes bearing phenyl cinnamate mesogens as a method of liquid-crystal elastomer synthesis by photo-crosslinking¹⁵. It appears from the development of a long-wavelength absorbance in the u.v. spectra of crosslinked samples that photo-Fries rearrangement is also a competing process in the photolysis of those materials.

Isothermal phase transitions

In the light of the above discussion it is not surprising that the result of isothermal irradiation of polymer 1 in the liquid-crystalline state does not show a simple photoinduced phase transition. Of all of the situations studied, irradiation in the liquid-crystalline state gives the least selectivity in the photochemistry. The measured loss of birefringence (*Figure 13*) occurs undoubtedly as a result of a photoinduced phase transition. However, the material is clearly not in equilibrium, as may be observed by a second heating cycle. Competing processes of the photo-Fries rearrangement include photochemical crosslinking (which can be shown to have occurred by the insolubility of the irradiated films) and photo-isomerization about the carbon-carbon double bond, although no evidence for this can be seen in the u.v. spectra. It is not clear what combined effect these will have on the system under discussion: while crosslinking also results in the removal of the mesogenic nature of the side chains, crosslinking of liquid-crystalline polymers in the liquid-crystal state may also serve to lock in the anisotropy of the backbone and hence of the side chains. This latter process is the basis of the memory effect in liquid-crystal elastomers¹⁶. These opposing effects limit the effectiveness of the photo-Fries rearrangement as a means of inducing isothermal phase transitions to the isotropic state. Essentially, although the composition of the material may be changing through the photo-Fries process, the resultant structural rearrangements that would lead to a phase transition are inhibited by the crosslinked structure. The crosslinking produces a network, which seems unfortunately to lock in a non-equilibrium but anisotropic structure. The correlation of irradiation time against ΔT , the data shown in *Figure 14*, is prone to large variations but there is a clear trend. The feature at around $\Delta T = 4\text{--}5^\circ\text{C}$ could be related to the nematic to smectic phase transition, which occurs at 7.5°C below T_{N-I} in the unirradiated polymer. Thus in the liquid-crystal phase, phase depressions of $5\text{--}10^\circ\text{C}$ may be easily achieved, in contrast to $60\text{--}70^\circ\text{C}$ realizable when the photo-Fries process is activated (*Figures 6, 7 and 8*).

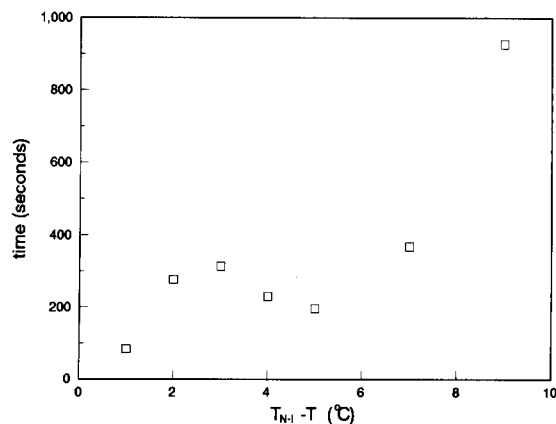


Figure 14 Plot of time for transmitted light intensity to fall by 90% of maximum value for samples of polymer 1 between crossed polarizers, against ΔT

SUMMARY

Solution experiments establish the photo-Fries rearrangement of cinnamate esters to be an extremely effective method of selectively altering the composition, and hence the liquid-crystal properties, of a mesogenic copolymer in an irreversible manner. Depressions of the clearing temperature of the order of $60\text{--}70^\circ\text{C}$ are possible with only 20 mol% of the photoactive units. These properties would seem to make this photoactive liquid-crystal polymer suitable for use as an optical recording medium. However, when the polymer is irradiated in the liquid-crystalline state, photo-Fries rearrangement is suppressed to some extent and crosslinking predominates, and rather limited photoinduced phase depressions are observed.

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