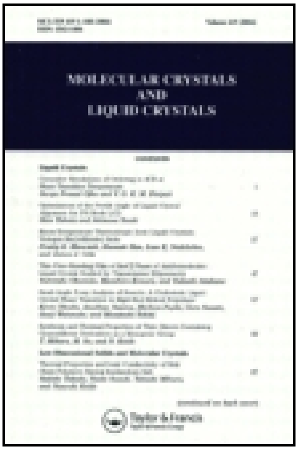

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Photochemical Crosslinking of Novel Polycinnamate Main Chain Mesogens

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PHOTOCHEMICAL CROSSLINKING OF NOVEL POLYCINNAMATE MAIN CHAIN MESOGENS

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Abstract A prototype cinnamate based main chain liquid crystalline polymer was synthesized and characterized. Its photochemistry was studied in the form of a thin film. The polymer undergoes photochemical crosslinking. Major photoreactions are postulated as 2+2 cycloaddition and photo-Fries rearrangement.

INTRODUCTION

Polymers with cinnamate ester appendages such as poly(vinyl cinnamate) are quite photochemically reactive. Thorough investigations by Reiser and coworkers[1] have shown that such polymers undergo a high yield crosslinking reaction which proceeds by a photocycloaddition process between the carbon-carbon double bonds of the cinnamate ester side chains. As a result of this efficient photoinduced crosslinking process, poly(vinyl cinnamates) have found success as photoresists[2].

Another class of macromolecules which have received widespread attention due to their unique ordering characteristics are thermotropic liquid crystalline polymers. Liquid crystalline polymers combine orientational ordering with the ability to flow under moderate stress. Applications for liquid crystalline polymers are under continued investigation in many laboratories. They range from use as nonlinear optical materials to high strength plastics and fibers. Liquid crystalline polymers often have mesophases at high temperatures which may require processing under stringent conditions.

This paper describes a preliminary report of the synthesis and photolysis of a thermotropic liquid crystalline polymer with a cinnamate ester group in the polymer backbone. It contains a siloxane linkage which provides some degree of flexibility to the polymer and results in a nematic liquid crystalline polymer at relatively low temperatures. In addition, because of the reactive cinnamate ester chromophore in the backbone, it crosslinks by a photocycloaddition process. There is an interesting patent by Charbonneau[3] which describes various liquid crystalline polymers of 3-methoxy-4-hydroxycinnamic acid (ferulic acid) which are said to be capable of photo-crosslinking, but no details are provided.

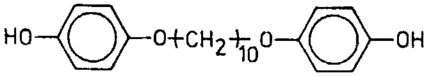
EXPERIMENTAL

GENERAL

Melting points (uncorrected) for all monomers and their precursors were determined using a Thomas-Hoover capillary melting point apparatus. Proton NMR spectra were obtained on a Varian EM-360 spectrometer using tetramethylsilane as internal reference. Infrared spectra were obtained on a Mattson Polaris FT-IR spectrophotometer. Elemental analyses on all new compounds were performed by Galbraith Laboratories, Knoxville, TN. All UV spectra were recorded on a Perkin-Elmer Model 552 spectrophotometer. Polarized light microscopy was conducted using a Reichert-Thermovar microscope equipped with a Mettler FP-52/5 hot stage. The photocrosslinking work was done using a Bausch and Lomb SP 200 high pressure Hg lamp source with monochromator. A Lauda K-2/R thermal circulator was used to perform both the UV absorption studies and the photocrosslinking experiments as a function of temperature. Differential scanning calorimetry was performed on a Du Pont 9900 Thermal Analysis System using a model 910 DSC cell. All temperatures quoted are in degrees Celsius.

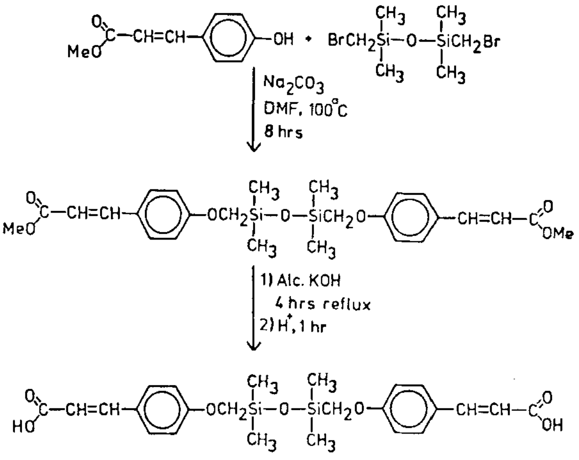
MONOMER SYNTHESIS

Diphenol 1 was synthesized using the procedure of Griffin and Havens[4]. Melting point and other physical data are comparable to those previously obtained.



4,4'-dihydroxy-1,10-diphenoxydecane 1

Compound 2 was synthesized according to the scheme shown below.



Synthesis of Diacid 2

1,3-bis[4-(methyl acrylate)phenoxymethyl]tetramethyl disiloxane was prepared by adding a solution of p-hydroxymethyl cinnamate (20 g, 0.112 mol) in DMF (35 mL) to 1,3-bis(bromomethyl)tetramethyl disiloxane (17.98 g, 0.056 mol) in the presence of anhydrous Na_2CO_3 (14.84 g, 0.14 mol) and heating for 8 h at 100°C. The mixture was then cooled to room temperature and poured into 400 mL of ice water and filtered. The crude product was washed several times with water and then air dried. The solid was recrystallized from 75% ethanol:50% yield, M.P. 83-85°C.

1,3-bis[4-(acrylic acid)phenoxymethyl]tetramethyl disiloxane 2 was prepared from the above methyl ester (15 g, 0.029 mol) by vigorously refluxing it with 10% alcoholic KOH (350 mL) for about 4 h. The solution was then poured into about 300 mL of water and the solution acidified with concentrated HCl. It was stirred for 1 h and the precipitated diacid was filtered and washed thoroughly with water and dried. The crude diacid was recrystallized from EtOH/DMF:75% yield, M.P. 211-213°C. NMR ^1H (DMSO-d_6) δ 0.23 (s, 12H), 3.70 (s, 4H), 6.43 (d, 2H), 6.86-7.96 (m, 10H). IR(KBr) cm^{-1} 2964, 2595, 1687, 1678, 1601, 1509, 1241, 1213, 1167. Anal ($C_{24}H_{30}O_7Si_2$) Calcd: C, 59.26; H, 6.17. Found: C, 59.15; H, 6.03

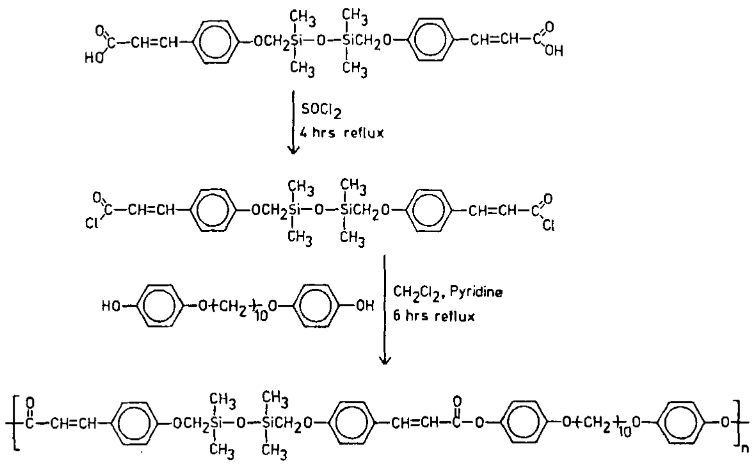
POLYMER SYNTHESIS

Diacid 2 was refluxed with an excess of thionyl chloride for 4 h after which thionyl chloride was removed with a rotary evaporator. The residual diacid chloride was washed with small amounts of petroleum ether, isolated by filtration, and then dried under aspirator vacuum for about 20 min. It was used as such for the polymerization. Diphenol 1 (3.677 g, 7.02 mmol) was dissolved in pyridine (20 mL), and separately the diacid chloride was dissolved in methylene chloride (ca. 75 mL). The two solutions were mixed and heated at reflux for 6 h. The solution was then poured into acetone (ca. 400 mL) and filtered to give a yellow solid polymer. This was redissolved in 1,1,2,2-tetrachloroethane and boiled with decolorizing carbon for about 5-10 min., filtered, and then reprecipitated from EtOH/H_2O. The polymer was then thoroughly dried under vacuum at room temperature. The presence of the cinnamate chromophore was confirmed by UV spectroscopy. The nematic liquid crystalline nature of the polymer (called SiC10) was established by polarizing microscopy and DSC. The inherent viscosity of the polymer was 0.14 g/dL in chloroform at 25°C. NMR ^{1}H ($CDCl_3$) δ 0.23 (s, 12H), 1.26 (s, 16H), 3.5 (s, 4H), 3.7 (s, 4H), 6.33 (d, 2H), 6.53-7.56 (m, 16H), 7.69 (d, 2H). IR(KBr) cm^{-1} 2935, 2854, 1603, 1509, 1503, 1245, 1195, 1169, 1140. Anal calcd: C, 68.31; H, 6.93. Found: C, 67.48; H, 7.07.

PHOTOCROSSLINKING PROCEDURE

The polymer was cast as a thin film on the outside of a 1 cm quartz cell by spin-coating from a solution of the polymer in chloroform. The initial spectrum before irradiation was recorded at room temperature. Photolysis of the polymer film was carried out at 313 nm through the high intensity B & L monochromator. The quartz cell was placed at a distance of 7 cm from the monochromator exit.

Film photolysis was carried out as a function of temperature and phase type. When operating above room temperature, the temperature of the quartz cell was varied by filling it with ethylene glycol, placing it in a thermostated cell holder and circulating ethylene glycol at various temperatures using a Lauda K-2/R thermal circulator. The extent of crosslinking was estimated by



Polymerization Scheme

washing the film after irradiation in chloroform for 1 min., drying, and then measuring the absorbance again at 313 nm. From this an estimate of the insoluble polymer formed could be obtained. The UV spectrum of the polymer film, cast as above, was recorded after heating to different temperatures using the apparatus described previously. Continuous heating of the polymer film at 130°C over a period of 4 h was also performed to ensure that there was no degradation of the polymer.

RESULTS AND DISCUSSION

The results and discussion section will be divided into three parts. The first section describes the liquid crystalline characteristics of the polymer used in this study. The second section deals with UV changes of the SiC10 polymer with temperature. The final section presents results for photolysis of the SiC10 polymer (UV study). The photolysis study is particularly important in ultimately establishing the crosslinking properties of cinnamate ester containing polymers. Taken together, all three sections should shed light on the structural-spectroscopic-photochemical properties of this unique type of liquid crystalline polymer.

CHARACTERIZATION

The liquid crystalline polymer used in this study was synthesized, as described in the experimental section, by reaction of a biscinnamic acid derivative containing a flexible disiloxane linkage with a diphenol having a decamethylenedioxy spacer between the two phenolic groups. The resulting polymer (SiC10), in addition to containing a photochemically reactive cinnamate ester chromophore spaced periodically in the backbone, has a relatively low temperature liquid crystalline phase (below 120°C). When cast at room temperature from chloroform on the quartz cell, SiC10 exists as a clear, transparent amorphous film. On first heating it experiences a transition to a nematic liquid crystalline phase (confirmed by optical microscopy) at about 70°C followed by a clearing transition at approximately 120°C. Upon cooling a nematic liquid crystal is formed at 110°C. The nematic optical texture is retained down to room temperature. A change in the heat capacity is seen (DSC) on cooling at 35°C, with no optical change. A second heating cycle indicates a very weak second order T_g transition presumably to a nematic structure at 35°C. Again, as in the first heating cycle, clearing to an isotropic melt is achieved at 120°C.

DSC of SiC10 (Fig. 1) shows, in addition to the clearing transition, three overlapping endotherms (55-95°C) on the first heating cycle and a single exotherm on the subsequent cooling cycle. Optical microscopy does not provide unambiguous assignment of phases in this region of 55-95°C on first heating. However, it is apparent from microscopy that the mesophase is present by approximately 70°C on this first heating cycle. The clearing transition corresponds to a peak maximum at 114°C on first heating and is nicely reversible occuring at 110°C on the subsequent cooling run. The cooling curve is featureless below the isotropic-mesophase transition back to near room temperature where at 35°C an apparent glass transition occurs. Second heating of the polymer shows what appears to be a glass transition at 35°C and no other endotherms until the clearing transition again at 114°C (peak maximum) unchanged from the first heating cycle. Presumably the first thermal cycle anneals out some residual solid structure which is lost thereafter resulting in a mesomorphic main chain polymer with only a glass transition into the mesophase on heating.[5] This implies, and is confirmed by microscopy, that the polymer retains nematic order on cooling (room temperature). The mesophase structure and morphology is frozen into the solid, i.e., a glassy mesomorphic solid at room temperature.

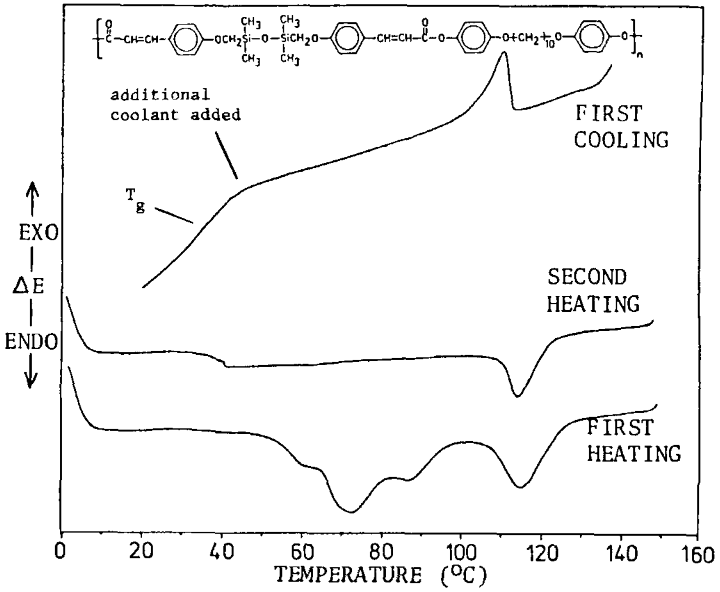


FIGURE 1. DSC of SiC10 Polymer.

In general, both DSC analysis and optical microscopy indicate the formation of a nematic liquid crystalline phase for the SiC10 polymer film which clears at about 120°C. Upon initial casting from solvent an amorphous film is formed which converts to a liquid crystalline phase above 70°C. After the first heating cycle, the film, when cooled to room temperature, retains a glassy nematic structure. Upon heating, a fluid nematic mesophase is formed above 35°C via a glass transition.

UV SPECTRAL ANALYSIS

Figure 2 shows the UV spectrum of a solvent cast film of the SiC10 polymer at three different temperatures; 30°C (amorphous film), 90°C (nematic liquid crystal), and 136°C (isotropic melt). At both 30°C and 136°C the UV spectra are essentially identical having maxima at 313 nm and 303 nm with a shoulder at 287 nm. The fact that the spectrum in the isotropic state closely resembles that of the amorphous film, without any thermal history, suggests that the same sort of randomness in the orientation of the chromophores exists in both states. The drop in the intensity and change in structure of the absorption spectrum at 90°C may well be due to aggregation of the chromophores in the nematic mesophase reminiscent of the spectral changes observed in certain crystals. (It is highly unlikely that any macroscopic orientation could be caused by the quartz surface and thus be responsible for the large changes that we see).

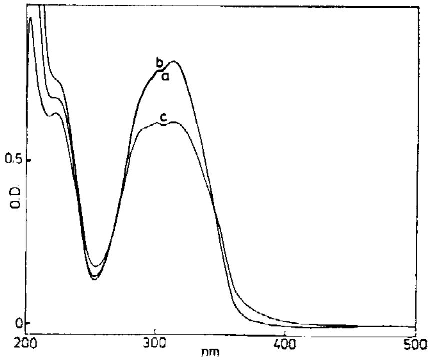


FIGURE 2. UV Absorption Spectra Taken While Heating the SiC10 Polymer Film from 15 to 136°C a) 30°C (Amorphous Solid), b) 136°C (Isotropic Melt) and c) 90°C (Nematic Mesophase).

On slowly cooling the polymer from the isotropic melt through the mesophase back to room temperature, the UV spectral (Figure 3) change is totally different from that observed upon heating the polymer. First, there is a tremendous drop in the intensity of the spectrum on cooling to the nematic mesophase (see spectrum at 76°C). On further cooling, the nematic mesophase is locked into the solid film at 30°C and the UV spectrum remains essentially the same as at 76°C. Finally, in order to rule out any possibility of thermal degradation effects during the heating-cooling cycle, the polymer film was heated continuously for 4 h at 130°C. No change in the UV spectrum could be detected during this heating period.

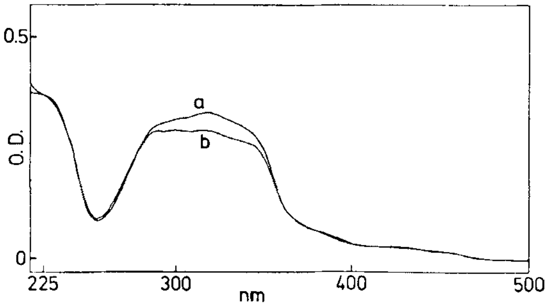


FIGURE 3. UV Absorption Spectra Taken While Cooling the SiC10 Polymer Film from Isotropic Melt to a) 76°C and b) 30°C.

In summary, the UV spectral changes observed on going from the isotropic to the nematic mesophase are consistent with the DSC-microscopy analysis in the previous section. Although we cannot confirm the mechanism responsible for the UV spectral distribution change in the mesophase, it is speculated that it may be due to some type of aggregation of cinnamate ester groups between units on adjacent polymer chains. Actual analysis of this phenomenon is under continued investigation and other interpretations of the UV spectral changes in Figures 2 and 3 may certainly be possible.

PHOTOLYSIS

Photolysis at 313 nm for 1 h of the solvent cast (non-annealed or heat cycled) SiC10 films (few microns thick) at slightly above room temperature (30°C) results in a highly (∿90%) crosslinked film which is yellow colored and solvent resistant. The FT-IR stretching peak at 1,631 cm^{-1}, due to the carbon-carbon double bond of the cinnamate ester group, rapidly disappears. In addition, a solid state

^{13}C-NMR of the crosslinked film shows the appearance of a new peak at 45 ppm (shift from tetramethylsilane) which is tentatively assigned to a cyclobutane ring structure. All of these results combine to indicate a fairly efficient crosslinking reaction for the SiC10 polymer film at room temperature, probably by a 2+2 cycloaddition process. Such a process is well known for conventional poly(vinyl cinnamate) type photoresists[1].

In Figures 4-7, UV spectra for photolysis (λ_{ex} = 313 nm) of the amorphous film at 30°C, the nematic film at 88°C, the isotropic melt at 128°C, and a polymer solution (0.55 mg/dL) at 30°C are shown. Basic similarities for the photolyses in Figures 4-7 exist. 1) In each case, there is a reduction in the intensity of the UV spectrum between 287 nm and 313 nm on continued irradiation. 2) There is an increase in absorbance above 350 nm in each case.

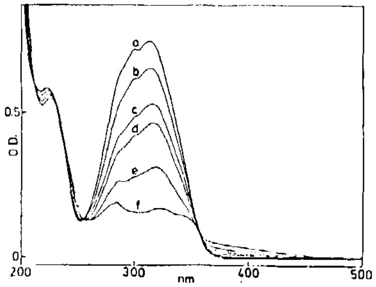


Fig. 4

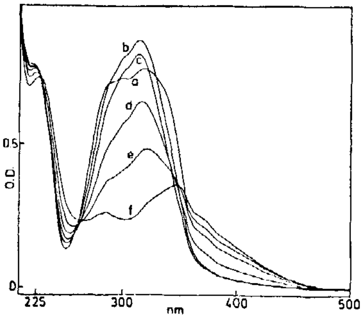


Fig. 5

FIGURE 4. Film Photolysis of SiC10 Polymer at 313 nm and 30°C for a) 0 sec, b) 30 sec, c) 2 min, d) 3 min, e) 7 min, and f) 20 min.

FIGURE 5. Film Photolysis of SiC10 Polymer at 313 nm and 88°C (Nematic Mesophase) for a) 0 sec, (Spectrum Recorded After Equilibrating at Specified Temperature), b) 10 secs, c) 30 secs, d) 3 min, e) 7 min, and f) 20 min.

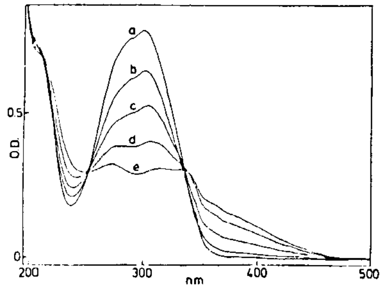


Fig. 6

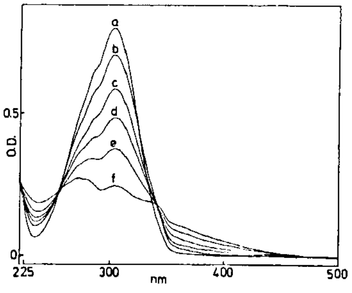


Fig. 7

FIGURE 6. Film Photolysis of SiC10 Polymer at 313 nm and 128°C (Isotropic Melt) for a) 0 sec (Spectrum Recorded After Equilibrating at Specified Temperature), b) 30 secs, c) 3 min, d) 10 min, and e) 20 min.

FIGURE 7. Solution Photolysis of SiC10 Polymer at 313 nm for a) 0 sec, b) 30 secs, c) 2 min, d) 5 min, e) 10 min, and f) 20 min.

In addition to the similarities in Figures 4-7, there are some obvious differences. 1) The intensity of the long wavelength absorbance above 350 nm for a given photolysis time varies depending on the sample temperature. 2) Photolysis in the nematic mesophase at 88°C is characterized by an initial increase in absorbance between 287 nm and 313 nm at short photolysis times followed by the characteristic reduction in intensity at longer photolysis times.

From a small molecule model compound study currently being conducted in our laboratory, it is postulated that the red-shifted absorption spectrum above 350 nm is due to an ortho photo-Fries rearrangement product (see typical structure below). Laser flash photolysis of both the SiC10 polymer and appropriate small molecule models[6] provide[5] strong evidence for a phenoxy radical intermediate in a non-concerted photo-Fries rearrangement process. It is however, highly unlikely that a cross photo-Fries rearrangement between radicals on two different polymer chains could lead to a crosslinking reaction.

The increase in absorbance at short photolysis times (Fig. 5) is only observed in the mesophase, not in the frozen nematic or the isotropic phases. This effect is similar to what one would expect for a change from an aggregate state to an amorphous or isotropic state (see Fig. 2). One possible explanation is that it is caused by a high quantum yield trans to cis photoisomerization which disrupts the stacking of chromophore pairs in the aggregates. If ε_{cis} is greater than $\varepsilon_{aggregate}$, then an initial increase in absorbance would be expected until a photostationary state is reached with a fixed cis/trans ratio. Eventually the occurrence of lower quantum efficiency cyclobutane formation and photo-Fries reactions would lead to a slower absorbance decrease, as is observed. That the absorbance increase is not observed in the frozen nematic state can be attributed to the preferential formation of cyclobutanes with $\varepsilon_{cyclobutane} < \varepsilon_{aggregates}$ and a much smaller disruption of chromophore stacking. Isomerization in this more rigid medium is presumably much less likely. In the isotropic state (Fig. 6) there is no evidence for aggregation and the observed reduction in absorbance at 300 nm is probably due to all of the three postulated reactions: cyclobutane formation, photo-Fries reaction, and isomerization.

One final UV spectral result deserves attention. Figure 8 shows the UV spectral changes both before (curve a) and after (curve b) exhaustive photolysis (1 h at 313 nm) of the SiC10 polymer as cast at 30°C. Also shown (curve c) is the UV spectrum of 3-(4-methoxyphenyl)propanoic acid in ethanol (1.30 mg/dL). This compound serves as a model (at least from a UV absorption standpoint) for a cyclobutane type adduct, which we have already provided evidence for earlier in this section. The similarities in the UV spectral peaks for the photolyzed SiC10 polymer (curve b) and the saturated model (curve c) are striking and provide supplemental support (in addition to the ^{13}C and FT-IR results) for a photocycloaddition reaction.

Finally, drawing both from our results as well as expected reactions[7] for cinnamate esters, the following general Scheme is proposed to account for our cumulative observations of the photolysis of the SiC10 polymer. The basic phenyl cinnamate chromophore can react photolytically by three processes; cycloaddition (only one possible isomer of which is shown in the Scheme), photo-Fries rearrangement,

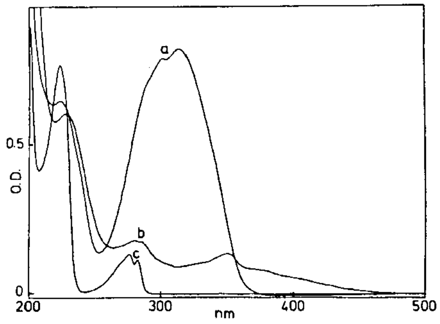
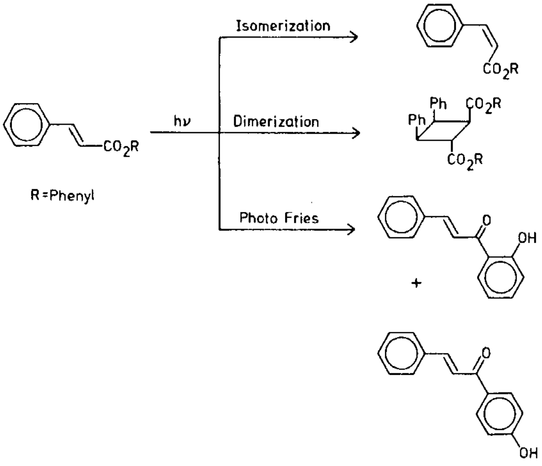


FIGURE 8. a) UV Absorption Spectrum of SiC10 Polymer Film, Deposited from Chloroform, at 30°C.
b) UV Absorption Spectrum of SiC10 Polymer Film Used in (a) after 1 h Irradiation at 313 nm.
c) UV Absorption Spectrum of 3-(4-methoxy phenyl) Propanoic Acid, A Model Chromophore for Photodimerized Cinnamate, in Ethanol.



Aryl Cinnamate Photoreactions

and isomerization. Although we have no direct information at this time concerning the isomerization process, one might expect it to be more likely the more mobile are the polymer chains. We expect the probability of isomerization to increase in the order frozen nematic < nematic < isotropic liquid. Initial evidence presented in this section suggests that both the cycloaddition process and the ortho photo-Fries rearrangement occur. At high temperatures in the isotropic state (130°C) the photo-Fries process is apparently enhanced, while in the initial cast amorphous film at 30°C photo-Fries product formation is quite low. Photolysis in the mesomorphic state (88°C) represents an intermediate case.

CONCLUSIONS

In summary, a siloxane based liquid crystalline polymer with a cinnamate ester group in the main chain has been synthesized and characterized by microscopy, DSC, and UV. The siloxane spacers incorporated into the polymer backbone were successful in lowering transition temperatures and providing solubility. The cinnamate ester moieties can be crosslinked by photolysis at rather short exposure times. The photolysis process has been postulated to generate at least two species, a cycloadduct and a photo-Fries rearrangement product.

Future work will concentrate on confirmation of photoproduct structure and quantitative analysis of product yield. Photolysis of the glassy nematic liquid crystalline polymer at room temperature produced after the first heating cycle is currently under way. Results will be published in the near future. Exhaustive investigation of the photolyzed films are being carried out in an effort to determine the effect of crosslinking of the SiC10 polymer on such physical properties as elasticity and tensile modulus. In addition, its suitability as a room temperature liquid crystalline photoresist is under consideration.

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