for porphyrin cation radicals.[7] The new spectral features disappear after 10–15 min with the appearance of bands due to (F8-TPP)Fe(III)F_2^- (a split Soret band is observed at 406 and 454 nm with an additional band at 576 nm, Figure 2b).

The EPR spectrum for the MCPBA-oxidized product shows the presence of three distinct signals at $g = 4.38$, 3.11, and 2.70 at 80 K (a broad $g = 2$ signal due to destruction product is present if a large excess of MCPBA is added to bleach the porphyrin). The solution magnetic moment (210 K) is $4.1 \pm 0.2\ \mu_B$. Detection of EPR signals characteristic of a $S = {}^3/_2$ species at moderate temperature in concert with the magnetic moment is consistent with generation of an iron(V) porphyrin species, since an iron(IV) porphyrin complex ($S = 1$) is expected to be EPR silent. Other possible structures such as the (oxo)iron(IV) porphyrin π-cation radical species would be expected to show a blue shift in the Soret band,[7] unlike the optical spectra observed here.

These spectroscopic results are observed only in the presence of a large excess of fluoride ion. Hence coordination of a fluoro ligand or ligands is suggested for the iron(V) complex. Double oxidation of the metal center is favored in this case by virtue of a relatively electron deficient porphyrin framework. On the basis of the observed results, a structure with coordinated fluoro ligands or a combination of oxo and fluoro ligands is suggested for the iron(V) porphyrin species.

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Chromophore Aggregation and Concomitant Wavelength-Dependent Photochemistry of a Main-Chain Liquid Crystalline Poly(aryl cinnamate)

David Creed,* Anselm C. Griffin, Charles E. Hoyle, and Krishnan Venkataram

Departments of Chemistry and Biochemistry and of Polymer Science, University of Southern Mississippi Hattiesburg, Mississippi 39406-5043

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The unique combination of order and mobility has made liquid crystalline (LC) media attractive for photochemical studies, and there are now many examples[1] of such uses of low molar mass LC materials. We have recently reported the first observations[2] of the effects of LC behavior on main-chain polymer photochemistry using a class of novel main-chain thermotropic LC polymers (e.g., **1**, Chart I), in which fairly rigid aryl cinnamate mesogenic groups are connected by flexible spacer groups. In our continuing efforts to delineate the influence of order and mobility on these photoreactions, we have obtained evidence that aggregation of the chromophores in parallel or near-parallel stacks leads to a wavelength dependence of the polymer photochemistry. This effect is most dramatic in the glassy nematic phase of the polymer and is the first such observation in the photochemistry of either a low molar mass or polymeric LC material.

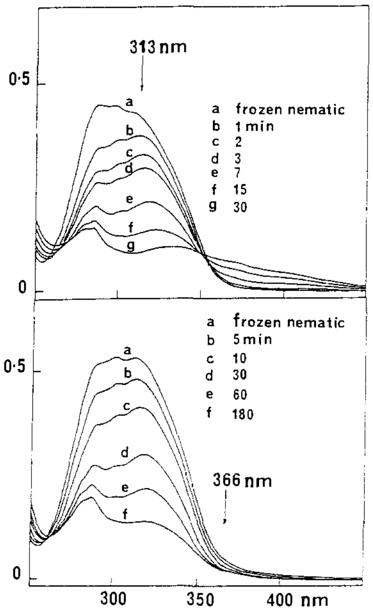

Figure 1. UV–vis spectral changes upon 313- and 366-nm irradiation of a glassy nematic film of polymer **1**. The remaining absorption at ca. 280 nm is attributed to cyclobutane photoproducts. The long-wavelength absorption stretching into the visible region is attributed to photo-Fries product.[2,7]

Polymer **1** is nonbirefringent[3] when cast from chloroform. The highest molecular weight preparations become nematic above 70 °C and finally isotropic above 120 °C. Clearing temperatures are molecular-weight dependent.[4] On cooling to room temperature, the nematic phase is retained in a glassy state in which LC order is frozen in. Drastic UV spectral changes are observed in the nematic state, and the overall broadening and increase in absorption to the blue and to the red of the original band that accompanies the drop in the optical density is attributed to the formation of aggregates by a significant fraction of the aryl cinnamate chromophores.[2] Additional evidence for this hypothesis comes from duplication of these spectral changes using dispersions of the small-molecule model copound, **2**, in poly(methyl methacrylate), PMMA. In dilute dispersions (<10% of **2**), the unaggregated monomer is observed at $\lambda_{max} = 317$ nm. With sufficiently high fractions of **2** in PMMA, a new blue-shifted band ($\lambda_{max} = 280$ nm) can be seen in the UV, with weaker absorption stretching into the visible. Such behavior is characteristic of near-parallel stacking of chromophores.[5] The magnitude of the hypochromic effect in the polymer is dependent on the molecular weight.[6] These effects will be discussed in more detail in a subsequent full paper.

Two major photochemical reactions occur[2] upon irradiation of films of **1** at 313 nm. These are cyclobutane formation, shown by UV absorption changes and solid-state ^{13}C NMR, and photo-Fries rearrangement, shown by comparison of a new UV–vis absorption band with the UV–vis absorption of the photo-Fries product, **3**, obtained from irradiation[7] of **2**. The UV-irradiated films become insoluble, indicating a significant amount of cross-linking, most probably via interchain cinnamate dimerization. A small fraction of other reactions leading to saturation of the cinnamate double bond cannot be completely excluded.[8] The

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(1) Weiss, R. G. *Tetrahedron* **1988**, *44*, 3413–3475 and references therein.

(2) (a) Creed, D.; Griffin, A. C.; Gross, J. R. D.; Hoyle, C. E.; Venkataram, K. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 57–71. (b) Haddleton, D. M.; Creed, D.; Griffin, A. C.; Hoyle, C. E.; Venkataram, K. *Makromol. Chem. Rapid Commun.* **1989**, *10*, 391–396.

(3) Freshly cast films of **1** show a slight opacity suggesting some local ordering of the chains. Moreover, samples with no thermal history exhibit a broad endothermic transition above 50 °C in DSC scans, that is absent in the (reproducible) second and subsequent heating cycles. This transition is also consistent with some local order present in the material before it is heated into the nematic or isotropic phases.

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(5) Kasha, M. *Radiat. Res.* **1963**, *20*, 55–71.

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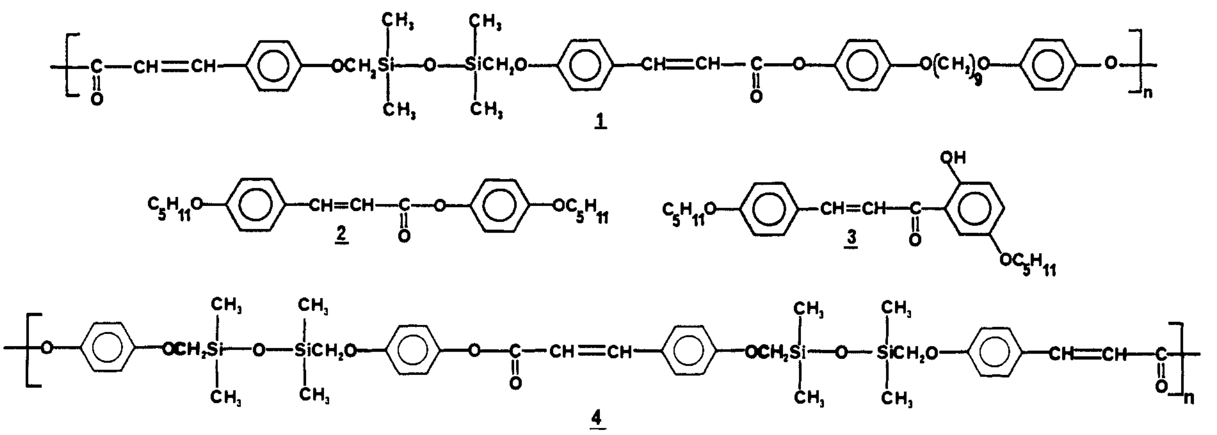
Chart I



photochemistry of the isolated aryl cinnamate chromophore has also been explored by using solid solutions of **2** in PMMA. If these solutions are sufficiently dilute, the only reaction observed upon irradiation is the photo-Fries reaction. The isosbestic point observable under these conditions indicates that trans–cis isomerization is not occurring in this highly viscous medium, and this is probably also true for the rigid phases of the polymer although it cannot be excluded in the more mobile nematic phase[2] and in the isotropic melt.

The photochemistry of **1** is wavelength dependent. This effect is quite dramatic in the nematic phases. Irradiation of films at 366 nm, where virtually all the light energy is absorbed by aggregates, leads to the UV–vis changes attributable to cinnamate photodimerization and almost none of the long wavelength absorption increase attributable to photo-Fries reaction. However, irradiation at 313 nm produces both the dimer and the Fries products (Figure 1). Upon exhaustive 366-nm irradiation, not all the absorption due to the aryl cinnamate chromophores disappears. That this residual absorption is due to unreacted aryl cinnamate can be shown by the appearance of the absorption due to the photo-Fries product upon 313-nm irradiation of these exhaustively 366 nm irradiated films. All of these observations tend to suggest that a significant fraction of chromophores is present in aggregates and that dimerization is the only photochemical process that occurs upon specific excitation of these aggregates. Exhaustive irradiation at 366 nm converts all aggregated pairs to dimers, and the remaining isolated chromophores, having very little absorptivity at 366 nm, are relatively insensitive to further 366-nm irradiation. However, 313-nm irradiation causes them to undergo the alternative, *unimolecular* photo-Fries reaction. This effect is most pronounced in the glassy nematic state, where a greater fraction of chromophores is aggregated. In this state, we estimate, at least 70% of the original chromophores are aggregated on the basis of the cinnamate absorption remaining after exhaustive 366-nm irradiation.

Compared to these dramatic effects, there is no observable wavelength dependence upon 313- compared to 366-nm irradiation of the isotropic melt at 123 °C. This parallels the observation[2] of loss of the hypochromic effect when the UV–vis spectra of films are run in the isotropic melt. Some wavelength dependence is, however, observed upon irradiation of "amorphous" (i.e., nonbirefringent[3]) films of **1** and upon irradiation of a polymer, **4**, with the same chromophore as **1** but which is not liquid crystalline. In these cases, the main evidence for wavelength dependence is a delay between chromophore disappearance and the appearance of the characteristic absorption due to Fries product when irradiation is at 366 nm, and the absence of such a delay upon 313-nm irradiation. Qualitatively this effect is more pronounced in the case of "amorphous" **1** compared to non-LC **4**. In both these cases, short-range ordering of chromophores presumably occurs during casting of the films. Our photochemical observations thus clearly parallel the photophysical observations of Reiser and his coworkers[9] in which ground-state aggregation of *p*-phenylenediacrylate chromophores in a main-chain polyester is apparent from fluorescence intensity and lifetime studies.

We are currently quantitating the photoproduct ratios in the different phases as a function of wavelength and temperature. Preliminary results indicate that the dimer/Fries ratios are higher in the more organized and less mobile phases. This may be advantageous for applications such as the development of biaxially strengthened films or photoresists, for which photochemical cross-linking is the most important reaction.

Acknowledgment. We thank Armstrong World Industries, the National Science Foundation (Grant No. RII-8902064), the State of Mississippi, and the University of Southern Mississippi for their support of this work and Professor R. G. Weiss for helpful discussions.

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Structure, Dynamics, and Reactivity of an Alkoxy Intermediate Formed from Acetylene on Zeolite Catalysts: An in Situ Solid-State NMR Study

Noel D. Lazo, Jeffery L. White, Eric J. Munson,
Marsha Lambregts, and James F. Haw*

Department of Chemistry, Texas A&M University
College Station, Texas 77843

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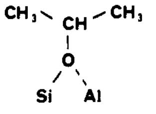
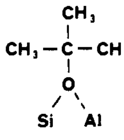
Recently, there has been much interest in reactive intermediates formed by the adsorption of organic compounds on zeolites and alumina.[1-3] In a low-temperature in situ NMR study of the oligomerization of propene on zeolite HY, Haw and co-workers[1] proposed that alkoxy species of type I, formed between protonated alkenes and the zeolite framework, are long-lived intermediates.[4]



I



II

$\mathrm{Al{-}O{-}CH_2{-}(CH_2)_2{-}CH_3}$

III

$\mathrm{Al{-}O{-}CH{=}CH_2}$

IV

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* Author to whom correspondence should be addressed.

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