The Effect of Two-dimensional Ordering on Photoreactions of Long-chain Unsaturated Carboxylic Acids

Bo Zhang Guo,[a] Sadhana Tripathi,[a] D. Martin Taylor,*[b] and Charles J. M. Stirling*[†][a]

[a] *Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, UK*
[b] *School of Electronic Engineering Science, University of Wales, Bangor, Gwynedd LL57 1UT, UK*

Long chain alkanoic acids with terminal alkenyl and alkynyl groups are subjected to UV irradiation in ordered (Langmuir–Blodgett) and disordered films; polymerisation occurs in the LB films but only dissociation and desorption in the disordered films.

Langmuir–Blodgett (LB) films provide ordered films of organic substrates and Ringsdorf[1] has shown that when these substrates possess in-chain alkenyl groups, polymerisation occurs upon UV irradiation. Such behaviour is not, of course, characteristic of such substrates in liquid solution, in melts or crystals. We now report on the behaviour of *terminally* unsaturated carboxylic acids **2** when exposed to UV irradiation in LB films and contrast the behaviour of the same substrates in disordered thin films of roughly comparable mass area^{-1}.

Acids **2** were obtained by the routes shown in Scheme 1. Monolayers spread on water[‡] were transferred at constant surface pressure to aluminium coated slides at a dipping rate of 1 cm min^{-1}. Disordered films were obtained by dipping the slides in dilute solution of the substrates until the intensity of ATR (attenuated total reflectance)–FTIR[§] spectra were comparable with those of the LB films.

Monolayers of these unsaturated acids showed normal π-A characteristics giving, at 35 mN m^{-1}, areas per molecule of 20.5 and 22.5 Å^2 respectively. The effect of irradiation (254 nm principal wavelength) was monitored by ATR–FTIR and by surface potential measurements.[¶]

The IR spectra for acid **2a** are shown in Fig. 1. The carboxy groups are partially converted to carboxylate at the subphase pH as evidenced by the absorptions at 1700 and 1530 cm^{-1} respectively. In addition, the $\nu_{C=C}$ and $\delta_{=CH_2}$ bands show clearly at 1633 and 1427 cm^{-1} respectively [Fig. 1(*a*)]. After irradiating for 1 h, the latter bands were not observed [Fig. 1(*b*)] exposing the bands at 1454 and 1404 cm^{-1}; the ν_{CH_2} band

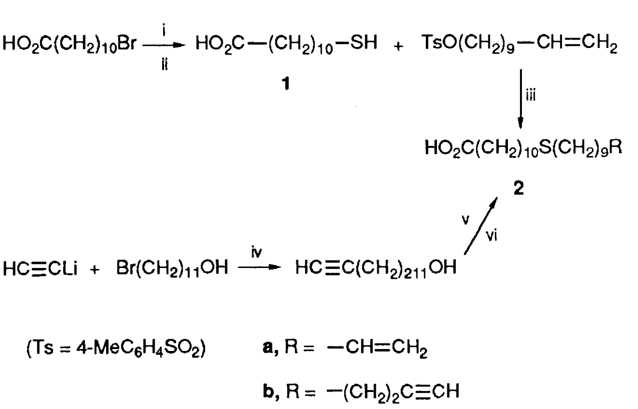
---

[†] *Present address*: Department of Chemistry, The University, Sheffield S3 7HF, UK.

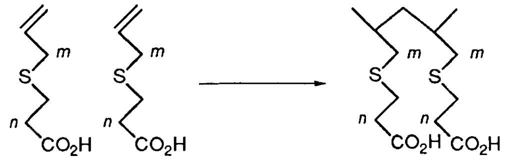
[‡] Obtained from a Millipore Super Q system 10^{-4} mol dm^{-3} in $BaCl_2$ at 20 ± 1 °C and pH 5.7 ± 0.1. Compression rate 0.2–0.4 nm^2 molecule^{-1} s^{-1}.

[§] ATR–FTIR spectra were measured with a Mattson Cygnus instrument using opposed parallel mirrors bearing the films set about 2 mm apart and allowing *ca.* −25 reflections before the beam reached the detector. Spectra (Fig. 1) are calibrated with 3% transmission bars.

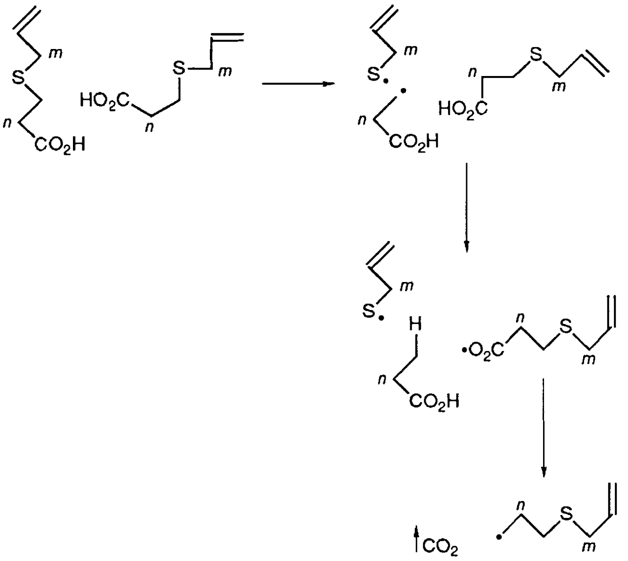
[¶] Surface potential measurements were made with a Trek 320B instrument using clean mirrors for reference potentials.



Scheme 1 *Reagents and conditions*: i, thiourea/EtOH; ii, NaOH–EtOH; iii, EtONa-EtOH; iv, THF/dry DMSO; v, TsCl-pyridine/$CHCl_3$; vi, **1** and EtONa-EtOH



Scheme 2



Scheme 3

at 2916 cm^{-1} also shifts to higher wavenumber (2924 cm^{-1}). Additionally, the carboxy carbonyl stretching frequency splits in two (ν, 1728 and 1703 cm^{-1}). We believe that these changes result from polymerisation of the terminal alkenyl function. The shifts in the carboxy absorptions are consistent with observations of Davies *et al.*[2] who found that temperature-induced disorder in LB films disrupted inter-layer cyclic dimerisation leading to intra-layer sideways dimerisation. In the present case, but not apparently in Davies', these changes are irreversible.

The surface potential of the film decreased steadily from 180 mV to 59–60 mV[3] during irradiation (1 h). Such changes are consistent with a reduction in the effective dipole moment of the distal group on polymerisation (Scheme 2). Also consistent is the observation that the films, before irradiation, are readily washed off the mirrors by immersion in diethyl ether or hexane but are resistant to wash-off after irradiation.[4]

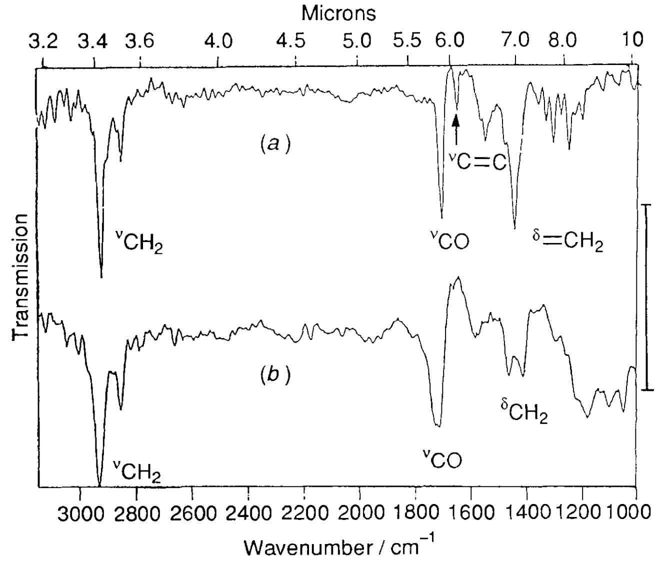


Fig. 1 FTIR spectra (32 scans) of 7 monomolecular layers of alkene-S-acid, (*a*) as deposited; (*b*) after 1 h of UV irradiation

In complete contrast, irradiation of disordered films of alkene–sulphide-acid **2a** produced no evidence for polymerisation. Before irradiation, ATR–FTIR spectra showed clearly the alkene $\nu_{C=C}$ vibration at 1635 cm^{-1} albeit slightly shifted from those recorded for ordered films. On irradiation, little change occurs in the IR spectra other than progressive diminution in intensity, and at all stages the film is readily removable by solvent. It was established that: (*i*) the film temperature did not exceed 33 °C, (*ii*) irradiation under Ar rather than air had no effect, (*iii*) the film did not disappear if a filter (<330 nm) was interposed. Desorption of LB films of magnesium and cadmium arachidate salts by UV irradiation (254 nm) has been demonstrated[5] but in parallel experiments with disordered stearic acid films, we observed little weakening of the FTIR intensities during the first hour of irradiation. Photodecarboxylation of carboxylic acids has also been observed[6] but clearly the processes must be different for stearic acid and for acid **2a**. We further tested the behaviour under irradiation of bulk samples in quartz cells; **2a** rapidly released CO_2 into the argon gas space (FTIR) and stearic acid only slowly. We think that the much more rapid reaction of **2a** is due to S–C bond fission under irradiation as demonstrated for bulk (liquid) samples of simple alkyl sulphides.[7] The radicals produced lead to low M_w fragments that escape, in the case of the disordered films, from the mirrors. A possible course of reaction is shown in Scheme 3. ‖

Similar experiments were performed with the alkyne terminated substrate **2b**. A film of three monolayers gives the ATR–FTIR spectrum in Fig. 2. While the $\nu_{C\equiv C-H}$ vibration at 3303 cm^{-1} is weak, irradiation for 1 h produces a strong band at 1597 cm^{-1} assigned to the C=C stretching vibration of a conjugated carbon–carbon double bond. 1,3-Butadiene also shows this band. The resonance splitting effect** on methy-

---

‖ H-atom abstraction from a carboxy group is probably rather exothermic but these are photoprocesses in the solid state. Since submission of this manuscript, Professor B. C. Gilbert has kindly informed us that decarboxylation of radical cations occurs readily, probably *via* intramolecular electron transfer, giving a labile carboxyl radical mediated decarboxylation of methionine.[8] In the present cases, as alternatives to the sequence of Scheme 3, photolytic ejection of an electron from sulphur might produce a labile carboxyl radical cation, which might also be produced by electron transfer from sulphur to a radical produced by S–C fission. There is no direct evidence for any of these suggestions.

** SPR measurements were taken with a Kretschmann-type arrangement.

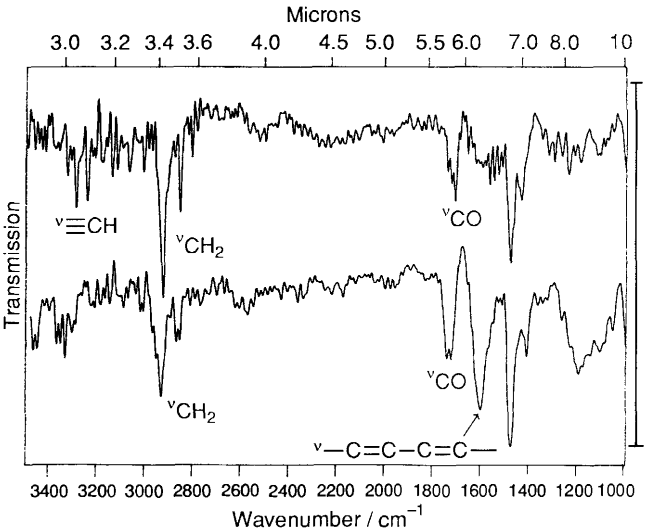


Fig. 2 FTIR spectra (32 scans) of 3-monomolecular layers of alkyne-S-acid, (*a*) as deposited; (*b*) after 1 h UV irradiation

lene adjacent to the C=C was observed. Effects on the carboxy group are as for acid **2a** and the wash-off behaviour is analogous. These changes are again consistent with polymerisation of the alkynyl group and intriguingly, surface plasmon resonance (SPR)** measurements on the films before and after irradiation show first an *increase* in the resonance angle from 44.55° to 45.76° (40 min irradiation) and then a *decrease* to 44.83° after a further 100 min. Increase in the resonant angle indicates an increase in the refractive index of the film which is consistent with polymerisation of the terminal alkynyl group to a polyene ('polyacetylene') system. The subsequent decrease in the resonant angle indicates cross-linking.

Irradiation of disordered films of **2b** gave the same results as that of **2a**.

We again emphasise the difference in behaviour between ordered and disordered films. Our results highlight the fact that when functional groups are in enforced juxtaposition, their behaviour can be quite different from that shown by random arrangements of functional groups notwithstanding that both are in the solid state. Our observations lead to a number of speculations. These include the possibilities of ordering adsorbed molecules on ordered surfaces and the investigation of a range of inter-functional reactions not realisable in disordered phases, but which can be achieved in ordered arrangements.

We thank the SERC (Grant No. GR/F 82863) for the support of this work and Drs O. N. Oliviera, Jr. and J. P. Llewellyn for advice and help with surface potential and surface plasmon resonance measurements respectively.

Received, 3rd October 1990; Com. 0/04441E

References

1 H. Ringsdorf and H. Schapp, *Macromol. Sci. Chem.*, 1981, **15**, 1015.
2 G. H. Davies, J. Yarwood, M. C. Petty and C. A. Jones. *Thin Solid Films*, 1988, **159**, 461.
3 D. M. Taylor, O. N. Oliveira Jnr. and H. Morgan, *J. Colloid Interface Sci.*, 1990, **139**, 508.
4 Typical conditions: immersion in Et_2O at 20 °C for 2 min and drying in air (5 min). Films produced by polymerisation of inchain alkenes have earlier been shown to be resistant to solvent removal: A. Barraud, C. Rosilio, and A. Ruaudel-Teixier, *J. Colloid and Interface Sci.*, 1977, **62**, 509.
5 P. Tippmann-Krayer, L. A. Laxbuber and H. Mohwald, *Thin Solid Films*, 1988, **159**, 387.
6 A. Ruaudel-Teixier, *Mol. Cryst. Liq. Cryst.*, 1983, **96**, 365.
7 C. S. Smith and A. R. Knight, *Can. J. Chem.*, 1973, **51**, 780; P. M. Rao and A. R. Knight, *Can. J. Chem.*, 1972, **50**, 844.
8 M. J. Davies, B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc., Perkin Trans.* 2, 1983, 731.