

## Photopolymerization in Monolayers of an Amphiphilic Diacetylene Derivative containing a Ferrocene Group

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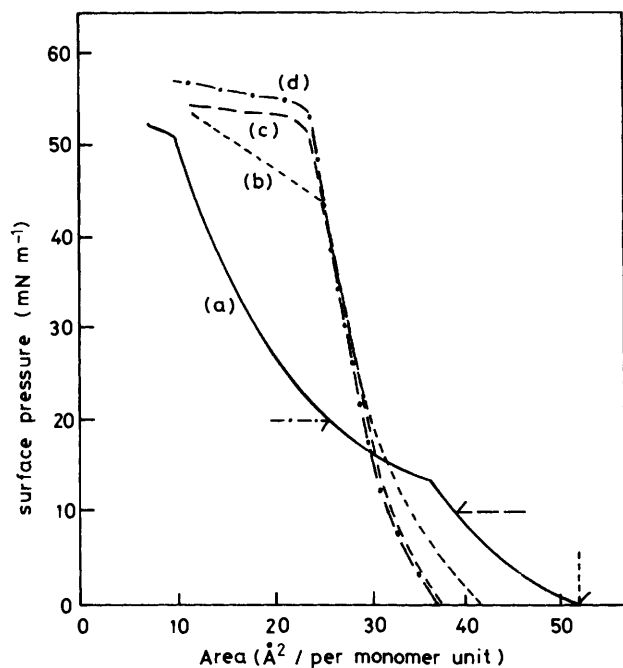
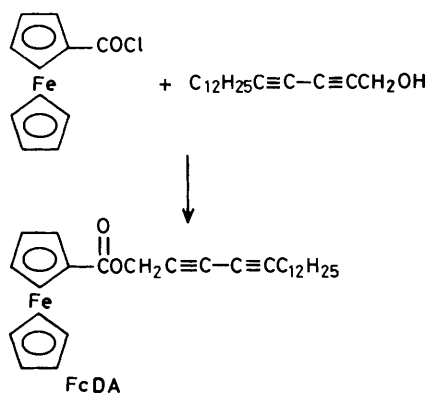
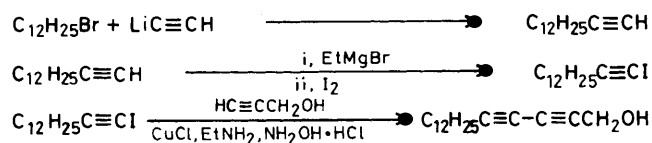
The photopolymerization of heptadeca-2,4-diynylferrocenecarboxylate in the monolayer on a water surface was investigated by studying pressure–area isotherms and electronic spectra; the polymerization behaviour was found to depend markedly on the molecular packing in the monolayer.

Two-dimensional arrays of organometallic complexes in monolayer assemblies are of interest for molecular electronic devices. In previous papers<sup>1,2</sup> we have reported that different orientations of ferrocene nuclei can be achieved in Langmuir–Blodgett (LB) films of amphiphilic ferrocene and biferrocene derivatives, depending on the numbers of long-chain substituents. Recently, a photodiode and modified electrodes with LB films of long-chain ferrocene derivatives have been studied.<sup>3–5</sup> We considered that the introduction of a diacetylene group in addition to ferrocene into the film materials, and subsequent polymerization in the monolayer or in the multilayer, would provide a potential structure for various applications. In this paper, we report a study of the photopolymerization of heptadeca-2,4-diynylferrocenecarboxylate in the monolayer on a water surface.

Heptadeca-2,4-diynylferrocenecarboxylate (FcDA) was synthesized by refluxing heptadeca-2,4-diyn-1-ol with ferrocene carbonyl chloride, as shown in Scheme 1. The structure of the product was identified by elemental analysis and mass [ $m/z$  462 ( $M^+$ )], u.v., i.r., and <sup>1</sup>H n.m.r. spectra.

The monolayer of FcDA was spread from chloroform solution onto distilled water and surface pressure( $\pi$ )–area( $A$ ) isotherms were measured with a Lauda film balance. The polymerization was carried out by exposing the monolayer on the water surface to a 500 W Xenon lamp at a distance of 40 cm. Absorption spectra of the monolayers were measured with a multi-channel photodetector (Otsuka Electronics), which consisted of a halogen lamp connected to a photodiode array by an optical fibre to measure the transmittance of the monolayer on the water surface through reflection from a mirror on the bottom of the trough.

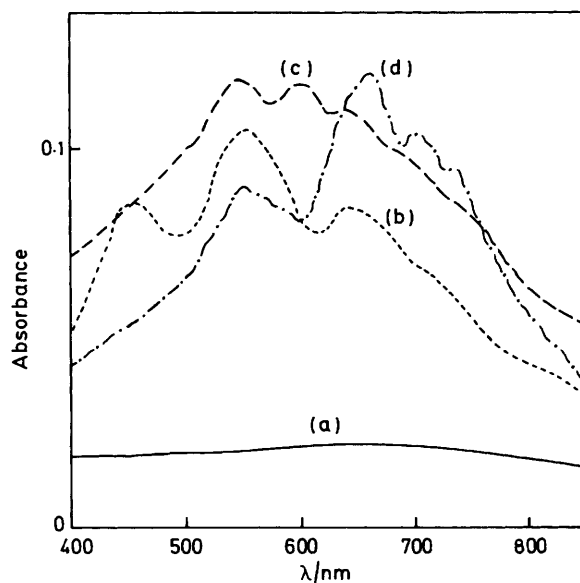
Figure 1 shows  $\pi$ – $A$  isotherms for the monolayers of FcDA before and after irradiation. The limiting area  $A_{\pi \rightarrow 0}$  for the first condensed region of the monomer before irradiation (a) is about 45 Å<sup>2</sup>; thus the cyclopentadienyl rings of the ferrocene nuclei seem to be oriented perpendicular to the surface. On compression beyond the transition point (at 14 mN m<sup>-1</sup>), change in molecular orientation and packing, or slight dissolution into the subphase may occur. The  $\pi$ – $A$  isotherms (b)–(d) for the monolayers after irradiation at specified



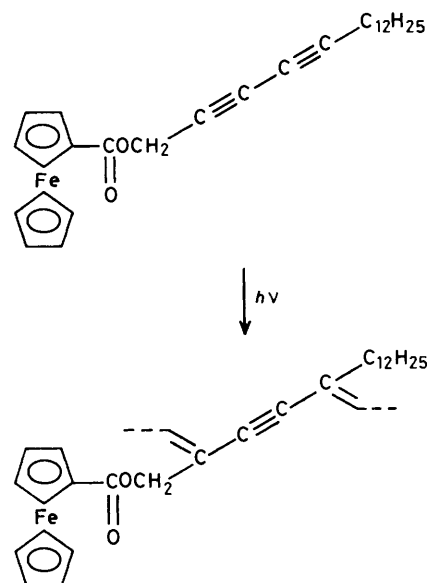
**Figure 1.** Surface pressure–area isotherms for the monolayers of FcDA before (a) and after irradiation at 14 °C under different pressures: (b) 0, (c) 10, and (d) 20 mN m<sup>-1</sup>, as indicated by arrows.

pressures (indicated by arrows on the monomer isotherm) are characterized by a decrease in the limiting area and an increase in stability with increased pressure during irradiation. This suggests progressive photopolymerization of the diacetylene derivative in the monolayer: higher packing density and strength are characteristic of polymer films. The polymerization in the monolayer was confirmed by monitoring changes in absorption spectra.

Figure 2 shows the visible spectra of the monolayer on the water surface after irradiation for about 2 h at various pressures (at 14 °C). The increase in absorbance in the visible region indicates that the photopolymerization proceeds in the monolayer (Scheme 2). However, the spectra depend markedly on the surface pressure during the irradiation. A broad



**Figure 2.** Visible absorption spectra for the monolayer of FcDA on water before (a) and after irradiation for about 2 h at 14 °C under surface pressures of (b) 0, (c) 10, and (d) 20 mN m<sup>-1</sup>.



band appeared around 540 nm on irradiation at 0 mN m<sup>-1</sup>, around 500–600 nm on irradiation at 10 mN m<sup>-1</sup>, and around 650 nm on irradiation at 20 mN m<sup>-1</sup>. The bands at 540 and 640 nm correspond to a red and a blue form of the polymer, respectively, as reported;<sup>6–9</sup> the broad bands around 600–500 nm (purple form) seem to be due to an intermediate state between the red and blue forms. Study of the effect of temperature on the photopolymerization at 10 mN m<sup>-1</sup>, showed that the red form was obtained at a higher temperature (21 °C) than the purple form (14 °C). In addition, the blue form obtained at 20 mN m<sup>-1</sup> changed to the red form on further irradiation at elevated temperature.

These differences in the resultant polymers can be seen also in the  $\pi$ -A isotherms after irradiation, as shown in Figure 1. The collapse pressure of the polymerized films was highest for the blue form (d), less for the purple form (c), and least for the

red form (b). Further, the areas occupied by the monomer unit in lower pressure region were largest for the red form. These results seem to be due to differences in higher order structure of the polymer, such as distortion of main and/or side chains. Previously, other investigators have identified the blue and red forms of polydiacetylenes as acetylenic and butatrienic structures, respectively.<sup>10</sup> However, our u.v. photoelectron spectroscopic study of polydiacetylene-monocarboxylic acid in LB films has revealed that the polymer chain is of the acetylenic type, rather than the butatrienic type, irrespective of colours.<sup>11</sup>

In conclusion, it has been found that the polymerization behaviour of FcDA and the polymer structure are significantly influenced by the orientation and packing of the monomer molecules in the monolayer. FcDA monolayers polymerized on a water surface can be transferred onto solid supports by the LB method. Cyclic voltammetric studies of the LB films of polymerized FcDA are now in progress.

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