

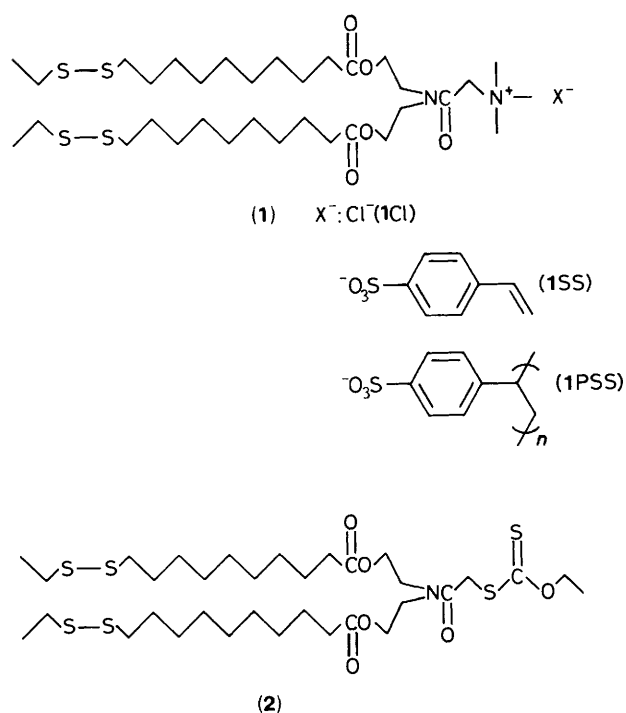
A Novel Two-dimensional Photopolymerization at an Ordered Monolayer Surface on Gold

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A two-dimensional photopolymerization has been successfully carried out in the presence of a photoinitiator fixed near the polymerizable groups at a spontaneously adsorbed monolayer surface on gold.

Polymerization of two-dimensional molecular aggregates (bilayers, monolayers, and Langmuir-Blodgett multilayers) is of wide interest owing to the practical and biological importance of polymerized aggregates with enhanced stabilities, and also the interest in the low-dimensional reaction. We have reported that ultra-high molecular weight polymers in a bilayer state can be produced under mild conditions by taking advantage of the well-defined bilayer surface and fixation of the photoinitiator at an effective position for initiation,¹ and that the molecular weight of polymers can also be controlled by the phase separation of bilayers.²



We have prepared a spontaneously-assembled polymerizable monolayer on gold and revealed the photopolymerization behaviour at its two-dimensional surface by electrochemical methods. Nuzzo and Allara³ have shown that well organized monolayers can be readily prepared on gold by spontaneous adsorption of organic thiols⁴ and disulphides. We used freshly prepared (1SS)[†] and (2)[†] as polymerizable-amphiphile and photoinitiator, respectively, containing disulphide groups in the hydrophobic tails. The polymeric amphiphile (1PSS), which has poly(styrene sulphonate) as a counterion in place of the styrene sulphonate of (1SS), was also used for comparison. Monolayers were formed by immersing gold-mirror plates (prepared by evaporation of gold onto glass plates) or gold electrodes in solutions of the disulphide compounds in chloroform for 2 h[‡] at room temperature. The total concentration of disulphides was kept constant at 1 mM. We used two independent techniques, contact angle measurement of water and cyclic voltammetry, to obtain information regarding the monolayer surface. The contact angles (θ) of water provide useful measures of wettability. The (1Cl)⁺ monolayer predictably afforded a very hydrophilic surface with a contact angle θ of 42°. When the counterion of (1) was exchanged from chloride to styrene sulphonate (1SS), the contact angle remarkably increased up to 82°, dependent upon the hydrophobicity of the counterion. A further increase in hydrophobicity was observed in the case

[†] The new compounds (1) and (2) were prepared as follows. *O,O'*-di[(11-ethylthio)undecanoyl]diethanolamine was prepared from 11-(ethylthio)undecanoic acid⁵ and diethanolamine. This ester was treated with chloroacetyl chloride and then allowed to react with trimethylamine or sodium *o*-ethylxanthate to give (1Cl) or (2), respectively. (1SS) and (1PSS) were prepared by an anion-exchange reaction of (1Cl) with sodium styrene sulphonate or poly(sodium styrene sulphonate), respectively. The structure was confirmed by NMR spectra and elemental analyses.

[‡] Initial monolayer formation is very rapid, with limiting properties reached after a few minutes.

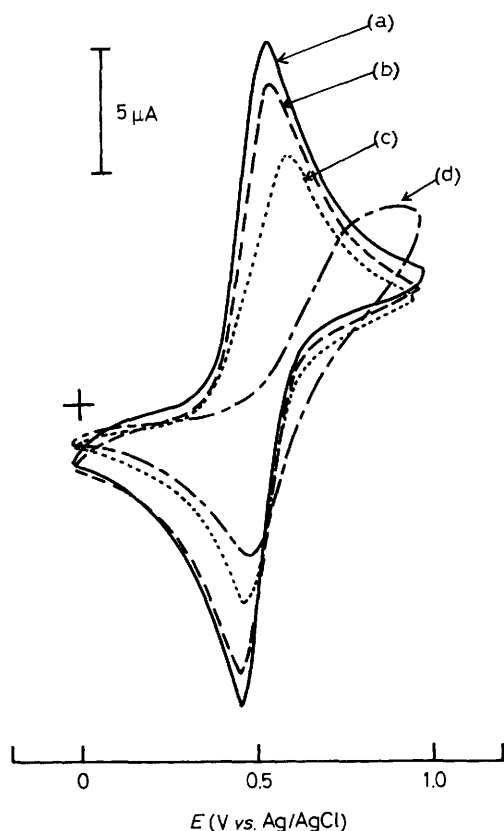


Figure 1. Cyclic voltammetric current response vs. applied potential for (a) bare gold, (b) (1Cl)/Au, (c) (1SS)/Au, and (d) (1PSS)/Au. The solutions are $K_4[Fe(CN)_6]$ (3 mM) in KCl (1 mM). The sweep rate is 100 mV s^{-1} .

of the (1PSS) monolayer (θ 87°). This suggests that the hydrophobicity of the monolayer surface could be readily controlled by changing the counterion of (1), as supported by electrochemical measurements for monolayers on gold electrodes.

These measurements were carried out under nitrogen at 20°C with a CV-1B Cyclic Voltammograph (BAS). The gold substrates were mounted in a conventional three-electrode cell with an exposed area of 0.02 cm^2 . All potentials were measured with respect to a Ag/AgCl (saturated NaCl) reference electrode. The redox reaction between $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ was employed. Figure 1 shows the cyclic voltammetric potential-current ($E-i$) curves for (1)-modified gold with $K_4[Fe(CN)_6]$ (1 mM) as the electroactive species and KCl (1 M) as the electrolyte. These show an apparent decrease of the redox peak currents and increase of the peak-to-peak separation, which indicate that contact of $Fe(CN)_6^{4-}$ with the surface of the electrode was restricted. Such electrochemical barrier properties increased in the following order: (1PSS) > (1SS) > (1Cl), corresponding to the results obtained by contact angle measurements. In particular, there is a significant difference in electrochemical barriers between (1SS) and (1PSS). Thus the polymerization process of the (1SS) monolayer on gold can be traced electrochemically using the above redox system. The mixed monolayer of (1SS) and (2) [(2)/(1SS) 1/200] on the gold electrode was prepared in a similar manner to that described above. Photopolymerizations were performed upon UV irradiation with a low pressure Hg lamp and simultaneously detected by cyclic voltammetry. Figure 2 (inset) shows the UV irradiation time dependence of the cyclic voltammograms; a decrease in the redox peak

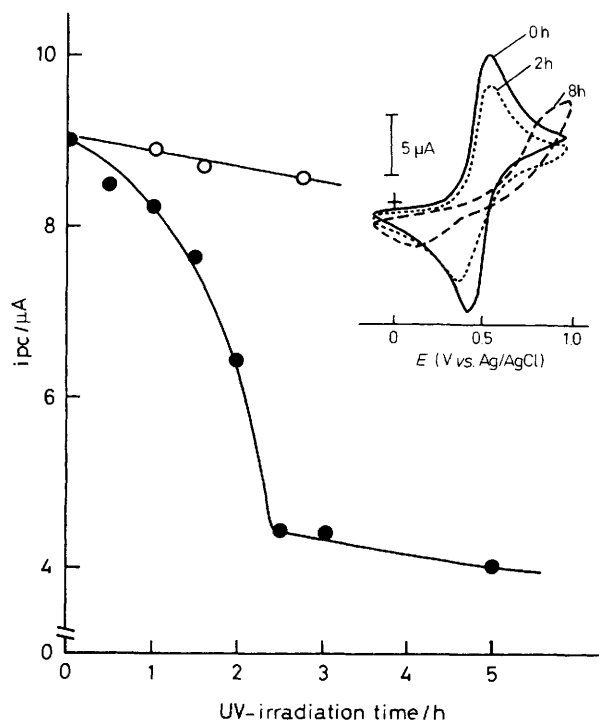


Figure 2. Changes in cyclic voltammograms of the monolayers of pure (1SS)/Au (—○—) and [(2)/(1SS)] (= 1/200)/Au (—●—) upon UV irradiation at 20°C .

current and increase in the peak-to-peak separation were observed with irradiation. Figure 2 also gives plots of the maximum reduction currents (i_{pc}) vs. irradiation time on the basis of the cyclic voltammograms. Three hours irradiation was found to be sufficient for completing the polymerization of the (1SS) monolayer in the presence of the photoinitiator. In contrast, in the absence of (2) the cyclic voltammograms did not show any significant change upon UV irradiation for ≤ 3 h. This implies that the photoinitiator (2) fixed near the polymerizable groups at the monolayer surface plays an important role in initiation of the polymerization. Further, the electrochemical barrier for the postpolymerized monolayer was apparently enhanced compared with that for the prepolymerized monolayer (1PSS).

In conclusion, this communication provides the first example of two-dimensional polymerization, detectable by an electrochemical method, at a spontaneously adsorbed monolayer on gold. Photopolymerization proceeded smoothly in the presence of the photoinitiator, which was fixed close to the polymerizable groups. Attempts to reveal the structural properties of polymerizable and polymerized monolayers on gold are now in progress.

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