

Specific Adsorption of Ferrocene-terminated Poly(oxyethylene) at Self-assembled Monolayers of Poly(methacrylic acid)-based Amphiphiles on Gold Electrodes

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Self-assembled monolayers of poly(methacrylic acid)-based amphiphiles (1_n) on gold electrodes have the ability to discriminate against the chain-length of ferrocene-terminated poly(oxyethylene) (2_m) on the basis of an electrochemical measurement.

The interaction between two different macromolecules plays a key role in living systems since biological phenomena such as enzymatic processes and protein syntheses are indebted mainly to specific intermacromolecular interactions and to a peculiar aggregation state. We have focused on the design and preparation of polymeric amphiphiles carrying a poly-electrolyte segment such as poly(methacrylic acid) (PMAA) and their monolayer properties on water.¹ These polymer assemblies have provided unique characteristics different from those in homogeneous media. The amphiphiles of PMAA connected at one terminus with long alkyl chains have been aligned at the air-water interface, and their monolayers were found to recognize the chain length of the corresponding guest polymers such as poly(oxyethylene) (POE) added into

the subphase owing to multiple hydrogen bonding between polymers.²

We report herein a specific adsorption of poly(oxyethylenes) (2_m , $m = 10-120$)[†] at self-assembled monolayers of PMAA-based amphiphiles (1_n , $n = 35$ and 63) on gold electrodes. One terminus of the POE chains is labelled with ferrocene as a redox-active moiety to detect electrochemically

[†] Ferrocene-labelled poly(oxyethylenes) (2_m) were prepared according to the similar manner to that of Murray *et al.*³ ω -Hydroxy- α -methoxy-poly(oxyethylenes) (Japan Catalytic Chemical Industry Co., Ltd) with various chain lengths (average degree of polymerization, $m = 10-120$) were used as a starting material.

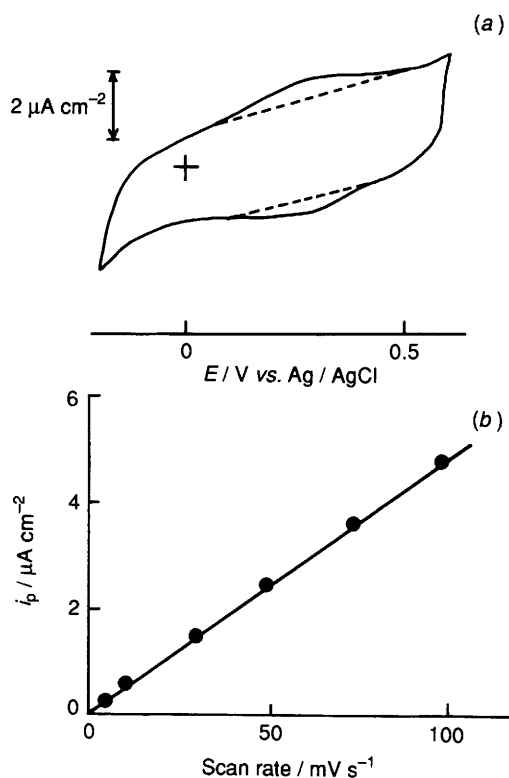
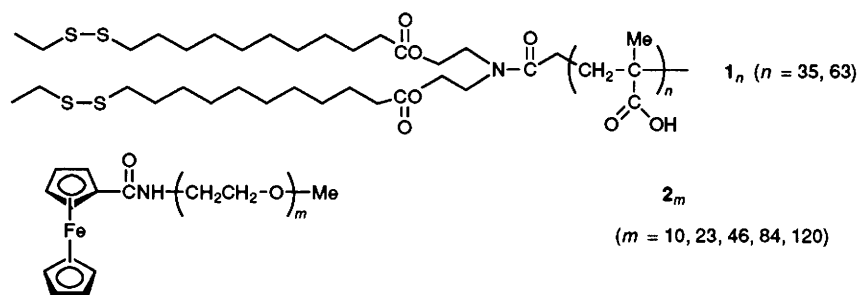


Fig. 1 (a) Cyclic voltammograms acquired at a scan rate of 100 mV s⁻¹ of a 1₆₃ monolayer covered gold electrode (dashed) and the same electrode after adsorption of 2₄₆ on the 1₆₃ monolayer (solid). In both cases, the supporting electrolyte is 0.1 mol dm⁻³ KCl at pH 4.0. (b) Plot of peak current (i_p) vs. scan rate. Solution conditions are the same as in (a). Electrode area = 0.02 cm².

the amount of POE adsorbed on 1_n-monolayers. The preparation of 1_n and their adsorption properties on gold substrates have been described elsewhere.⁴ Self-assembled monolayers of 1_n have been formed spontaneously on gold substrates from aqueous solutions, and the packing density of 1_n molecules within the monolayers has been successfully controlled based upon the conformational size of the PMAA segment adopted in the solution with a prescribed pH.⁴

The preparation of 1_n monolayers was performed by immersing clean gold electrodes in aqueous solutions containing 1_n (1 mmol dm⁻³) for 10 h[‡] at pH 6.0, at which the packing of 1_n in the resultant monolayers is relatively loose because the PMAA segments are considered to provide an expanded conformation. Such a loose-packing of the PMAA

[‡] Initial monolayer formation was rapid, with limiting properties reached after a few hours, *i.e.* no significant change in electrochemical properties estimated by using a redox probe such as Fe(CN)₆^{3-/4-} was detected.

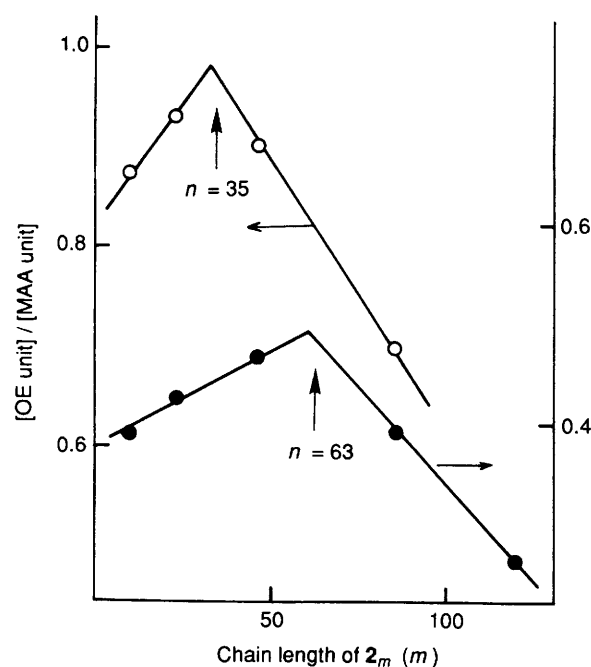


Fig. 2 Relationship between the ratio of oxyethylene unit of the 1_n monolayer-bound 2_m ([OE unit]) to methacrylic acid unit of the 1_n monolayer ([MAA unit]) and the chain length of 2_m (m) for the cases of a 1₃₅ monolayer (upper) and a 1₆₃ monolayer (lower)

segments of 1_n is expected to give a favourable cavity for the guest 2_m. The 2_m adsorption process was carried out by immersing the 1_n-modified electrodes in aqueous solutions of 2_m (1 mmol dm⁻³) and allowing 2 h for equilibration. The pH of the solutions was kept at 4.0 during the adsorption experiment since the CO₂H groups in the PMAA segment were protonated at that pH region. After equilibration, the electrodes were washed with water (pH 4.0) to remove free guest polymers. Fig. 1(a) shows a typical cyclic voltammogram obtained for 2₄₆ adsorbed on the 1₆₃-modified electrode with 0.1 mol dm⁻³ KCl as an electrolyte at pH 4.0. The peaks are due to the one-electron oxidation and reduction of adsorbed 2₄₆. Rinsing the electrode with water (pH 4.0) four additional times resulted in nearly identical current-voltage traces, which demonstrated that desorption is negligible. Fig. 1(b) displays a plot of peak current against scan rate. The peak current is found to vary linearly with scan rate. This indicates that 2₄₆ is surface-bound to the 1₆₃ layer and is not subject to diffusion to the electrode. When this electrode was treated with water at pH 8.0, at which the CO₂H groups of the 1₆₃ layer are considered to be completely deprotonated, *i.e.* they exist as a carboxylate anion, the redox peaks disappeared from the cyclic voltammogram. The binding of 2₄₆ to the 1₆₃ layer is, therefore, mainly due to multiple hydrogen bonding between CO₂H groups in 1₆₃ and ether oxygen atoms in 2₄₆. A

similar trend was discerned for the other combinations of 1_n and 2_m

For each combination of 1_n and 2_m , surface coverages (Γ_2 , mol cm⁻²) of 2_m bound to the 1_n layer were estimated by integration of the charge beneath the voltammetric waves. The surface coverages (Γ_1) of 1_n on the bare gold electrodes were computed elsewhere⁴ by assuming a disk-shaped model.^{5,6} By using the values of Γ_1 and Γ_2 , the ratios§ of oxyethylene unit of the 1_n layer-bound 2_m ([OE unit]) to methacrylic acid unit of 1_n layer ([MAA unit]) were calculated and plotted against the chain length (m) of 2_m in Fig. 2. As can be clearly seen from Fig. 2, the ratios ([OE unit]/[MAA unit]) give maxima for both monolayers of 1_{35} and 1_{63} , and interestingly the chain length of 2_m at each maximum ratio is well consistent with that of 1_n layer. These results suggest that

§ The ratios ([OE unit]/[MAA unit]) have been calculated from both the surface coverage of 2_m bound to 1_n layer (Γ_2) and that of 1_n on the gold electrode (Γ_1) with the following equation: [OE unit]/[MAA unit] = ($m\Gamma_2$)/($n\Gamma_1$), where m and n are the number-average degree of polymerization (chain length) of the POE segment and the PMAA segment, respectively.

1_n monolayers have the ability to discriminate against the chain length of guest 2_m s. Effects of a cavity size of host monolayers changeable by their conformation on guest polymers are now in progress.

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