In Situ Monitoring of Specific Adsorption Processes of Poly(ethylene glycol) at Monolayers of Poly(methacrylic acid)-based Amphiphiles deposited on a Quartz Crystal Microbalance

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The specific adsorption of poly(ethylene glycol)s onto monolayers of poly(methacrylic acid)-based amphiphiles is successfully monitored *in situ* using a quartz crystal microbalance.

Biological phenomena such as enzymatic processes, protein syntheses and molecular recognition on biomembrane surfaces rely primarily on specific inter-macromolecular interactions and higher-ordered aggregation structures. To model and elucidate such interactions, we have devised a strategy in which synthetic polyelectrolytes, as biopolymer models, are aligned two-dimensionally at the air–water interface[1] or on a solid substrate.[2,3] These polymer assemblies have provided unique properties different from those in homogeneous media; for example, self-assembled monolayers of poly(methacrylic acid) (PMAA)-based amphiphiles on gold electrodes were found to have the ability to discriminate against the chain-length of ferrocene-terminated poly(oxyethylene) on the basis of an electrochemical measurement.[3]

We report herein a specific adsorption process of poly(ethylene glycol)s PEGs; ($\mathbf{2}_m$, m = 4–170) at deposited monolayers of PMAA-based amphiphiles ($\mathbf{1}_n$, n = 41, 61) on quartz crystal microbalances (QCMs). QCMs are known to provide very sensitive mass measuring devices because of the resonance frequency changes upon the deposition of a given mass on the QCM electrode.[4–7] Recently, the QCM has been proved to be a useful tool for the characterisation of Langmuir–Blodgett (LB) films in water phases.[8] Here, it occurred to us that if the frequency changes upon adsorption of guest polymers on the host polymer monolayers could be monitored sensitively, information regarding a chain-length recognition mechanism would be more directly obtainable.

The host amphiphiles $\mathbf{1}_n$ were prepared by the manner described previously.[1] PEGs with different chain-lengths as the guest polymer were purchased commercially. The monolayers were obtained by spreading benzene–ethanol (8 : 2, *v*/*v*) solutions of $\mathbf{1}_n$ on highly purified water (Milli-Q system, Millipore). The concentration of the spreading solution was about 1.0 mg cm^{-3}. Surface pressure (π)–area (*A*) curves were measured at 20 °C, as described previously.[7] The amphiphiles ($\mathbf{1}_{41}$ and $\mathbf{1}_{61}$) were found to form stable monolayers with collapse pressures of 38 and 35 mN m^{-1}, respectively, from their π–*A* isotherms at pH 4.0 (not shown here). The QCM plate[†] was lowered at a speed of 5 mm min^{-1} through the monolayer on a subphase at 25 mN m^{-1}, pH 4.0, and one-layer LB films in which the PMAA segments of $\mathbf{1}_n$ were exposed on the aqueous phase were deposited on each side of the QCM plate. Fig. 1 shows the frequency changes of the QCM deposited with $\mathbf{1}_{61}$ LB film when it was immersed in an aqueous solution of $\mathbf{2}_{170}$ (1 mmol dm^{-3}) at 20 °C. The pH of the solution was kept at 4.0 during the adsorption experiment, since the CO_2H groups of the PMAA segment were protonated in this pH region. The frequency decreased gradually upon immersion. When the pH of the solution was increased to 9.0 at which the CO_2H groups of the $\mathbf{1}_{61}$ layer are considered to be deprotonated, *i.e.* they behave as a carboxylate anion, by adding the required amount of NaOH, the frequency conversely increased, though it did not completely revert to the original value. This fact definitely demonstrates that the observed frequency decrease stems from the binding of guest $\mathbf{2}_{170}$ to the surface of the $\mathbf{1}_{61}$ layer, mainly through multiple hydrogen bonding between the CO_2H groups of the host monolayer and the oxyethylene units of the guest PEG (CO_2H---OCH_2CH_2). A similar trend was discerned for the other combination of $\mathbf{1}_{41}$ and $\mathbf{2}_{170}$. It can also be seen from Fig. 1 that adsorption of $\mathbf{2}_{170}$ takes about 20 min for equilibration. Here, we assumed that the mass (Δ*M*, ng) of surface-bound guest polymers $\mathbf{2}_m$ to the $\mathbf{1}_n$ layers can be estimated from the frequency change (ΔF_{eq}, Hz)[‡] at equilibration, so that the chain-length effect of guest $\mathbf{2}_m$s on binding properties would be revealed.

For each combination of $\mathbf{1}_{41}$ or $\mathbf{1}_{61}$ and $\mathbf{2}_m$, the amounts (M_2, nmol) of $\mathbf{2}_m$ bound to the $\mathbf{1}_n$ layer were estimated by the frequency changes (ΔF_{eq}). The amounts (M_1) of $\mathbf{1}_n$ on the QCMs were also estimated from the frequency difference before and after monolayer deposition. By using the values of M_1 and M_2, the ratios of oxyethylene unit of the $\mathbf{1}_n$ layer-bound $\mathbf{2}_m$ ([OE unit]) to methacrylic acid unit of the $\mathbf{1}_n$ layer ([MAA unit]) were calculated using the following equation: [OE unit]/[MAA unit] = $(mM_2)/(nM_1)$, where m and n are the chain-lengths of the PEG and PMAA segments, respectively, and

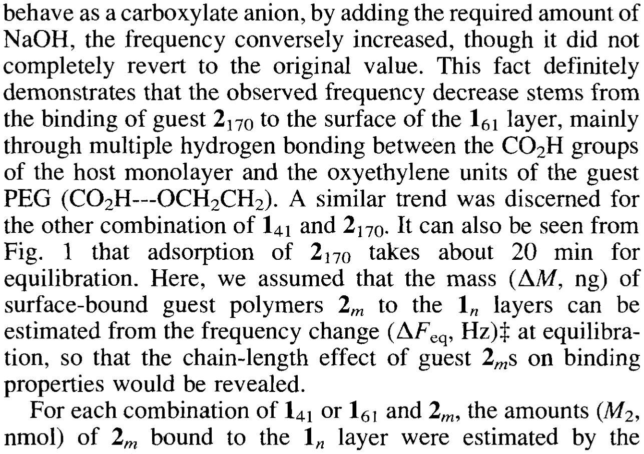
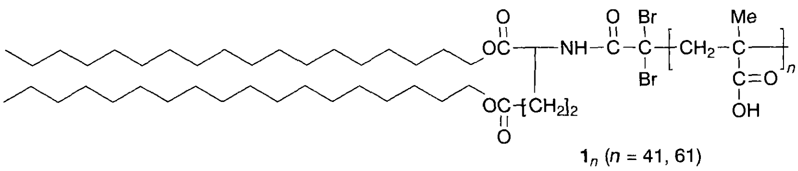


Fig. 1 Frequency change of the QCM deposited with the $\mathbf{1}_{61}$ monolayer on each side of the quartz when immersed in an aqueous solution of $\mathbf{2}_{170}$ (1 mmol dm^{-3}) at 20 °C



$\mathbf{1}_n$ (n = 41, 61)

$HO{-}\!\!\left[CH_2CH_2O\right]\!\!{-}H$ $\mathbf{2}_m$ (m = 4, 23, 33, 45, 76, 170) were plotted against the chain-length (m) of **2**$_m$ in Fig. 2. The ratios give maxima for both LB film-deposited QCMs of **1**$_{41}$ and **1**$_{61}$, and the chain-length of **2**$_m$ at each maximum ratio agrees well with that of the **1**$_n$ layer, suggesting that a cooperative interaction between the PMAA segment of **1**$_n$ and the guest PEG was most effectively enhanced when m became equal to n.

In summary, a specific polymer–polymer interaction can be monitored successfully as a frequency change on QCM in water. The **1**$_n$ LB film-deposited QCMs have the ability to recognize the chain-lengths of guest **2**$_m$s. Since all experiments in the present study were carried out in water, influences of a viscoelasticity[10] induced with the interpolymer complexation on the frequency change may not be excluded. Elucidation of chain-length specificity in a *dry* system is now in progress.

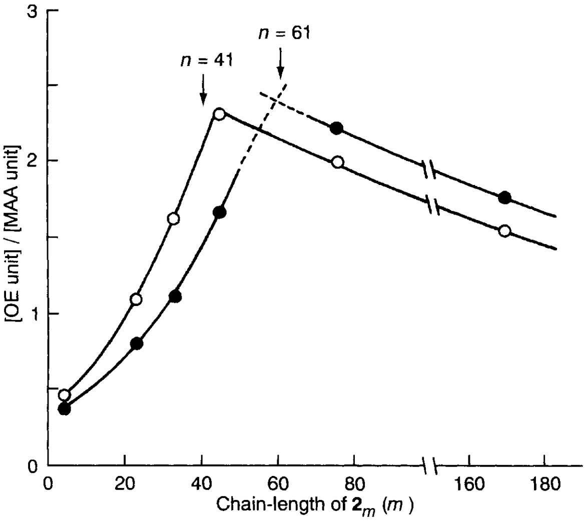


Fig. 2 Relationship between the mole ratio of oxyethylene unit of the **1**$_n$ monolayer-bound **2**$_m$ ([OE unit]) to methacrylic acid unit of the **1**$_n$ monolayer ([MAA unit]) and the chain-length of **2**$_m$ (m) for the cases of a **1**$_{41}$ monolayer (○) and a **1**$_{61}$ monolayer (●)

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Footnotes

† AT-cut quartz crystal plates (9 MHz) were used throughout. The quartz crystal plate was mounted in an oscillator (USI system), which was connected to an Iwatsu frequency counter (SC 7201 model) attached to the microcomputer system (NEC, PC9801 model).

‡ The following equation has been obtained for the AT-cut shear mode QCM:[7,9] $\Delta F = -2F_0\Delta M/A(\rho_q\mu_q)^{1/2}$, where ΔF is the measured frequency shift, F_0 the parent frequency of QCM, ΔM the mass change, A the electrode area, ρ_q the density of quartz, and μ_q the shear modulus. Calibration of the QCM used in this study showed that a frequency change of 1 Hz corresponded to a mass change of 1.0 ± 0.1 ng on the electrode of QCM.

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