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Determination of both wet and dry mass of water-soluble polymers adsorbed on planar silica using a quartz crystal microbalance

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Abstract. It is well-established that polymer adsorption at a model planar interface can be studied using a quartz crystal microbalance (QCM). Normally, this technique reports both the adsorbed mass of polymer chains plus any bound or entrained solvent molecules. Thus the total adsorbed amount significantly exceeds that reported by other methods such as optical reflectometry or adsorption isotherms obtained for colloidal substrates using a supernatant depletion assay. Herein we report a new QCM approach whereby the dry adsorbed amount, Γ_{dry}, is obtained directly from the wet (solvated) adsorbed amount, Γ_{wet}, by switching from liquid flow to a flow of nitrogen gas. The latter conditions lead to complete removal of the solvent, leaving only the desolvated adsorbed polymer chains. This strategy is exemplified for the adsorption of two well-known non-ionic water-soluble polymers, poly(ethylene glycol) (PEG) and poly(*N*-vinylpyrrolidone) (PNVP), onto a model planar substrate (silica). These two systems were selected to facilitate direct comparison with literature data, which validates this new approach.

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Introduction. The adsorption of polymer chains onto colloidal particles and at planar surfaces is of fundamental interest for understanding (i) colloidal stability (e.g. steric stabilization and bridging flocculation)[1] and (ii) lubrication mechanisms.[2] Langmuir-type isotherms up to monolayer coverage are typically observed for the adsorption of many polymers at various interfaces.[3,4] In the specific case of adsorption of water-soluble polymers from aqueous solution, polyelectrolytes tend to adopt a relatively flat conformation – and attain only submonolayer coverage – when adsorbing onto oppositely charged surfaces.[5] In contrast, non-ionic polymer chains such as poly(ethylene glycol) (PEG) or poly(*N*-vinylpyrrolidone) (PNVP) tend to adsorb as perturbed random coils.[6] Traditionally, the adsorbed amount, Γ_{dry}, can be determined for colloidal substrates using a suitable supernatant depletion assay. This may involve a colorimetric method, UV, IR or NMR spectroscopy or a more general method such as solution densitometry.[7–9] For planar substrates, Γ values can be obtained by optical reflectometry.[10,11] In both cases, the adsorbed amount, Γ_{dry}, corresponds to that for the 'dry' polymer chains. In contrast, the quartz crystal microbalance (QCM), which was originally developed to monitor gas adsorption,[12] can be used to measure the mass of the adsorbed polymer chains, any bound water molecules, and all the entrained (unbound) water molecules located within the hydrated layer.[13,14, 15, 16, 17] Typically, the overall mass of solvent (water) significantly exceeds that of the adsorbed polymer chains.[15] In principle, the extent of hydration of the adsorbed polymer chains can be examined by determining the dissipation (D), which also provides information regarding the viscous nature of this layer. [17,18,]

QCM can be used to assess the adsorption of polymers[15] or nanoparticles[19] at a planar surface, as well as the swelling and collapse of polymer brushes,[20] and polyelectrolyte multilayer formation.[21] Suitable model surfaces include silica,[22] gold,[23,24] and stainless steel,[19] but various alternative substrates are also available.[24] One of the major advantages of QCM compared to other analytical techniques is its high sensitivity: it can detect a change in mass within the nanogram range.[25]

The QCM technique is based on the piezoelectric effect, which induces vibrational oscillations in a quartz crystal subject to an alternating potential within the MHz range.[26] The frequency of such oscillations depends on the change in mass at the sensor surface. The adsorbed mass per unit area (or absorbed amount) can be calculated from the change in frequency, Δf, using various well-established models.[26–28] For example, the Sauerbrey[12] and Kelvin-Voigt[29–31] models are commonly used to interpret the adsorption of rigid and viscoelastic polymer layers, respectively. The latter model requires the thickness, density, viscosity and shear modulus of the adsorbed thin film. In practice, some of these parameters may not be accurately known, which incurs experimental error. For example, uncertainty in the mean film thickness can lead to an error of approximately 10% in the adsorbed mass per unit area.[32]

According to the Sauerbrey equation, the change in adsorbed mass, Δm, is proportional to the change in frequency, Δf, as indicated by equation (1):

$$\Delta m = -C \cdot \Delta f / n \qquad (1)$$

Where C is the mass sensitivity constant and n is the overtone number. The Sauerbrey model neglects viscoelastic effects and may lead to an underestimate of the adsorbed mass per unit area.[25] Strictly speaking, the Sauerbrey equation is only valid for uniform, rigid thin films where the change in dissipation energy is close to zero. In practice, even highly rigid layers may exhibit a small change in dissipation. Analysis of the dissipation energy in the plateau region provides useful insight regarding the viscoelastic nature of the adsorbed polymer layer. In certain cases, this may justify use of the Sauerbrey equation.[27]

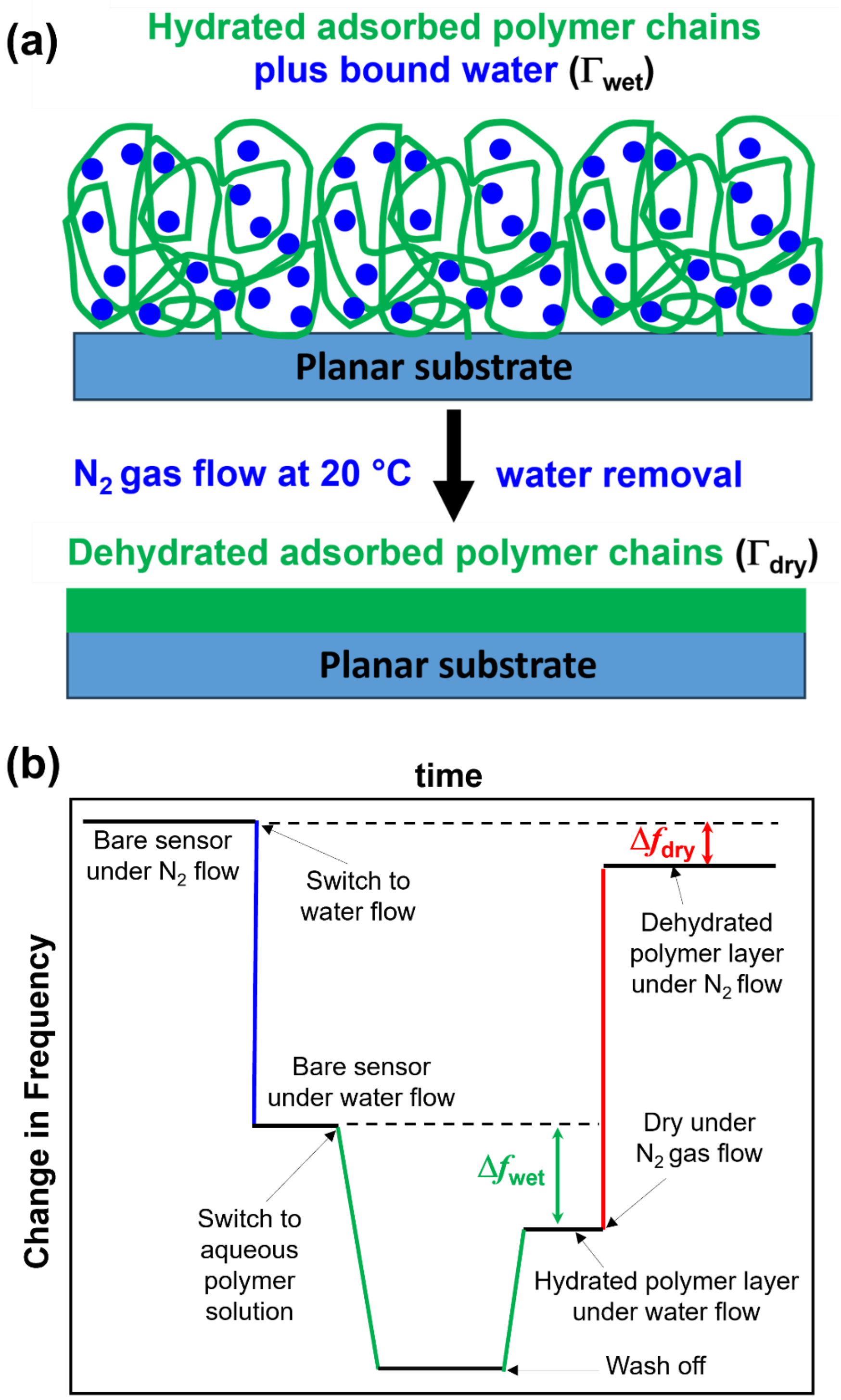
According to the literature, one approach to estimate the water content, W, of an adsorbed polymer layer is to compare the adsorbed mass per unit area (Γ_{dry}) obtained from a polymer adsorption isotherm to that calculated for the solvated polymer chains by QCM (Γ_{wet}) using equation (2):[13, 33]

$$W = (\Gamma_{wet} - \Gamma_{dry}) / \Gamma_{wet} \qquad (2)$$

However, this method requires two independent measurements of polymer adsorption using complementary analytical techniques. Moreover, there may be subtle differences between the two substrates (e.g. colloidal vs. planar silica) used for such experiments. For example, the surface density of silanol groups differs significantly for various types of colloidal silica (e.g. hydrophilic[34] vs. fumed silica[15]). Moreover, the precise protocol (piranha solution vs. UV/ozone treatment) used to clean planar silica substrates is also known to affect the surface density of silanol groups, thereby influencing the effect of solution pH on the extent of polymer adsorption.[35,36]

An alternative approach to calculate *W* involves measuring the change in frequency arising from the replacement of bound and unbound H_2O with D_2O, since the latter species should cause a greater frequency shift.[21,37] However, this method assumes that the polymer interaction with D_2O and H_2O is identical and that all the initially bound water is replaced by heavy water. Moreover, determining the water content for very thin polymer films (< 20 nm) becomes problematic owing to a lack of sensitivity so this method is not well-suited for studies of monolayer polymer adsorption.[37]

Herein we report using QCM to determine adsorbed amounts for two well-known water-soluble polymers (poly(ethylene glycol), PEG and poly(*N*-vinylpyrrolidone), PNVP) on a model planar substrate (silica). Our strategy is to first determine the adsorbed amount, Γ_{wet}, for a monolayer of *hydrated* PEG (or PNVP) chains in a conventional QCM experiment and then immediately switch the flow from deionized water to nitrogen gas. This leads to *in situ* dehydration of the hydrophilic polymer chains adsorbed at the surface of the QCM sensor, which enables the determination of the adsorbed amount of *dehydrated* PEG (or PNVP) chains, Γ_{dry} (see **Scheme 1**).



Scheme 1. (a) Schematic representation of a monolayer of hydrated adsorbed polymer chains (green) containing both bound and entrained water molecules (blue) when adsorbed at a planar surface (e.g. silica). Switching the flow from liquid (deionized water) to nitrogen gas causes dehydration of the adsorbed polymer chains to produce a dry polymer layer. (b) Schematic representation of the new QCM experiment performed in the present study. Δf_{wet} is determined from the baseline difference before and after polymer adsorption (green arrow) and hence Γ_{wet} is calculated using the Sauerbrey equation. Similarly, Δf_{dry} is calculated from the baseline difference before and after drying the adsorbed polymer chains (red arrow) under a continuous flow of nitrogen gas at 20°C and the corresponding Γ_{dry} is determined using the Sauerbrey equation.

The difference between these two adsorbed amounts ($\Gamma_{wet} - \Gamma_{dry}$) indicates the mass of water molecules bound/entrained within the adsorbed layer of hydrophilic polymer chains. Such QCM data are compared to that obtained from conventional adsorption isotherms constructed for the same water-soluble polymers adsorbed onto hydrophilic silica nanoparticles using a supernatant depletion assay based on solution densitometry. Our findings are compared with the relevant literature data for the adsorption of a series of PEG (and PNVP) homopolymers of varying molecular weight adsorbed onto both planar and colloidal silica substrates.[38,10]

Experimental

Materials

Poly(ethylene glycol) (PEG, nominal molecular weight, MW = 6,000) was supplied by BDH Chemicals (Poole, UK). PEG samples (nominal MW = 10,000, 20,000, 100,000 and 200,000) were supplied by Sigma-Aldrich (Gillingham, UK) and used as supplied [N.B. This polymer is sometimes denoted as 'poly(ethylene oxide)' in the literature]. Poly(*N*-vinylpyrrolidone (PNVP; MW = 360,000) was supplied by Sigma-Aldrich (Gillingham, UK). PNVP (nominal MW = 67,000) was kindly donated by Ashland (Delaware, USA) and used as supplied. Deionized water (15 MΩ cm^{-1} resistivity; pH 6.5 ± 0.2) was used in all experiments and obtained from an Elga PURELAB Option source. Silica nanoparticles (manufacturer nominal diameter = 250 nm) were supplied by Blue Helix (Crawley, UK) and subjected to a washing process to remove surface-adsorbed ethanol. First, the nanoparticles were dispersed in deionized water for 48 h followed by centrifugation for 1 h at 13,000 rpm. The aqueous supernatant was removed and the sedimented silica nanoparticles were dried at 30 °C under vacuum for 48 h. The purified silica nanoparticles were then evaluated for ethanol contamination by redispersion in water in deionized water followed by centrifugation for 1.5 h at 13,000 rpm. Subsequently, the density of the aqueous supernatant was determined by solution densitometry. This density corresponded to that of deionized water, so the nanoparticles were deemed to be sufficiently pure for polymer adsorption experiments.

Supernatant depletion assay. Solution densities (± 0.000005 g cm^{-3}) were determined using an Anton Paar DMA 5000 densitometer operating at 20 °C. A series of known polymer concentrations were prepared by dissolving each polymer in deionized water (3.00 mL) with magnetic stirring for 24 h. Each aqueous PEG concentration was injected in turn into a U-shaped borosilicate glass tube. After each measurement, this U-tube was rinsed five times with water and dried with air. Calibration plots of solution density, ρ, against polymer concentration were constructed for each PEG homopolymer (see **Figure S1**). Within the relatively low polymer concentration range investigated herein, such plots are linear to a good approximation.

For the silica adsorption measurements, the desired mass of polymer (0.5 – 20 mg) was weighed into a glass vial followed by the addition of purified silica nanoparticles (150.0 mg) and deionized water (3.00 mL). Each aqueous silica-polymer mixture was stirred at 20 °C for 48 h and the resulting dispersions were then centrifuged at 13,000 rpm for 1.5 h. The resulting aqueous supernatants were carefully extracted via syringe without disturbing the sedimented nanoparticles. For the lowest polymer concentrations, the corresponding aqueous silica-polymer mixture were scaled up by a factor of five to minimize weighing errors. The density of each aqueous supernatant was used to calculate the remaining polymer concentration and the adsorbed amount, Γ, was determined by difference using the following equation:

$$\Gamma = \frac{(C_i - C_f) \cdot V}{SA} \qquad (3)$$

Where *SA* is the total surface area of the silica nanoparticles in m^2 (i.e. the BET specific surface area multiplied by the mass of silica), C_i and C_f are the initial and final concentrations in mg cm^{-3} and *V* is the total solution volume in cm^3.

Scanning Electron Microscopy (SEM). SEM images were obtained using an FEI Inspect-F instrument operating at an accelerating voltage of 10 kV.

Dynamic Light Scattering (DLS). All measurements were conducted at 20 °C using a Malvern Zetasizer Nano ZS instrument (ZEN3600 model) equipped with a 4 mW He-Ne solid-state laser ($\lambda = 633$ nm); backscattered light was detected at 173°. A 0.01% w/w aqueous dispersion of purified silica nanoparticles was allowed to reach thermal equilibrium for 2 min prior to each experiment. Triplicate measurements were conducted, each consisting of ten runs of 10 s duration. The hydrodynamic z-average diameter was calculated from the nanoparticle diffusion coefficient using the Stokes-Einstein equation, which is valid for isolated, monodisperse spherical particles.

Helium Pycnometer. Prior to their analysis, purified silica nanoparticles were dried in a vacuum oven at 30 °C overnight to remove any water. Their solid-state density was found to be 2.06 g cm^{-3} as determined using a calibrated Micromeritics AccuPyc II 1345 gas pycnometer at 20 °C.

BET Surface Area Analysis. BET surface area measurements were conducted at 77 K using a Quantachrome NOVA 1000e instrument with nitrogen gas as the probe gas. Silica nanoparticles were degassed under vacuum at 100 °C overnight. The specific surface area was calculated using NovaWin software according to the BET method,[39] which utilizes the BET equation:

$$\theta = \frac{cp}{(1 - p/p_0)(p_0 + p(c - 1))} \qquad (4)$$

where c is the BET constant, p is the vapor pressure of the adsorbed gas, p_0 is the saturated pressure of adsorbate gas and θ is the surface coverage. A twenty-point absorption isotherm was constructed (see **Figure S2**). BET analysis indicated a specific surface area, A_s, of 10.1 m^2 g^{-1}, which is in satisfactory agreement with the specific surface area of 11.9 m^2 g^{-1} calculated using $A_s = 3/(\rho.r)$, where r is the mean nanoparticle radius (122.5 nm) estimated by SEM analysis and ρ is the silica nanoparticle density (2.06 g cm^{-3}).

QCM-D sensor treatment. Silica sensors (5 MHz; supplied by Biolin Scientific Ltd., Gothenburg, Sweden) were cleaned by UV-ozone treatment ($\lambda = 250$ nm) for 30 min, then immersed in a 2.0% w/w aqueous solution of sodium dodecyl sulfate for 30 min and thoroughly rinsed with deionized water. After drying under a stream of compressed air, each sensor was subjected to a further UV-ozone treatment for 30 min.

QCM-D experiments. All measurements were performed using an openQCM NEXT instrument equipped with a temperature control unit. Python openQCM 0.1.1c software was used for data acquisition. In the conventional QCM experiment, deionized water was allowed to flow through the QCM cell at 0.1 mL min^{-1} until a stable baseline was established prior to any polymer adsorption studies. The desired 1.00 % w/w aqueous polymer solution was then introduced at the same flow rate of 0.1 mL min^{-1} until the reduction in frequency, Δf, attained a plateau value with minimal drift. At this point, the flow over the QCM sensor was switched from the aqueous polymer solution back to deionized water to remove any weakly adsorbed polymer, which typically resulted in a modest increase in frequency.

In some experiments, a three-way tap was used to switch the flow through the QCM instrument from deionized water to nitrogen gas. Prior to polymer adsorption experiments, each sensor was equilibrated under a constant flow of nitrogen (3.00 dm^3 min^{-1}) until a stable baseline was established. A QCM-D experiment was then conducted in which an initial flow of deionized water at 1.0 mL min^{-1} was switched to a dilute aqueous polymer solution and then back to deionized water [N.B. A higher flow rate was used for such gas flow experiments because the small frequency change that occurs on switching from gas to liquid (or liquid to gas) is minimized under such conditions. We emphasize that this higher flow rate has no impact on the final adsorbed amount]. After any weakly-adhering polymer chains had been removed, the three-way tap was switched to introduce nitrogen gas at a constant flow rate of 3.00 dm^3 min^{-1} for 20 to 80 min at 20 °C, which led to a reduction in mass owing to dehydration of the adsorbed polymer chains. The QCM sensor was then allowed to equilibrate under the same continuous flow of N_2 gas and was judged to be dry once a stable plateau value was obtained for the third overtone, Δf_3, which was chosen because it is known to be less prone to experimental artifacts.[40,41] The dry mass of adsorbed polymer was calculated by subtracting the original baseline frequency obtained under a constant N_2 gas flow from the final plateau frequency achieved under the same conditions.

Results and Discussion

PEG Adsorption on Silica Nanoparticles: Supernatant Depletion Assay by Solution Densitometry

SEM studies (**Figure 1a**) of the purified silica nanoparticles confirmed a well-defined spherical morphology and a number-average diameter of approximately 245 ± 11 nm (based on the analysis of 100 nanoparticles), while DLS analysis (**Figure 1b**) indicated a z-average diameter of 270 nm and a DLS polydispersity (PDI) of 0.11. Hence these nanoparticles were judged to be an appropriate model colloidal substrate for polymer adsorption.

The adsorption of a series of five PEG homopolymers (nominal manufacturer molecular weights = 6,000, 10,000, 20,000, 100,000 and 200,000, respectively) onto the silica nanoparticles shown in **Figure 1a** from water at 20 °C was studied using a supernatant depletion assay based on solution densitometry, after centrifugal sedimentation of the PEG-coated silica nanoparticles. Langmuir-type adsorption was observed for each PEG homopolymer, as expected.[38] A representative isotherm is shown in **Figure 1c** for PEG 6,000; the other four isotherms are shown in **Figure S3**.

According to the literature, the adsorption of PEG on silica involves hydrogen bonding between the surface silanol groups and the ether oxygen atoms in the polymer chains.[42] The equilibrium adsorbed amount, Γ_{dry}, corresponds to monolayer coverage and can be estimated from the knee of the isotherm. As expected, Γ_{dry} increases with MW for all five PEG samples shown in **Table 1**.[43] This is illustrated by plotting Γ_{dry} against molecular weight (see **Figure 2**). Also included in this plot are two data sets obtained for near-monodisperse PEG samples using optical reflectometry, as reported by Mubarekyan and Santore[10] and Postmus et al.[11] respectively. Inspecting **Figure 2**, it is clear that significantly higher adsorbed amounts (and reduced scatter) are observed in the present study.

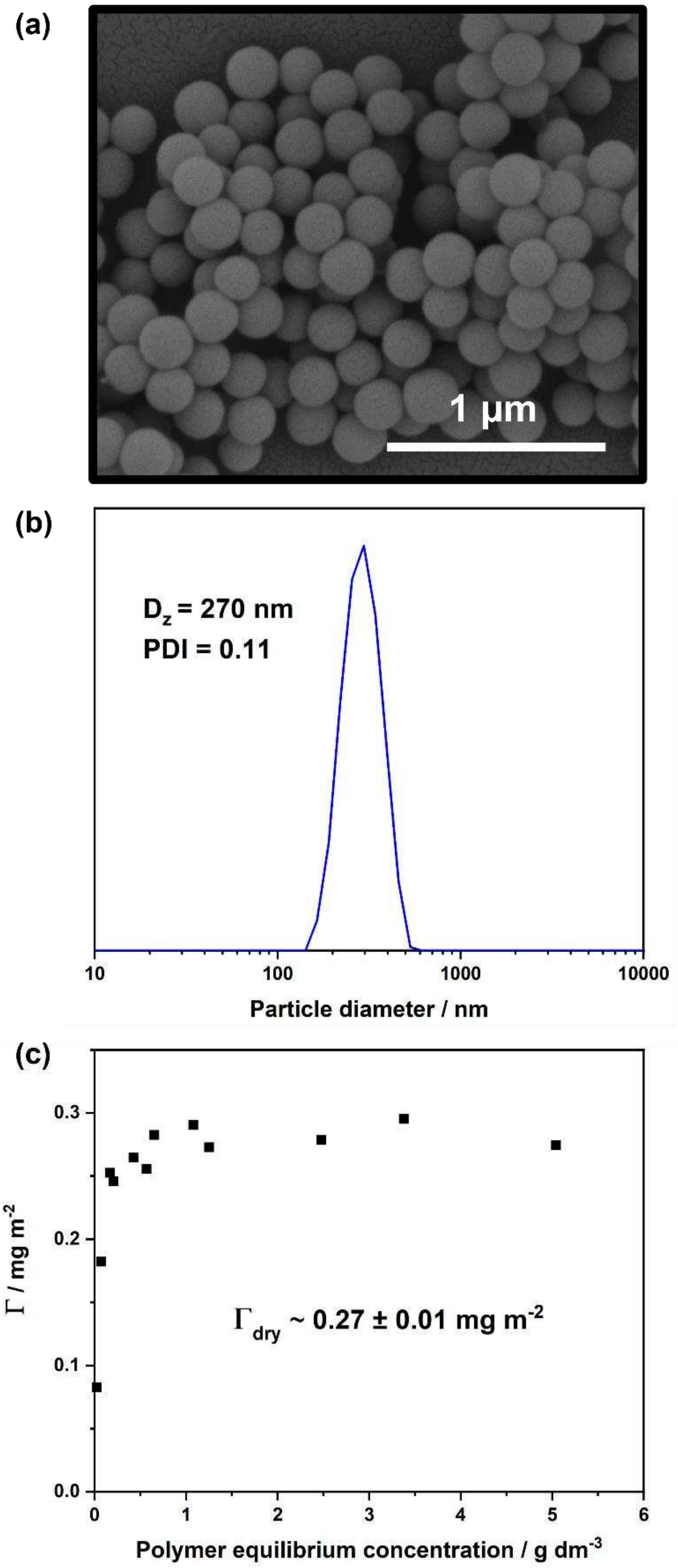


Figure 1. (a) Representative SEM image recorded for the near-monodisperse silica nanoparticles used in this study. (b) Corresponding DLS particle size distribution curve recorded for the same silica nanoparticles. (c) Adsorption isotherm constructed for the adsorption of PEG 6,000 onto silica nanoparticles at 20 °C via supernatant depletion assay using solution densitometry. The adsorbed amount, Γ_{dry}, is estimated by averaging the data points in the plateau region of the isotherm.

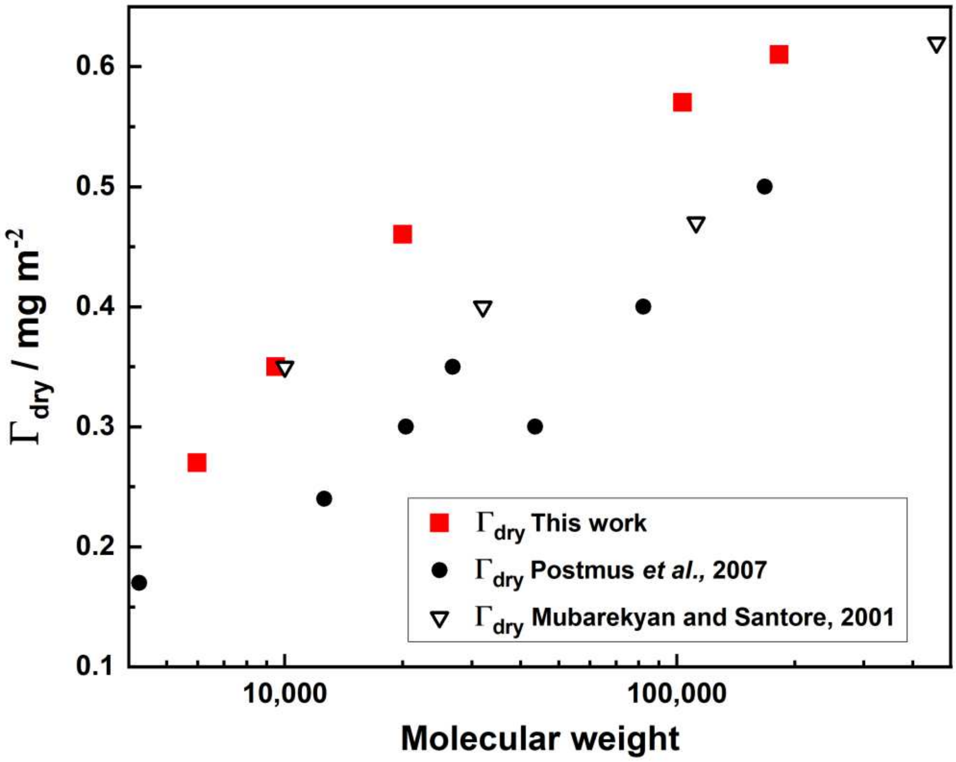


Figure 2. Adsorbed amount (Γ_{dry}, mg m^{-2}) as a function of molecular weight obtained for a series of PEG homopolymers on silica nanoparticles as determined by (i) supernatant assay using solution densitometry at 20 °C (red data set; this study) and (ii) optical reflectometry data (taken from the literature; temperature not stated by the authors).[10, 11]

An adsorbed amount, Γ_{dry}, of 0.27 ± 0.01 mg m^{-2} was obtained for PEG 6,000 at 20 °C (see **Figure 1c**). On the other hand, Killmann *et al*. reported a Γ_{dry} value of 0.37 mg m^{-2} for PEG 6,000 adsorbed onto 100 nm silica nanoparticles at pH 5.5.[44] In principle, this apparent discrepancy may be related – at least in part – to the subtle difference in solution pH: all measurements in the present study were performed using deionized water at pH 6.5 ± 0.2. This is because the degree of ionization of surface silanol groups is suppressed at lower pH, which leads to a greater propensity for H-bonding interactions with the PEG chains.[45] Indeed, Killmann *et al*. obtained a significantly higher Γ_{dry} value of 0.45 mg m^{-2} for PEG 6,000 adsorbed onto 100 nm silica nanoparticles at pH 2.3.[44]

Our Γ_{dry} value of 0.35 ± 0.01 mg m^{-2} for PEG 10,000 is in excellent agreement with that reported for a near-monodisperse PEG of the same molecular weight by Mubarekyan and Santore in their optical reflectometry studies of PEG adsorption at a planar silica substrate.[10] Similarly, our Γ_{dry} value of 0.55 ± 0.01 mg m^{-2} for PEG 100,000 seems to be reasonably consistent with a Γ_{dry} value of 0.40 mg m^{-2} for a near-monodisperse PEG 82,500 reported by Postmus *et al.,* who also used optical reflectometry to study PEG adsorption on planar silica. However, our Γ_{dry} value appears to be inconsistent with a Γ_{dry} value of 0.47 mg m^{-2} reported by Mubarekyan and Santore[10] for a near-monodisperse sample of PEG 112,000. It seems likely that such apparent discrepancies are related to subtle differences in the silica surface chemistry, solution pH, background salt and temperature.[9,35,45,46] Unfortunately, neither Mubarekyan and Santore nor Postmus *et al.* state the precise temperature at which their polymer adsorption experiments were performed.[10,11] Moreover, certain experimental details such as the buffer concentration are sometimes unclear.[10] Thus it is difficult to judge the effect of subtle differences in such parameters on the adsorbed amount of any given polymer. Moreover, the surface density of silanol groups on the planar silica substrates employed for optical reflectometry studies[10,11] is likely to differ from that of the colloidal silica nanoparticles shown in **Figure 1a**. This is an important point because Prescott and co-workers have demonstrated that the surface density of silanol groups can influence the adsorbed amount for non-ionic water-soluble polymers.[36] Indeed, we were inspired to develop a single analytical technique for assessing Γ_{wet} and Γ_{dry} values precisely to avoid such technical problems, which inevitably arise when comparing complementary techniques such as QCM, optical reflectometry and the construction of classical adsorption isotherms via supernatant depletion assay.

QCM-D studies of PEG adsorption on planar silica. First, deionized water (pH 6.5 ± 0.2) was introduced into the QCM cell to obtain a stable baseline at ~ 0 Hz, followed by switching to a 1.0%

w/w aqueous PEG solution. A rapid reduction in frequency to around –100 to –150 Hz was observed, indicating PEG adsorption onto the silica sensor at 20 °C. Once a stable baseline was obtained, the flow was switched from aqueous PEG solution back to deionized water to remove any weakly-adhering PEG chains (wash-off stage). This led to a new frequency plateau closer to the original baseline, which corresponds to monolayer coverage. The magnitude of this final frequency plateau (Δf_3) increases with PEG MW (see **Table 1**, **Figure 3** and **Figure S4**). All QCM measurements were performed in triplicate and reasonably consistent data were obtained for each PEG sample (**Table 1**). The adsorbed mass per unit area, Γ_{wet}, for the hydrated adsorbed PEG chains was calculated from Δf_3 using the Sauerbrey equation.[12] In principle, analysis of the dissipation energy (D) in the plateau region provides an insight into the viscoelastic nature of the adsorbed polymer layer. More specifically, Reviakine *et al.* proposed that, if $|\Delta D_n/(n.\Delta f_n)| << 4 \times 10^{-7}$ Hz^{-1} for a 5 MHz sensor, then the adsorbed layer should be sufficiently rigid for the Sauerbrey equation to be valid.[27] As expected, ΔD_3 increases with molecular weight for the hydrated PEG layers (5.01×10^{-7} for MW = 6,000 and 26.8×10^{-7} for MW = 200,000) layers (see **Figure 3)**: this indicates that longer PEG chains produce more viscoelastic hydrated layers. For PEG 6,000, the $|\Delta D_3/(3\Delta f_3)|$ value (where ΔD_3 denotes the difference in dissipation) for the frequency plateau was calculated to be 0.64×10^{-7} Hz^{-1}. The same analysis was conducted for the other four PEG homopolymers (see **Table 1**) and $|\Delta D_3/(3\Delta f_3)|$ ranged from 0.13×10^{-7} Hz^{-1} to 0.18×10^{-7} Hz^{-1}. This suggests that the Sauerbrey equation is indeed valid, at least for this particular polymer-solvent-substrate system. Notably, increasing the PEG molecular weight leads to a corresponding increase in Γ_{wet}. For example, Γ_{wet} is determined to be 1.42 ± 0.03 mg m^{-2} and 3.40 ± 0.08 mg m^{-2} for PEG 6,000 and PEG 200,000, respectively (see **Table 1** and **Figure 3**).

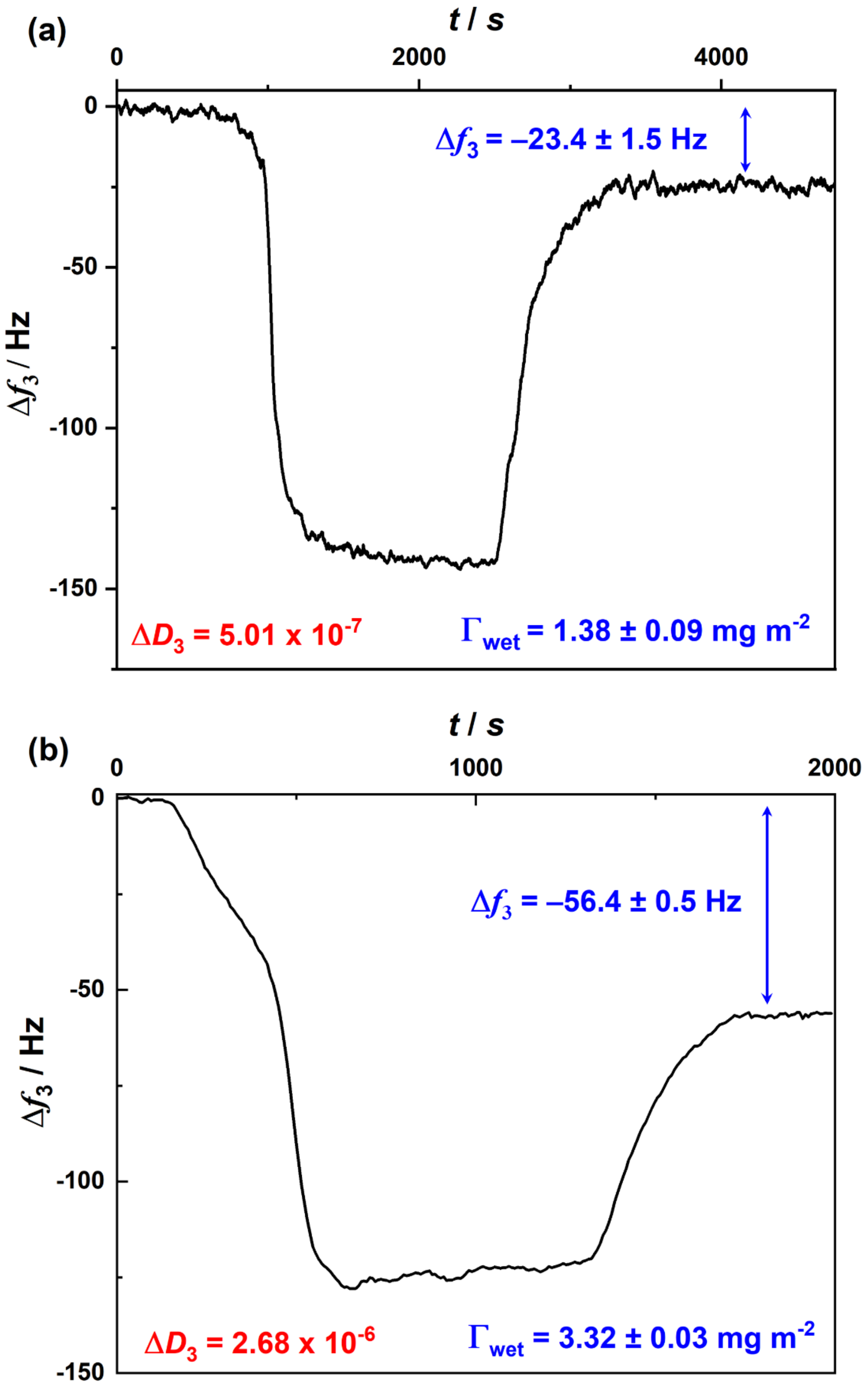


Figure 3. Change in QCM frequency observed over time during the adsorption of a series of two commercial PEGs with nominal molecular weights of (a) 6,000 and (b) 200,000. Adsorbed amounts were calculated for a planar silica sensor (5 MHz quartz) using the Sauerbrey equation. [N.B. Each QCM experiment was run in triplicate for each PEG. A typical run for each sample is shown here but mean values averaged over triplicate experiments are reported in **Table 1**].

A similar trend is observed for the Γ_{dry} values obtained using the classical adsorption isotherm method (see **Table 1**). The large difference between Γ_{wet} and Γ_{dry} indicates that a high proportion of the adsorbed mass associated with Γ_{wet} must be attributed to bound/entrained water within the surface-confined polymer chains.[43] Following the approach reported by Riley *et al.,*[13] we calculated the % water content, *W*, by difference using equation 2 (see **Table 1**).

Table 1. Summary of the effect of molecular weight for the adsorption of five PEG homopolymers onto colloidal or planar silica at 20 °C using either the classical adsorption isotherm method (based on a supernatant depletion assay) or QCM measurements, respectively (see main text for further details).

	PEG molecular weight				
Adsorption parameters	**6,000**	**10,000**	**20,000**	**100,000**	**200,000**
QCM Γ_{wet} mg m^{-2}	1.42 ± 0.03	1.70 ± 0.07	1.73 ± 0.01	3.18 ± 0.01	3.40 ± 0.08
QCM Γ_{dry} mg m^{-2}	0.31 ± 0.03	0.40 ± 0.05	0.51 ± 0.02	0.55 ± 0.07	0.66 ± 0.07
Isotherm Γ_{dry} mg m^{-2}	0.27 ± 0.01	0.35 ± 0.01	0.46 ± 0.02	0.55 ± 0.01	0.61 ± 0.01
Estimated[a] water content *W* %	81 ± 5	79 ± 8	73 ± 2	83 ± 1	82 ± 5
Calculated[b] water content *W* %	79 ± 8	77 ± 26	72 ± 17	76 ± 20	80 ± 8

[a] Estimated water content obtained using equation 2, where Γ_{dry} is calculated from adsorption isotherm data and Γ_{wet} is derived from a conventional QCM experiment.

[b] Calculated water content obtained using equation 2. In this case, Γ_{dry} and Γ_{wet} are obtained from a single gas flow QCM experiment: Γ_{dry} is calculated from the change in frequency observed after an initial hydrated polymer layer (Γ_{wet}) is dried to constant mass under a constant flow of N_2 gas.

Calculation of the dry adsorbed amount of polymer (Γ_{dry}) for PEG adsorption on planar silica

The new QCM approach reported herein was used for the analysis of PEG 6,000, 10,000, 20,000, 100,000 and 200,000 with the aim of determining Γ_{dry} directly from a single experiment performed on a particular polymer under a fixed set of reaction conditions using a given substrate. Typical results are shown in **Figures 4** and **5** for PEG 6,000 and PEG 200,000, respectively. Data obtained for the other three PEG samples are shown in **Figure S5**. **Figure 4** shows typical data obtained in a QCM experiment when switching from gas flow to liquid flow to gas flow for PEG 6,000. The frequency plateau observed for the sensor subjected to an initial N_2 gas flow is compared to that obtained for the final dehydrated chains after drying the hydrated adsorbed PEG layer corresponds to $\Gamma_{dry} = 0.31 \pm 0.03$ mg m^{-2}, which is in reasonably good agreement with $\Gamma_{dry} = 0.27 \pm 0.01$ mg m^{-2} calculated from the adsorption isotherm constructed using a supernatant depletion assay based on solution densitometry.

It is perhaps also worth noting that the intermediate Γ_{wet} value of 1.47 ± 0.05 mg m^{-2} is in good agreement with the mean Γ_{wet} value of 1.42 ± 0.03 mg m^{-2} calculated from triplicate experiments run in conventional QCM mode (i.e. with no N_2 gas flow either before or after PEG adsorption), see **Table 1**. From the above data, the estimated water content of the hydrated PEG 6,000 chains initially adsorbed onto silica is calculated to be 81 ± 5 % via equation 2 (where $\Gamma_{wet} = 1.42 \pm 0.03$ mg m^{-2} and $\Gamma_{dry} = 0.27 \pm 0.01$ mg m^{-2}) using data obtained from the supernatant depletion assay and conventional QCM experiments. However, as discussed above, this traditional approach involves comparison the adsorption of PEG onto colloidal and planar silica, respectively. For comparison, the QCM gas flow experiment performed using the same PEG adsorbed onto planar silica indicates a water content of 79 ± 8 %. These two W values are in reasonably good agreement, which suggests that there is minimal difference between the colloidal and planar silica substrates in this case.

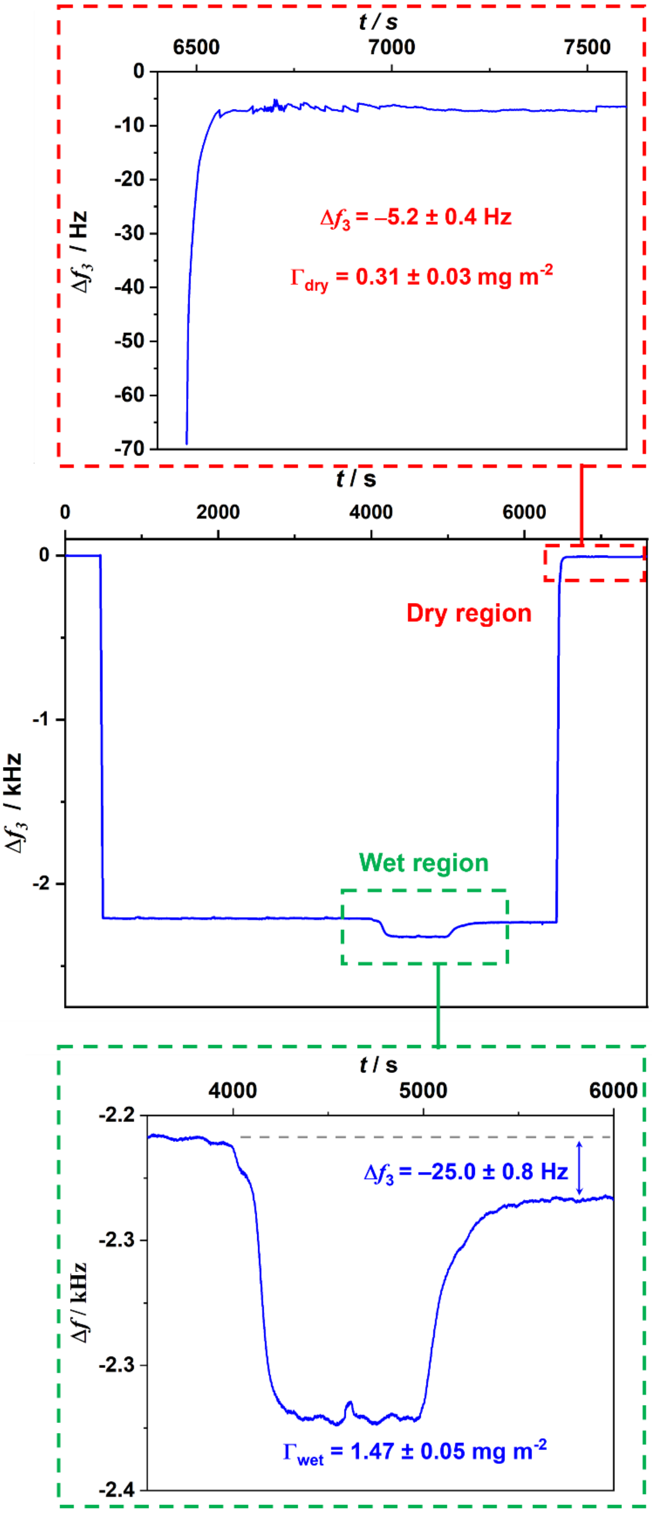


Figure 4. Change in QCM third overtone frequency vs. time observed for the adsorption of PEG 6,000 onto a planar silica sensor at 20 °C. Γ_{wet} is calculated from the change in frequency observed for the hydrated adsorbed PEG chains before and after wash-off to remove any weakly-adhering PEG. In contrast, Γ_{dry} is calculated from the frequency difference between the initial baseline (–1.7 ± 0.1 Hz) observed for the bare QCM silica sensor under a flow of N_2 gas and the final baseline (–6.9 ± 0.4 Hz) obtained after drying the adsorbed PEG chains to constant mass under a N_2 gas flow for 20 min (see **Scheme 1b**). [N.B. The experimental error in Γ_{dry} and Γ_{wet} is estimated from the noise in their respective baselines].

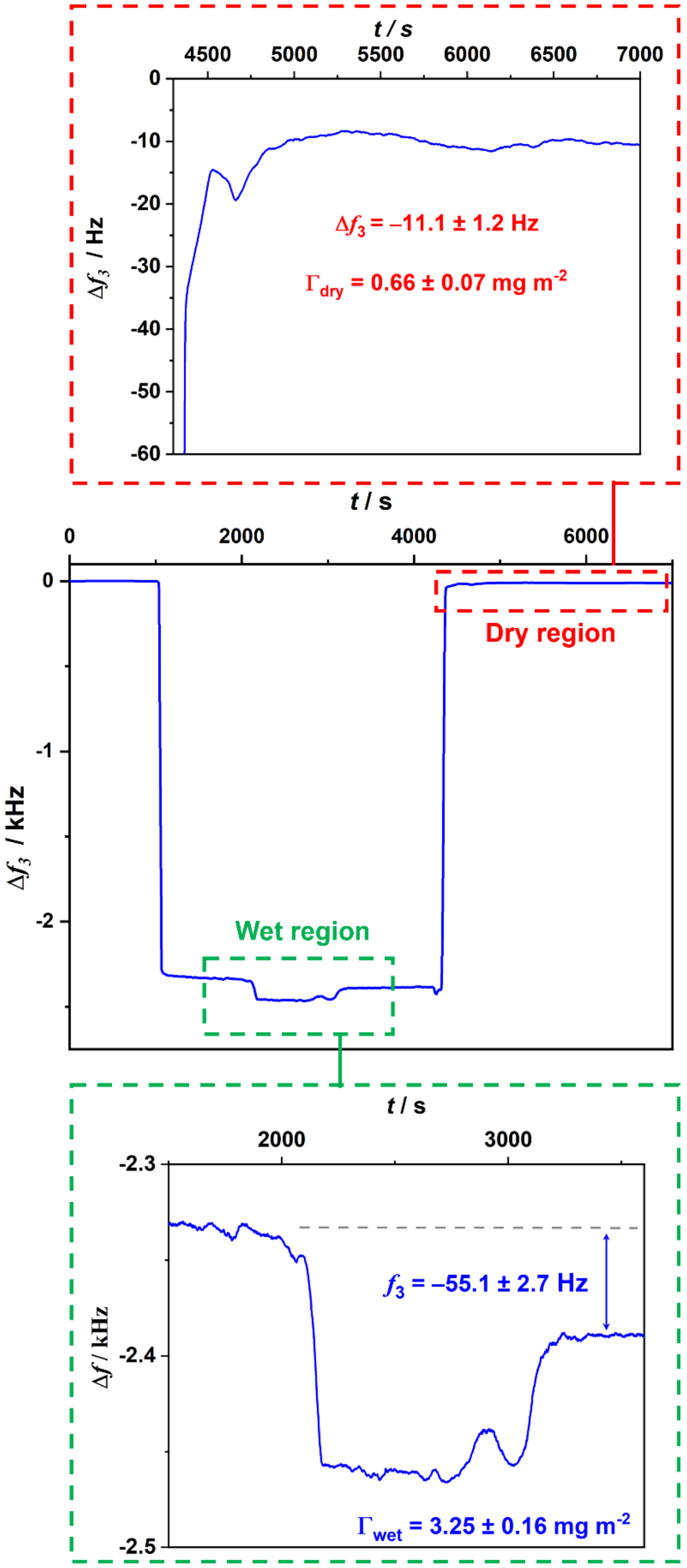


Figure 5. Change in QCM third overtone frequency vs. time observed for the adsorption of PEG 200,000 onto a planar silica sensor at 20 °C (central data set; see **Scheme 1b**). Γ_{wet} is calculated from the change in frequency observed for the hydrated adsorbed PEG chains before and after wash-off to remove any weakly-adhering PEG (lower inset). In contrast, Γ_{dry} is calculated from the frequency difference between the initial baseline (1.1 ± 0.8 Hz) observed for the bare QCM silica sensor under a flow of N_2 gas and the final baseline (-10.0 ± 0.9 Hz) obtained after drying the adsorbed PEG chains to constant mass under a N_2 gas flow for 45 min (upper inset). [N.B. The experimental error in Γ_{dry} and Γ_{wet} is estimated from the noise in their respective baselines].

Importantly, the significant difference in dissipation observed for the final dehydrated PEG layer after exposure to a continuous flow of N_2 gas ($\Delta D_3 \approx 0.72 \times 10^{-7}$) compared to that for the initial hydrated PEG layer ($\Delta D_3 \approx 1.22 \times 10^{-7}$) indicates (i) a substantial reduction in viscoelasticity on removal of the entrained/bound water and (ii) the final dry polymer layer is sufficiently rigid to justify use of the Sauerbrey equation. For PEG 200,000 (see **Figure 5**), the Γ_{dry} value of 0.66 ± 0.07 mg m^{-2} obtained from the QCM gas flow experiment is consistent with that determined from the corresponding adsorption isotherm data ($\Gamma_{dry} = 0.61 \pm 0.01$ mg m^{-2}).

Moreover, the Γ_{wet} value of 3.25 ± 0.16 mg m^{-2} calculated from the QCM gas flow experiment is consistent with the corresponding Γ_{wet} value obtained from the conventional QCM experiment run in triplicate (3.40 ± 0.08 mg m^{-2}). The corresponding water content, *W*, calculated from the QCM gas flow experiment is also consistent with the estimated value respectively (80% vs 82%, see **Table 1**). It is perhaps worth emphasizing the good agreement between Γ_{wet}, Γ_{dry} and *W* values obtained from the QCM and solution densitometry experiments. Furthermore, the new gas flow QCM experiments are sufficiently sensitive to monitor the increase in both Γ_{dry} and Γ_{wet} when varying the PEG molecular weight (see **Table 1**). Finally, the Γ_{dry} values obtained from the traditional supernatant depletion assay using silica nanoparticles are in reasonably good agreement with the corresponding data derived from the QCM gas flow experiments using planar silica. However, the latter data set are on average 9% higher, which leads to slightly lower calculated water contents (see **Table 1).**

Calculation of the dry adsorbed amount of polymer (Γ_{dry}) for PNVP adsorption on planar silica

Our new QCM gas flow method for the convenient calculation of Γ_{wet}, Γ_{dry} and *W* was further validated by investigating the adsorption of another commercial water-soluble homopolymer (PNVP). This non-ionic high MW water-soluble polymer was selected because (i) it is known to adsorb more strongly onto silica than PEG[7,35,38,47,48] and (ii) its highly hydrophilic character should ensure a relatively large mass fraction of bound/entrained water molecules. First, the adsorption behavior of PNVP 360,000 was examined by performing a conventional QCM experiment. This indicated a Γ_{wet}

value of 6.81 ± 0.09 mg m^{-2} (see **Figure S6**), which is significantly higher than that observed even for PEG 200,000 (see **Table 1**). Moreover, the $|\Delta D_3/(3\Delta f_3)|$ value corresponding to the frequency plateau was calculated to be 0.1×10^{-7} Hz^{-1}, thus confirming that the hydrated adsorbed layer of PNVP 360,000 is sufficiently rigid for the Sauerbrey equation to be valid.

Gratifyingly, the corresponding QCM gas flow experiment shown in **Figure 6** yielded a remarkably similar Γ_{wet} value of 6.83 ± 0.16 mg m^{-2}, while a Γ_{dry} value of 0.84 ± 0.04 mg m^{-2} was obtained after exposure of this hydrated PNVP layer to a stream of N_2 gas for approximately 40 min at 20 °C.

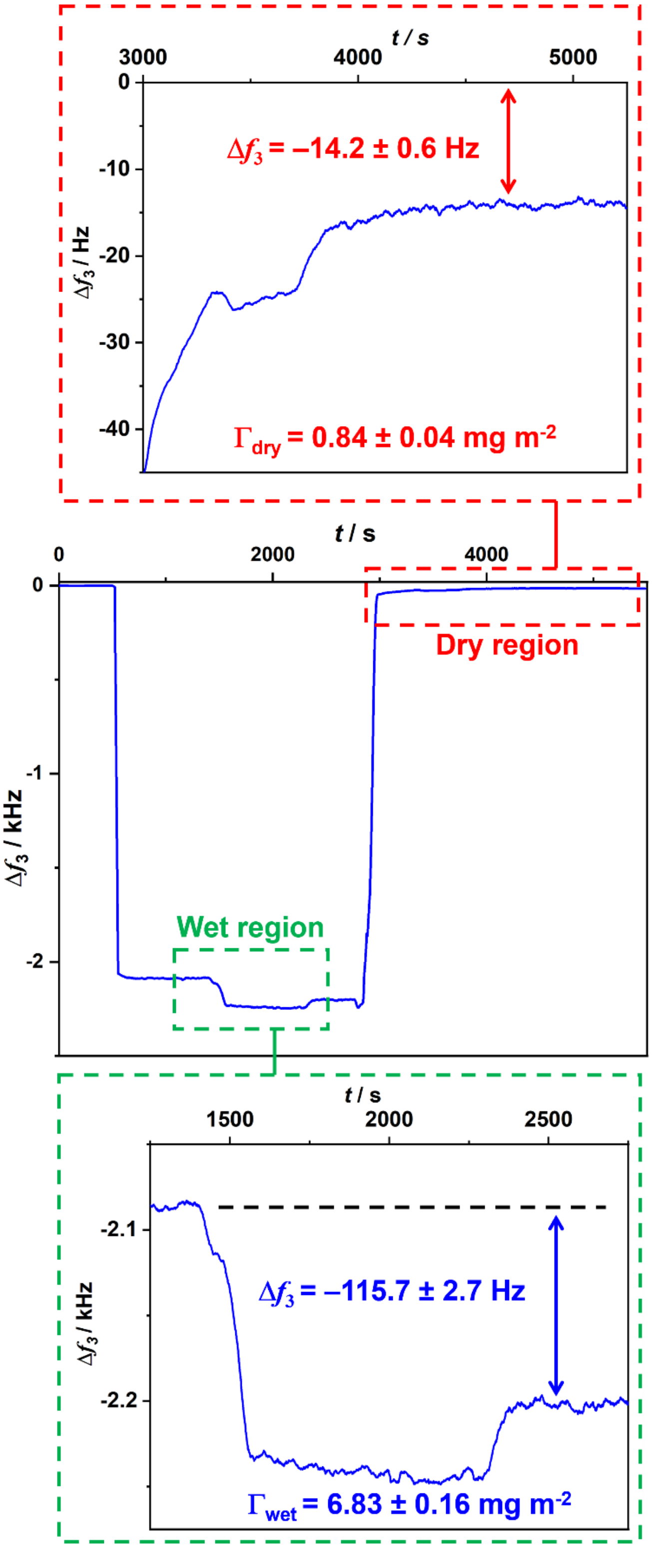


Figure 6. Change in QCM third overtone frequency vs. time observed for the adsorption of PNVP 360,000 onto a planar silica sensor at 20 °C (central data set; see **Scheme 1b**). Γ_{wet} is calculated from the change in frequency observed for the hydrated adsorbed PNVP chains before and after wash-off to remove any weakly-adhering PNVP (lower inset). In contrast, Γ_{dry} is calculated from the frequency difference between the initial baseline observed for the bare QCM silica sensor under a flow of N_2 gas and the final baseline obtained after drying the adsorbed PEG chains to constant mass under a N_2 gas flow for 40 min (upper inset). [N.B. The experimental error in Γ_{dry} and Γ_{wet} is estimated from the noise in their respective baselines].

The dissipation energy corresponding to the hydrated adsorbed PNVP chains ($\Delta D_3 \approx 11.0 \times 10^{-7}$) is significantly higher than that obtained for the dehydrated chains ($\Delta D_3 \approx 2.4 \times 10^{-7}$). Again, the corresponding change in dissipation energy normalized with respect to frequency ($|\Delta D_3/(3\Delta f_3)| = 0.06 \times 10^{-7}$ Hz^{-1}) indicated that the final dehydrated PNVP chains are sufficiently rigid to justify use of the Sauerbrey equation. As a comparison, Parnas *et al.* reported a Γ_{dry} value of 0.95 mg m^{-2} for PNVP 360,000 adsorbed onto 5 µm non-porous silica particles, as judged by a supernatant depletion assay based on UV spectroscopy.[49] Similarly, Harbottle and co-workers observed a Γ_{dry} value of approximately 0.90 mg m^{-2} for the same commercial PNVP adsorbed onto planar silica using optical reflectometry.[48] Accordingly, we used equation 2 to calculate a water content, *W*, of approximately 88 ± 21 % for PNVP 360,000 chains adsorbed onto planar silica from our QCM gas flow data. This seems to be physically reasonable given the strongly hydrophilic character of this water-soluble polymer (unlike PEG, PNVP does not exhibit inverse-temperature solubility behavior in aqueous solution).[50] However, this *W* value is somewhat higher than that reported by Harbottle and co-workers, who reported a *W* value of 55% (albeit with no estimated error).[48] We attribute this apparent discrepancy to the much lower PNVP concentration (≤ 1 ppm) used in this prior study. Indeed, Harbottle and co-workers observed a systematic reduction in Γ_{dry} when lowering the PNVP concentration from 1 ppm to 0.001 ppm. In contrast, the PNVP concentration used in the present study is 1.0% w/w (or 10,000 ppm). This most likely accounts for the higher Γ_{wet} value observed herein, which in turn leads to a higher *W* value via equation 2.

Finally, a lower molecular weight PNVP (MW = 67,000) was subjected to QCM analysis. Firstly, its adsorption behavior was examined by conducting a conventional QCM experiment in triplicate (see **Figure S7**). This yielded a mean Γ_{wet} value of 2.88 ± 0.11 mg m^{-2}, which is significantly lower than that obtained for PNVP 360,000 (6.83 ± 0.16 mg m^{-2}). These observations are comparable to the molecular weight-dependent Γ_{wet} values obtained for the series of five PEG samples.[38] The corresponding QCM gas flow experiment shown in **Figure 7** yielded a remarkably similar Γ_{wet} value of 2.88 ± 0.13 mg m^{-2}. After exposure of this initial hydrated layer of PNVP 67,000 chains to a stream of N_2 gas for approximately

65 min at 20 °C, a Γ_{dry} value of 0.79 ± 0.03 mg m^{-2} was obtained. This is consistent with supernatant depletion assay data obtained for 5 µm porous silica particles by Parnas *et al.,* who found that the adsorbed amount, Γ_{dry}, increased from 0.75 to 0.95 mg m^{-2} for PNVP 10,000 and 360,000, respectively.[49] In addition, Cohen-Stuart and co-workers found a Γ_{dry} value of approximately 0.81 mg m^{-2} for a fractionated PNVP sample with a viscosity-average molecular weight of 72,000.[38] A Accordingly, we used equation 2 to calculate a water content, *W*, of approximately 73 ± 9%. As expected, this is significantly lower than that obtained for PNVP 360,000 (*W* = 88 ± 5%) because the shorter PNVP chains form a thinner adsorbed hydrated layer containing less bound/entrained water.

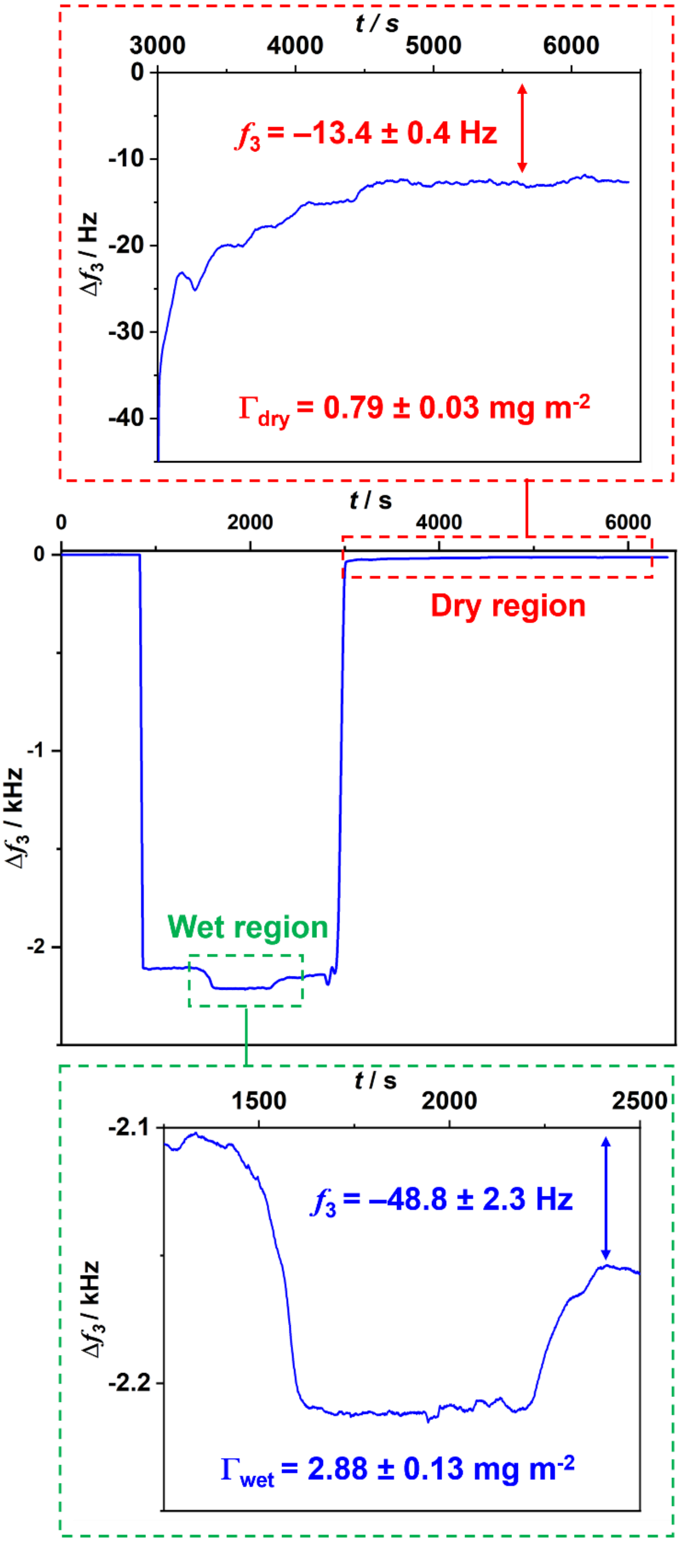


Figure 7. Change in QCM third overtone frequency vs. time observed for the adsorption of PNVP 67,000 onto a planar silica sensor at 20 °C (central data set; see **Scheme 1b**). Γ_{wet} is calculated from the change in frequency observed for the hydrated adsorbed PNVP chains before and after wash-off to remove any weakly-adhering PNVP (lower inset). In contrast, Γ_{dry} is calculated from the frequency difference between the initial baseline observed for the bare QCM silica sensor under a flow of N_2 gas and the final baseline obtained after drying the adsorbed PEG chains to constant mass under a N_2 gas flow for 40 min (upper inset). [N.B. The experimental error in Γ_{dry} and Γ_{wet} is estimated from the noise in their respective baselines].

Finally, one reviewer of this manuscript has pointed out that there have been at least two studies that have combined QCM with a second surface analytical technique to characterize polymer adsorption. Thus Domack and co-workers reported the combination of QCM with ellipsometry to study the thermally-induced swelling of polystyrene brushes in cyclohexane.[51] In addition, Bailey et al. utilized the combination of QCM with surface plasmon resonance (SPR) to monitor the physical adsorption of a polyfluoropolyether lubricant onto a planar silver surface.[52] Notwithstanding such pioneering studies, we believe that the simplicity and relatively low cost of our new QCM-only approach offers significant advantages for characterizing the extent of polymer adsorption on model planar substrates.

Conclusions

The quartz crystal microbalance is widely used to determine the extent of adsorption of soluble polymers onto various model planar substrates. However, this technique normally reports the solvated mass, i.e. the mass of polymer chains plus any entrained solvent. Such adsorbed amounts significantly exceed the adsorbed amount determined by (i) alternative analytical techniques such as optical reflectometry or (ii) adsorption isotherms constructed from supernatant assays. Herein we demonstrate that QCM can be used to determine not only the solvated adsorbed mass per unit area but also the dry adsorbed mass per unit area. This approach is exemplified for the physical adsorption of two well-known non-ionic water-soluble polymers on a model planar substrate (silica). A three-way tap is used to switch from deionized water to nitrogen gas after the initial QCM experiment (plus rinse step). This gas stream leads to gradual dehydration of the adsorbed polymer chains and ultimately affords the dry adsorbed mass per unit area. The data obtained from such experiments are broadly consistent with the relevant literature data. Given the straightforward experimental protocol and the recent availability of relatively cheap QCM instruments, we anticipate that this new approach will become popular amongst QCM users who wish to study the adsorption of either synthetic polymers and/or naturally-occurring biopolymers such as proteins.

Supporting Information Available

Calibration plots of solution density against PEG concentration; BET isotherm for the silica nanoparticles; adsorption isotherms for adsorption of four PEG of varying MW onto silica nanoparticles; conventional QCM experiment for the adsorption of PEG 10,000, 20,000 or 100,000 onto a planar silica sensor at 20 °C; QCM gas flow experiment conducted for the adsorption of PEG 10,000 or PEG 20,000 onto a planar silica sensor at 20 °C; conventional QCM experiment for adsorption of PNVP 360,000 and 67,000 onto a planar silica sensor at 20 °C.

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(43) One reviewer of this manuscript has asked whether the adsorbed monolayers of PEG or PNVP might contain residual water. It Is well-known that such water-soluble polymers are hygroscopic and often contain significant residual water (e.g. up to 5% w/w for PEG). We have not investigated this aspect, which is beyond the scope of the present study. In principle, drying at elevated temperature (our QCM cell can be heated up to 40 °C) should enable complete dehydration of the adsorbed polymer chains. We also not that residual water is likely to be a potential problem for other surface analytical techniques such as ellipsometry.

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