Effect of end-group modification on the adsorption of poly(ethylene oxide)-b-poly(butylene oxide) diblock copolymers at the solid–liquid interface

Mohammad Siddiq · Guangming Liu · Guangzhao Zhang · Abbas Khan · Peter M. Budd

Abstract   The adsorption of poly(ethylene oxide)-b-poly(butylene oxide) diblock copolymers at the solid–liquid interface was studied using a quartz crystal microbalance with dissipation monitoring (QCM-D). The effect of modifying the end group of the hydrophilic block was investigated by comparing the behaviour of trimethylammonium- and dimethylamino-tipped copolymers, designated as TE_mB_n and DE_mB_n, respectively. For adsorption from aqueous solution onto a gold surface, results for $DE_{49}B_{22}$ were similar to those of the T-analogue, but for $DE_{80}B_{34}$ adsorbed amounts were substantially higher, and for $DE_{27}B_{25}$ enormously higher, than for the T-analogue. It is suggested that very high levels of adsorption are associated with the formation of a multilayer structure.

Keywords   Diblock copolymers · Adsorption · Quartz crystal microbalance · Solid–liquid interface · Multilayer structure

Introduction

Adsorption of a diblock copolymer onto a solid surface from a selective solvent may give rise to a variety of surface structures (Fig. 1). If the non-soluble block has a high affinity for the surface and the soluble block is non-adsorbing, a monolayer is

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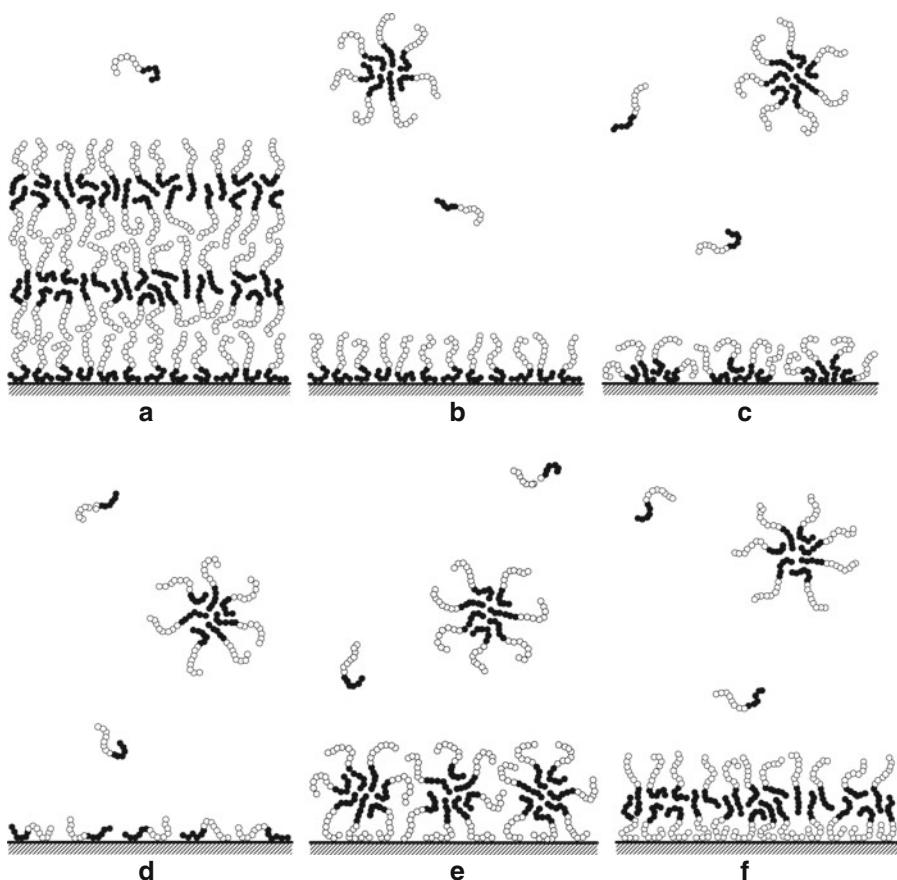
Fig. 1 Schematic illustration of possible surface structures arising from adsorption of a block copolymer from micellar solution: **a** multilayer, **b** monolayer, **c** 'hairy cap' surface micelles, **d** loop, tail and train, **e** surface micelles and **f** bilayer

expected to form, with the solvated soluble block extending away from the surface (Fig. 1b). In the extreme, where the density of adsorbed polymer molecules is so high that the chains are highly stretched, this may be referred to as a 'brush'. Under certain conditions, it is conceivable that further adsorption onto a monolayer may occur, giving a multilayer structure (Fig. 1a). In the case of a short non-soluble block that only partially wets the surface "hairy cap" surface micelles may exist in equilibrium with copolymer in solution (Fig. 1c) [1]. Alternatively, a 'loop, tail and train' structure may be envisaged (Fig. 1d), with more or less of each block in contact with the surface, depending on the nature of the surface and the composition of the copolymer [2]. If the soluble block has an affinity for the surface, direct adsorption of micelles may occur (Fig. 1e) [3] or a bilayer may form (Fig. 1f) [4]. Subtle modifications to the end group of the soluble block have the potential dramatically to change the adsorption behaviour. In this communication, we show

the difference in behaviour between dimethylamino-tipped poly(ethylene oxide)-b-poly(butylene oxide) diblock copolymers (DE_mB_n) and trimethylammonium-tipped copolymers (TE_mB_n) prepared from them by quaternization with iodomethane [5, 6]. For comparison, data are also presented for three conventional E_mB_n diblock copolymers. Adsorption from aqueous solution was studied by means of a quartz crystal microbalance with dissipation monitoring (QCM-D).

Experimental

Block copolymers

The block copolymers were synthesised in Manchester by sequential anionic polymerization in tetrahydrofuran of ethylene oxide, followed by butylene oxide. Standard vacuum line techniques were employed for the transfer of monomers.

Three diblock copolymers having the same hydrophobic block length but different hydrophilic block lengths, $E_{40}B_8$, $E_{80}B_8$ and $E_{120}B_8$, were prepared using previously published procedures [7]. The initiator was prepared by dissolving potassium metal in a five-fold excess of 2-(2-methoxyethoxy)ethanol.

Three dimethylamino-tipped copolymers, $Me_2N(CH_2)_2OE_{48}B_{22}$ (designated $DE_{49}B_{22}$, i.e. the analogous conventional copolymer is $E_{49}B_{22}$), $Me_2N(CH_2)_3OE_{79}B_{34}$ ($DE_{80}B_{34}$) and $Me_2N(CH_2)_3OE_{26}B_{25}$ ($DE_{27}B_{25}$) were prepared as described previously [5]. The initiator was 2-dimethylaminoethanol (for $DE_{49}B_{22}$) or 3-dimethylaminopropan-1-ol (for $DE_{80}B_{34}$ and $DE_{27}B_{25}$) partially converted to potassium alkoxide salt. Trimethylammonium-tipped copolymers, $I^-Me_3N^+(CH_2)_2OE_{48}B_{22}$ ($TE_{49}B_{22}$), $I^-Me_3N^+(CH_2)_3OE_{79}B_{34}$ ($TE_{80}B_{34}$) and $I^-Me_3N^+(CH_2)_3OE_{26}B_{25}$ ($TE_{27}B_{25}$), were prepared by quaternization of the dimethylamino-tipped copolymers with iodomethane in methanol at ambient temperature in the dark, as described previously [5].

The copolymers were characterized by gel permeation chromatography and ^{13}C-NMR spectroscopy. Values of critical micelle concentration (cmc) were determined on the basis of surface tension measurements, as described previously [6]. Table 1 shows polydispersities and cmc values for the E_mB_n and DE_mB_n copolymers.

Table 1 Polydispersity (M_w/M_n) from gel permeation chromatography and critical micelle concentration (cmc) for poly(ethylene oxide)-b-poly(butylene oxide) diblock copolymers

Copolymer	M_w/M_n	cmc (g cm^{-3})
$E_{120}B_8$	1.05	6.5×10^{-4}
$E_{80}B_8$	1.03	6.5×10^{-4}
$E_{40}B_8$	1.03	7.0×10^{-4}
$DE_{49}B_{22}$	1.14	4.5×10^{-4}
$DE_{80}B_{34}$	1.10	4.0×10^{-4}
$DE_{27}B_{25}$	1.13	4.0×10^{-4}

Quartz crystal microbalance measurements

Measurements were carried out using a Q-Sense QCM-D [8], with an AT-cut quartz crystal with a fundamental resonant frequency of 5 MHz and a diameter of 14 mm. The quartz crystal was mounted in a fluid cell with one side exposed to the solution. The constant (C) of the crystal used was 17.7 ng cm^{-2} Hz^{-1}. The frequency shift was measurable to within ± 1 Hz in aqueous medium. The effects of surface roughness were minimized by using highly polished crystals with a root-mean-square roughness <3 nm [9].

A measurement of adsorption was initiated by switching the liquid exposed to the quartz resonator from Milli-Q water to a copolymer solution with a concentration of $\sim 1 \times 10^{-3}$ g cm^{-3}. Note that all the copolymers form micelles in bulk solution at this concentration (see values of cmc in Table 1). Prior to each trial, the crystal resonator was cleaned using Piranha solution composed of one part H_2O_2 and three parts H_2SO_4, rinsed with Milli-Q water, and blown dry with a stream of nitrogen gas. Δf and ΔD values from the fundamental were usually noisy because of insufficient energy trapping and thus discarded. In the present study, all the results were obtained from the measurements of frequency and dissipation shifts in the third overtone ($n = 3$). All experiments were conducted at 20 ± 0.02 °C.

Results and discussion

E_mB_n copolymers

QCM-D was used to study the adsorption from aqueous solution of three E_mB_n block copolymers with the same, relatively short, B block length, but different E block lengths: $E_{40}B_8$, $E_{80}B_8$ and $E_{120}B_8$. The first of these is very similar to a polymer, B_8E_{41}, for which adsorption onto hydrophobic surfaces from dilute solution has previously been investigated by means of ellipsometry and surface force measurements [10]. In that case, a brushlike structure (Fig. 1b) was assumed to form, with the B block as anchor. The present work concerns solutions at a concentration above the cmc and we compare a hydrophilic silicon dioxide (SiO_2) surface, which has a typical contact angle between 20° and 25° [11], with a gold surface, for which a typical contact angle is 77° [12], although rigorous cleaning and protection from air can give much lower contact angles [13].

Figure 2a shows the changes in frequency (Δf) and dissipation (ΔD) of a SiO_2-coated quartz resonator immersed in aqueous solutions of each of the E_mB_n copolymers, as functions of time after each copolymer was introduced. In the simplest terms, Δf may be related to the mass of the adsorbed layer, whilst ΔD depends on the thickness and softness of the layer [14]. A softer layer, with more included solvent, has a larger energy dissipation. The adsorbed amounts show little dependence on the molecular weight of the polymer, similar to the behaviour of a homopolymer in a good solvent [15]. However, ΔD is significantly less for $E_{40}B_8$ than for the copolymers with longer E blocks, showing that in this case the fraction of B (0.17, as compared to 0.09 for $E_{80}B_8$ and 0.06 for $E_{120}B_8$) is sufficiently high as
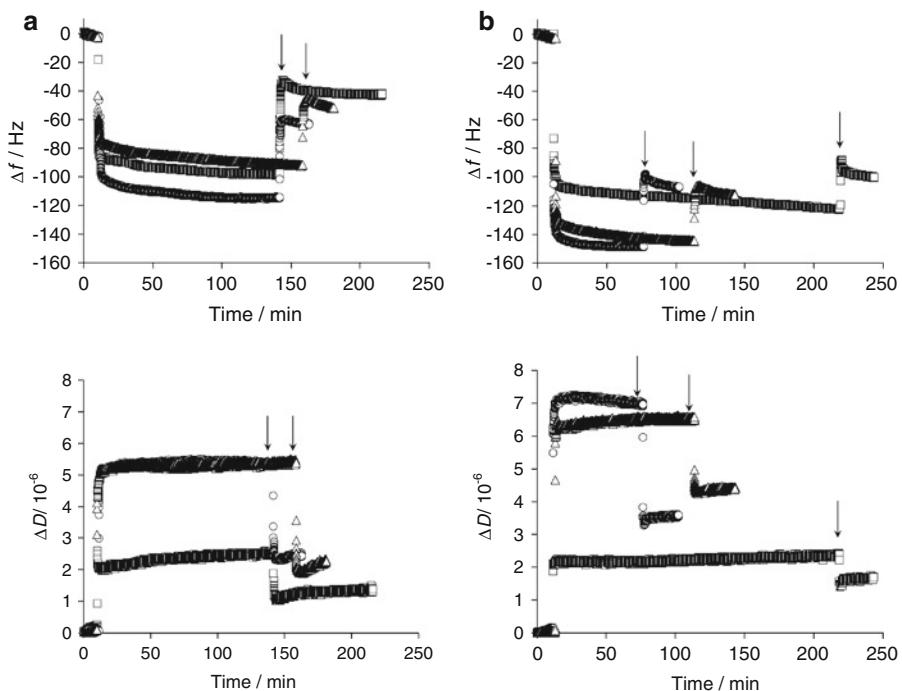
Fig. 2 Changes of frequency (*top*) and dissipation (*bottom*) of **a** SiO$_2$-coated quartz resonator and **b** gold-coated quartz resonator immersed in aqueous solutions of E$_{40}$B$_8$ (*square*), E$_{80}$B$_8$ (*circle*) and E$_{120}$B$_8$ (*triangle*) as functions of time after each copolymer was introduced; the *arrows* indicate rinsing

to give a harder structure. After a period, the resonator was rinsed with pure water, as indicated by arrows in the figure. It can be seen that much of the adsorbed polymer was readily removed on rinsing. We can conclude that the adsorption is dominated by weak interactions between the long E blocks and the hydrophilic surface. This most probably involves a 'loop, tail and train' structure (Fig. 1d), although adsorption of micelles (Fig. 1e) is a possibility.

Figure 2b shows data for a gold-coated quartz resonator with the same copolymers. The main differences, as compared to the more hydrophilic SiO$_2$-coated surface, are that the adsorbed amounts are a little higher and more is retained on rinsing. This suggests significant interaction between the hydrophobic B block and a gold surface, which is relevant to the discussion below of end group modified copolymers on a gold surface. For E$_m$B$_n$ copolymers with short B blocks, we may have a 'loop, tail and train' structure (Fig. 1d) or 'hairy cap' surface micelles (Fig. 1c).

Differences in the structure of the adsorbed layer are clearly shown by plots of ΔD versus Δf, in which the dissipation change per unit added frequency is indicated by the slope. Such plots are illustrated for E$_m$B$_n$ copolymers on both SiO$_2$ and gold surfaces in Fig. 3. A clear difference in behaviour, suggesting a harder structure, is seen for E$_{40}$B$_8$, as has been already discussed. Further work is required to clarify the details of the structure of the adsorbed layer in these systems.
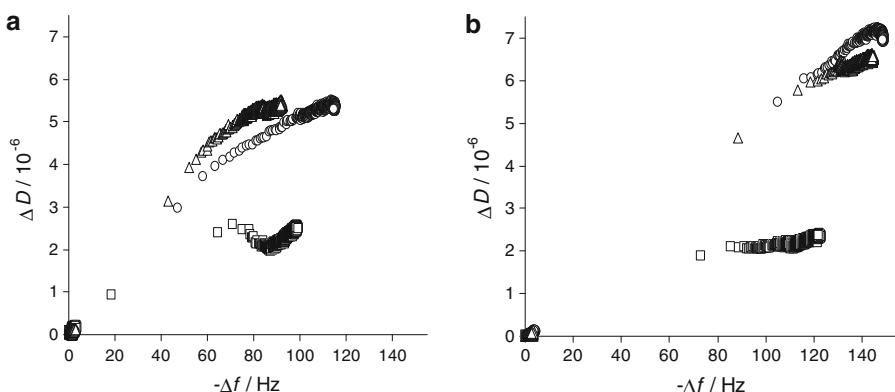
Fig. 3 Relationship between ΔD and Δf for $E_{40}B_8$ (*square*), $E_{80}B_8$ (*circle*) and $E_{120}B_8$ (*triangle*) on **a** SiO$_2$-coated and **b** gold-coated surface

TE_mB_n copolymers

The adsorption from aqueous solution onto a gold surface was studied for three trimethylammonium-tipped copolymers: $TE_{80}B_{34}$, $TE_{49}B_{22}$ and $TE_{27}B_{25}$. All these copolymers have longer B blocks than the E_mB_n copolymers discussed above and we can expect significant interaction between the B block and the gold surface. It is likely that a monolayer will form (Fig. 1b). The cationic tip may be expected to increase the excluded volume of the hydrophilic block, through hydration and repulsive interactions, and so limit the packing density of E chains.

The changes in Δf and ΔD of a gold-coated quartz resonator are shown for the TE_mB_n copolymers in Fig. 4. As might be expected, adsorbed amounts are higher than for the E_mB_n copolymers discussed above and there is only a small change on rinsing, indicating essentially irreversible adsorption. The magnitude of ΔD varies with the size of the E block, increasing in the sequence $TE_{27}B_{25} <$ $TE_{49}B_{22} < TE_{80}B_{34}$. This is also reflected in plots of ΔD versus Δf (Fig. 5).

DE_mB_n copolymers

The dimethylamino-tipped copolymers $DE_{80}B_{34}$, $DE_{49}B_{22}$ and $DE_{27}B_{25}$ show dramatic differences in adsorption behaviour, depending on copolymer composition. Changes in Δf and ΔD of a gold-coated quartz resonator for the DE_mB_n copolymers are compared with the corresponding TE_mB_n copolymers in Fig. 6. It can be seen that, whilst the results for $DE_{49}B_{22}$ are similar to those of the T-analogue, for $DE_{80}B_{34}$ the Δf and ΔD values are substantially higher than for the trimethlyammonium version, and for $DE_{27}B_{25}$ they are enormously so. Indeed, for $DE_{27}B_{25}$, the chamber was rinsed before equilibrium was reached, because of concern that the adsorption might overstep the metrical range of the apparatus. Despite the enormous differences in the magnitude of Δf and ΔD between the three D-copolymers, plots of ΔD versus Δf fall on a more or less common line (Fig. 7), which would suggest little change in polymer segment density.

Fig. 4 Changes of frequency (*top*) and dissipation (*bottom*) of gold-coated quartz resonator immersed in aqueous solutions of $TE_{80}B_{34}$ (*square*), $TE_{49}B_{22}$ (*circle*) and $TE_{27}B_{25}$ (*triangle*) as functions of time after each copolymer was introduced; the *arrows* indicate rinsing
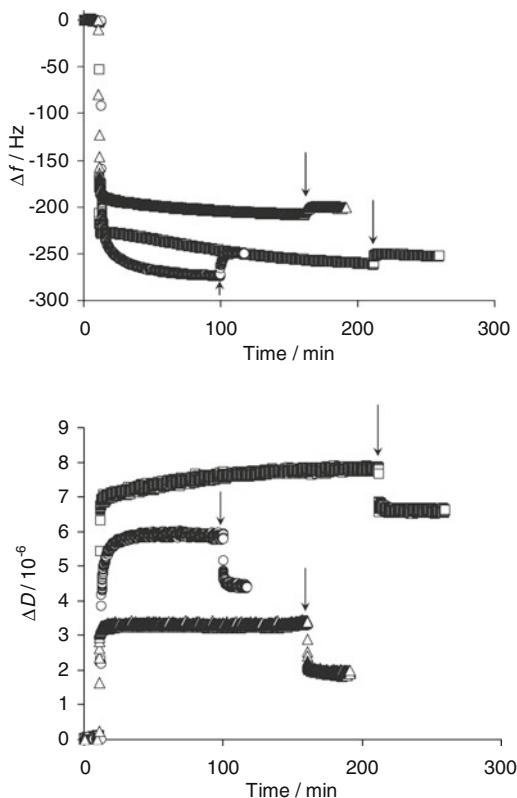
Fig. 5 Relationship between ΔD and Δf for $TE_{80}B_{34}$ (*square*), $TE_{49}B_{22}$ (*circle*) and $TE_{27}B_{25}$ (*triangle*) on a gold-coated surface
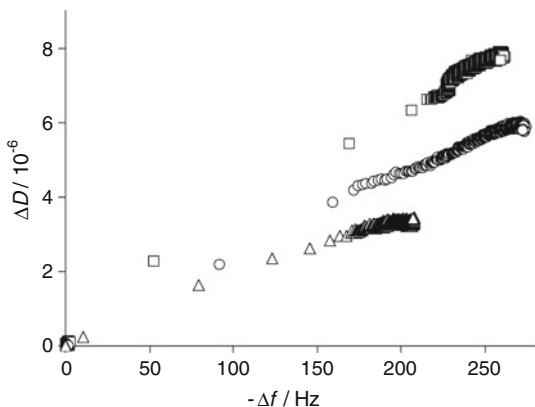
If it is correct that the T-copolymers form a monolayer (Fig. 1b), as suggested above, then it seems likely that $DE_{49}B_{22}$ also forms a monolayer. For $DE_{80}B_{34}$, it might be tempting to interpret the higher apparent loading compared to its T-analogue as formation of a more dense brush, but this would be expected to give a smaller dissipation per unit frequency. The best explanation is thus adsorption of a
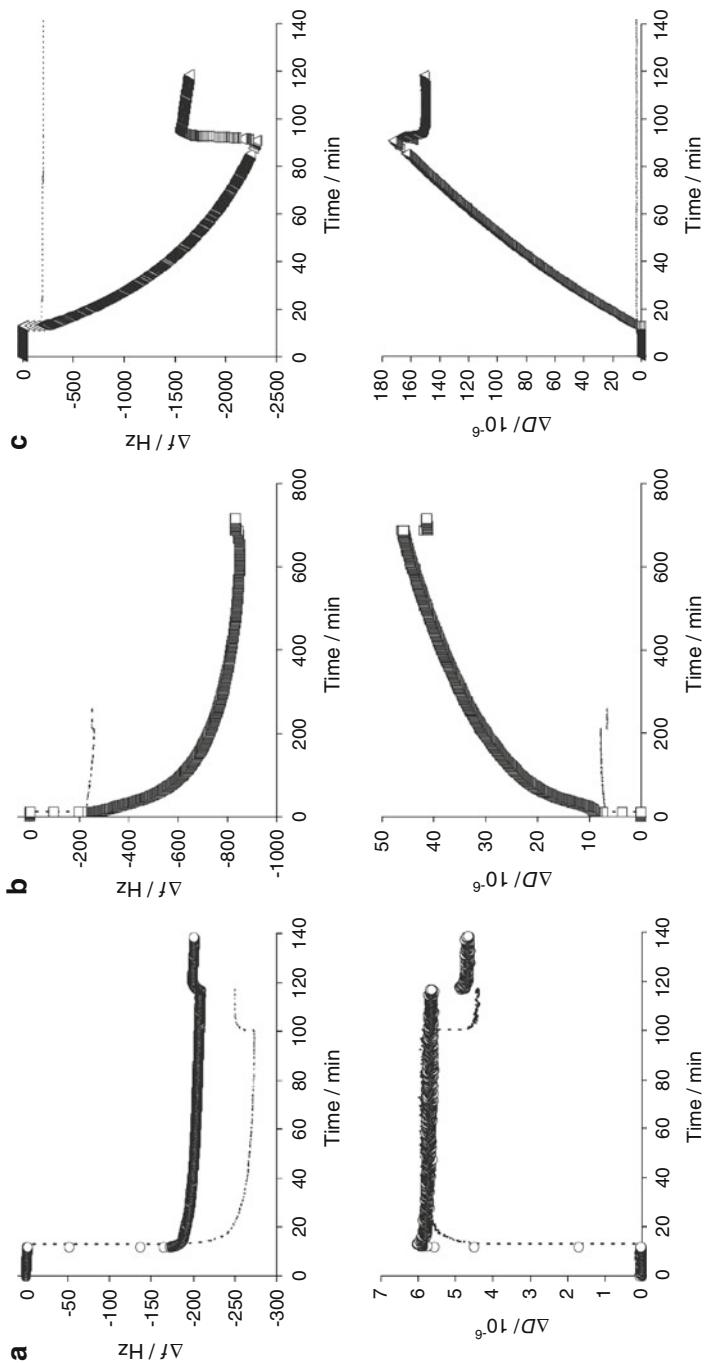
Fig. 6 Changes of frequency (*top*) and dissipation (*bottom*) of gold-coated quartz resonator immersed in aqueous solutions of **a** $DE_{49}B_{22}$, **b** $DE_{80}B_{34}$ and **c** $DE_{27}B_{25}$ as functions of time after each copolymer was introduced. The *dashed lines* indicate the results for the corresponding T-tipped copolymers

Fig. 7 Relationship between ΔD and Δf for $DE_{49}B_{22}$ (*circle*), $DE_{80}B_{34}$ (*square*) and $DE_{27}B_{25}$ (*triangle*) on a gold-coated surface
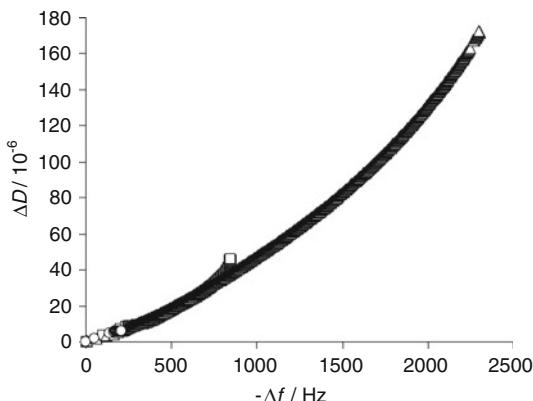
further layer or layers. For $DE_{27}B_{25}$ it is hard to explain the very high levels of adsorption other than in terms of a multilayer structure. Such a structure is not unreasonable, given that the two blocks are of similar length, which would tend to favour a lamellar structure. However, we have to explain why the behaviour of $DE_{27}B_{25}$ should be so dramatically different to that of $TE_{27}B_{25}$, where only the end unit of the hydrophilic block has been modified.

In order to understand such a pronounced effect, we have to consider the nature of the end group. In the case of a trimethylammonium-tipped (T) copolymer, there is a positive charge and associated counterion, which, as already indicated, is likely to give rise to a greater excluded volume for the hydrophilic block, as compared to a purely non-ionic polymer. A dimethylamino-tipped (D) copolymer is expected to be neutral at high pH and protonated at low pH, but the question arises as to what extent it will be protonated when the polymer is dissolved in pure water, as in the present study. The solutions were found to be of neutral pH, but this does not necessarily mean that the end groups are neutral, since there may be a different local pH in the immediate environment of the end group. Furthermore, because the amine is attached to an E chain, its local environment is effectively a mixed solvent of water and poly(ethylene glycol). For a low molar mass tertiary amine, such as triethylamine, the conjugate acid has a pK_a of about 11 at ambient temperature [16]. If the D-tip had a pK_a of this magnitude, it can be calculated that there would be at least 80% degree of protonation under the conditions of the experiments. However, for tertiary amines incorporated into surfactants, pK_a values appear to be lower [17]. On balance, we can expect that DE_mB_n copolymers will partially be protonated under the conditions of the experiments. A protonated DE_mB_n copolymer, like a TE_mB_n copolymer, will carry a positive charge. However, a significant difference is the presence of hydrogen in the DH^+ tip.

It is well established that ammonium ions can form complexes with polyethers and crown ethers, and that these complexes may involve $-NH^+\cdots O-$ ionic hydrogen bonds [18, 19]. For a tertiary ammonium ion, such as $(CH_3)_3NH^+$, interacting with a polyether, complex formation may be further reinforced by $-CH^{\delta+}\cdots O-$ bonds [19]. The complex of $(CH_3)_3NH^+$ with $CH_3(OCH_2CH_2)_3OCH_3$ (i.e. methoxy-tipped E_3) has a dissociation enthalpy of 145 kJ mol^{-1} in the gas phase [19]. In solution,

however, the stability of such complexes is strongly affected by the nature of the solvent [20]. In the present case of a tertiary ammonium ion in a polyether-rich environment, we can expect at least weak complex formation to occur. It is feasible that this could stabilize a multilayer structure and thus explain the dramatic difference in adsorption behaviour between $DE_{27}B_{25}$ and $TE_{27}B_{25}$.

Conclusions

This study has demonstrated a remarkable effect on the adsorption behaviour of certain poly(ethylene oxide)-b-poly(butylene oxide) diblock copolymers, arising from the modification of the end group of the hydrophilic block. Thus, very large adsorbed amounts were observed on a gold substrate for a dimethylamino-tipped copolymer, whereas the equivalent copolymer with a trimethylammonium tip showed much lower adsorbed amounts. The extremely high coverage achieved with the dimethylamino-tipped copolymer is best explained in terms of multilayer adsorption. It is possible that this is stabilized by the formation of tertiary ammonium–polyether complexes.

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