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Neutron Reflectivity of Adsorbed Water-Soluble Block Copolymers at the Air/Water Interface: the Effects of Composition and Molecular Weight

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ABSTRACT: We have used neutron reflection to follow the effects of composition and molecular weight on the structure of layers of poly(2-(dimethylamino)ethyl methacrylate-*block*-methyl methacrylate) copolymer (poly(DMAEMA-*b*-MMA)) adsorbed at the air/water interface. We had previously shown that for a 70% DMAEMA copolymer of M_n about 10K at a pH of 7.5 there is a surface phase transition from a layer about 20 Å thick to one about 40 Å thick and that the adsorbed layer at the higher concentration has a layered cross-sectional structure with the most hydrophobic part of the polymer forming a central layer rather than the outer layer in contact with air, as would be expected. The present work shows that copolymers containing 80% DMAEMA (about the same M_n) and 70% DMAEMA (M_n about 20K) form the same layered structure at the surface. The 80% DMAEMA copolymer is more surface active than the 70% copolymer, and this parallels the tendency to aggregate into micelles in bulk solution. The increase in molecular weight from 10K to 20K decreases the surface activity of the 70% DMAEMA copolymer. Addition of electrolyte enhances the formation of the layered structure at the interface but tends to equalize the surface activities of the three copolymers. Other surprising features are the increase of surface activity with increasing polyelectrolyte block size when the block is the larger component and the apparent suppression of ionization in the surface region.

Introduction

In earlier papers we have described neutron reflectivity measurements on layers of the water soluble diblock copolymer poly(2-(dimethylamino)ethyl methacrylate-*block*-methyl methacrylate) copolymer (poly(DMAEMA-*b*-MMA); 70 mol % DMAEMA, $M_n = 10$K) adsorbed at the air/water interface.[1,2] At low concentrations the adsorbed layer was found to consist of an approximately uniform distribution of the two blocks of the copolymer along the direction normal to the interface with about half of the layer immersed in the underlying water. At higher concentrations the adsorbed layer was found to have a layered cross-sectional structure with the majority of the more hydrophobic MMA forming a central layer with the outer layer next to air consisting largely of the polyelectrolyte DMAEMA component. The effect of lowering the pH is to increase the positive charge on the weak polyelectrolyte block, which has a pK_a of about 7.3. At pH 6.5 surface adsorption was found to be greatly reduced and the layer structure is no longer generated at the surface, although it is present at pH 7.5. Addition of electrolyte generally enhances the amount adsorbed and shifts the transition to the layered surface structure to lower bulk copolymer concentrations. Finally, the correlation between adsorbed amount and surface tension behavior was found to be somewhat erratic, indicating that care must be taken in using the surface tension behavior as a guide to the surface activity. The observed structures do not conform well with the types of adsorbed layer usually assumed in theoretical treatments. Since many theoretical predictions concern themselves with the effects of molecular weight and diblock composition, we have extended our previous work to include a diblock copolymer of the same molecular weight but different composition (80 mol % DMAEMA, $M_n = 10$K) and one of the same composition but different molecular weight (70 mol %, $M_n = 20$K).

Experimental Details

The preparation of poly (DMAEMA-*b*-MMA) and its partially deuterated version (dMMA) has already been described.[3] The isotopic species of the block copolymer used together with their characteristics are given in Table 1, where we use the shorthand notation % DMAEMA-d(h)-*M* where d or h indicates deuteration or not of the MMA block and M is the approximate molecular weight, as determined by GPC using PMMA calibration standards.

All the glassware and PTFE troughs were cleaned by soaking them in alkaline detergent overnight and then rinsing several times with ultrapure water (Elgastat UHQ, Elga, U.K.). The solutions were made by dissolving first in methanol and then diluting with water to reach a final methanol concentration of 4 vol %. The pH was adjusted using hydrochloric acid and maintained constant during the measurements by keeping the samples under a nitrogen or argon atmosphere. For the neutron measurements D_2O and methanol-d_4 were used as received from Aldrich. The surface

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Table 1. Characteristics of the DMAEMA-*b*-MMA Copolymers

copolymer	DMAEMA content (NMR)	DMAEMA content (elem. anal.)	DMAEMA homopolymer GPC,[a] M_n (M_w/M_n)	block copolymer GPC, M_n (M_w/M_n)
70%−d-10K		68	7600 (1.09)	10000 (1.11)
70%−h-10K	68	69	7400 (1.08)	10600 (1.09)
70%−d-20K		71.5	14250 (1.09)	19750 (1.10)
70%−h-20K	68.5	69.5	14300 (1.08)	20050 (1.10)
80%−d-10K		80	7500 (1.10)	8900 (1.12)
80%−h-10K	78.5	79	7800 (1.07)	9800 (1.09)

[a] PMMA calibration standards, THF eluent, refractive index detector, flow rate = 1 mL min^{-1}.

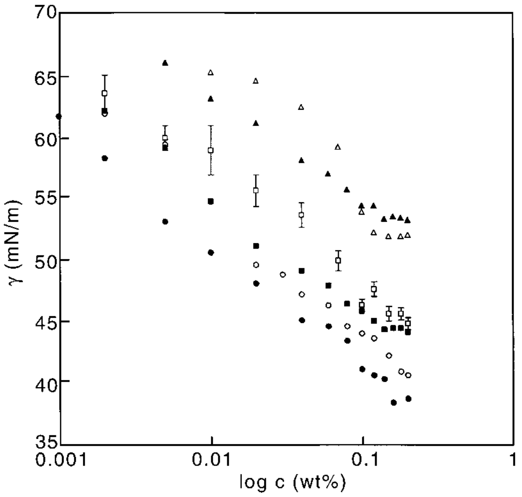

Figure 1. Surface tension of diblock copolymers containing 70% (open symbols) and 80% (closed symbols) DMAEMA residues as a function of copolymer concentration at pH 8.5 (○), 7.5 (□) and 6.5 (△).

tension of the aqueous copolymer solutions was determined on a Krüss K10T tensiometer using the du Noüy ring method with a Pt/Ir ring. The surfaces of such solutions often show time effects and all measurements were therefore made after the solution had stood for 10−30 min, the longer time being used only if necessary. Before each measurement, the ring was rinsed with pure water and flamed to remove contaminants. The temperature was maintained at 298 ± 0.2 K. The neutron reflection measurements were carried out on the reflectometers CRISP and SURF at Rutherford Appleton Laboratory (Didcot, U.K.). The instruments and the procedure for making the measurements have been fully described elsewhere.[4,5]

Results

I. Effect of Composition on the 10K Copolymers.

In comparison with the copolymer containing 70% DMAEMA the one containing 80% DMAEMA lowers the surface tension across the entire pH range studied. The variation of surface tension with concentration is shown for both copolymers at pH values of 6.5, 7.5 and 8.5 in Figure 1. The general pattern of the curves is similar for the two copolymers, and the increasing surface activity with pH is as expected from the decreasing ionization of the DMAEMA block as the pH is increased. A full discussion of the surface tension behavior of the 70% DMAEMA copolymer has been given in previous papers.[1,2]

The surface coverage of the copolymers was determined from neutron reflectivity measurements on the partially deuterated copolymers in null reflecting water (NRW). NRW has an isotopic composition such that its scattering length density is the same as that of air and therefore gives no reflected signal unless there is a layer of nonzero scattering length density material adsorbed at the surface. Partially deuterated copolymer will give such a signal and under these circumstances the signal is therefore entirely from the adsorbed polymer. Extensive numbers of such profiles have been shown for the 70% polymer in the previous two papers and we only show a small selection of reflectivity profiles here (Figure 2). The coverage and mean thickness of the adsorbed layer were determined by assuming that, for the partially deuterated polymer in NRW, the distribution of polymer along the normal direction z can be approximately represented by a Gaussian, giving the distribution of the scattering length density as

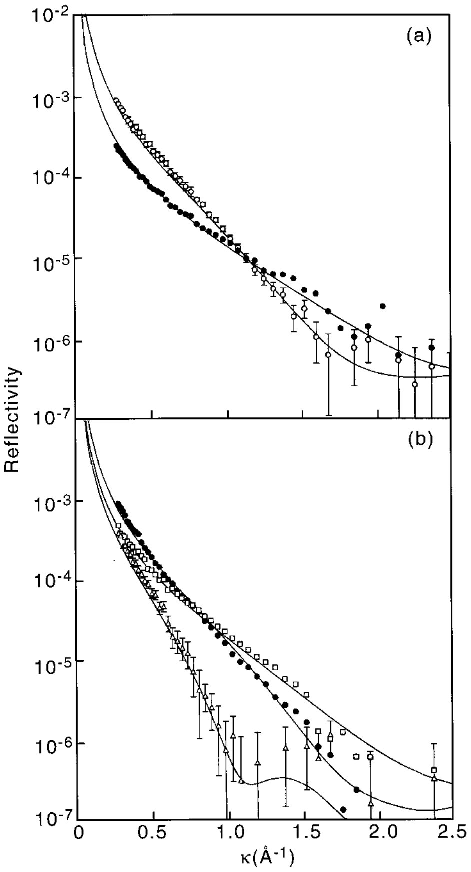

Figure 2. Neutron reflectivity profiles of partially deuterated copolymers in null reflecting water: (a) 80% DMAEMA copolymer at pH 7.5 and copolymer concentrations of (●) 0.02 and (○) 0.2 wt %; (b) pH 7.5, 0.1 M NaCl, and 0.2 wt % copolymer for (○) 70% and (□) 80% DMAEMA copolymer at molecular weight 10K and (△) 70% DMAEMA at 20K. The continuous lines are calculated using the parameters in Tables 3, 4, and 6.

$$\rho = \rho_0 \exp\left(-\frac{4z^2}{\sigma^2}\right) \qquad (1)$$

where σ is the full width at 1/e of the maximum. For

Table 2. Volumes and Scattering Lengths for Materials Used

unit	vol/Å^3	scattering length × 10^4 Å	scattering length density × 10^6/Å^{-2}
MMA-h_9	140	1.492	1.07
MMA-d_9	140	9.824	7.02
DMAEMA	225	1.798	0.80
H_2O	30	−0.168	−0.56
D_2O	30	1.914	6.34

this distribution the reflectivity R is given approximately by

$$\kappa^2 R \simeq \frac{16\pi^2 b_p{}^2 N_a{}^2 \Gamma_p{}^2}{10^{40}} \exp\left(\frac{-\kappa^2\sigma^2}{8}\right) \qquad (2)$$

where b_p is the known scattering length in Å of the copolymer (the scattering lengths of the different fragments are given in Table 2), κ is the momentum transfer ($=(4\pi \sin \theta)/\lambda$) (Å $^{-1}$) and the surface excess Γ_p is in mol m^{-2}. Hence

$$\ln(\kappa^2 R) = 2 \ln\left(\frac{4\pi b_p N_a \Gamma_p}{10^{20}}\right) - \frac{\kappa^2\sigma^2}{8} \qquad (3)$$

Thus the extrapolation of the linear plot of $\ln(\kappa^2 R)$ against κ^2 gives the surface excess, and although the polymer is not necessarily well represented by a Gaussian, the slope of the plot gives $\sigma^2/8$ and hence a measure of the relative thickness of the polymer layer. We have shown elsewhere that the value of the surface excess is accurately determined by this procedure even when the copolymer distribution is not well represented by a Gaussian. Some examples of these plots are given in Figure 3 using the reflectivity profiles shown in Figure 2. The surface excesses, most of them obtained by this means of analysis, are given in Table 3 for pH values of 2.5, 6.5, 7.5, and 8.5 and plotted for the last three values of the pH in Figure 4, where they are also compared with the values for the 70% polymer. In parallel with the lowering of the surface tension the surface coverage for the 80% copolymer is increased significantly relative to that for the 70% copolymer. Over much of the range of conditions studied the increase in coverage brought about by the higher DMAEMA content in the copolymer is about 50% and the most marked effect is at pH 2.5. At this pH the DMAEMA residues are expected to be completely ionized,[6,7] and yet the change from 70 to 80% DMAEMA more than doubles the surface coverage.

Added electrolyte might be expected to increase the surface activity because the electrolyte should screen the electrostatic interactions between charged DMAEMA fragments, making it behave more like an uncharged polymer. As expected, the addition of electrolyte indeed increases the surface activity of the 70% DMAEMA copolymer over most of the range of pH and concentration except at the highest surface coverages studied.[2] These effects are shown for pH 7.5 in Figure 5a. The corresponding changes in surface coverage, as determined from neutron reflection on the partially deuterated copolymers in NRW, follow a similar trend and are shown in Figure 5b, and the complete set of coverage measurements for the 80% copolymer are given in Table 3. For both copolymers, electrolyte lowers the surface tension at low copolymer concentration but raises it at high concentrations, and the crossover point occurs at a lower concentration for the 80% copolymer.

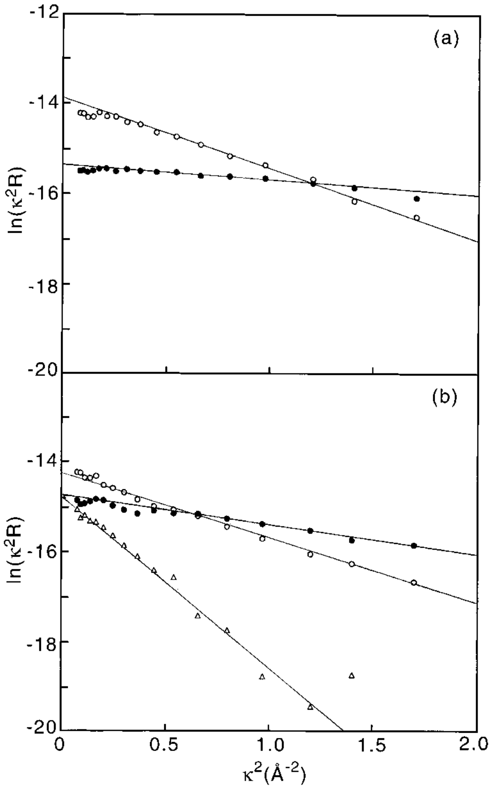

Figure 3. Determination of thickness and coverage of copolymer at the air/water interface using the linear plot of eq 3 on reflectivity of the partially deuterated copolymer in null reflecting water: (a) 80% DMAEMA copolymer at pH 7.5 and copolymer concentrations of (●) 0.02 and (○) 0.2 wt %; (b) pH 7.5, 0.1 M NaCl, and 0.2 wt % copolymer for (○) 70% and (●) 80% DMAEMA at molecular weight 10K and (△) 70% DMAEMA copolymer at 20K.

The weaker dependence of surface tension on copolymer concentration in the presence of electrolyte is reflected in the slower variation of surface coverage with copolymer concentration in Figure 5b for both copolymers. However, the marked decrease in surface coverage when electrolyte is added to the 80% copolymer is quite the opposite behavior from the 70% copolymer. The decrease in surface coverage on addition of electrolyte is shown more directly for a fixed concentration of the 80% copolymer in Figure 6. The effect of electrolyte at pH 8.5 was found to be qualitatively similar to that shown in Figure 5, but as shown in Table 3, addition of electrolyte at pH 6.5 increased the surface coverage over most of the concentration range.

In the previous papers we used neutron reflection from different isotopic species to show that there is a surface transition from a relatively uniform layer to a stratified structure with characterics that could correspond to a layer of adsorbed micelles. The reflectivities of three isotopic compositions, hDMAEMA−dMMA in NRW and in D_2O and hDMAEMA−hMMA in D_2O, were fitted to a common structure using the optical matrix method.[8] In the optical matrix method the model chosen for the surface layer is divided into a number of uniform layers, the Fresnel reflection and transmission coefficients are calculated for each interface, and these coefficients are then combined to give the total reflectivity from the composite surface layer. The calculation is exact for a given structural model. The model is adjusted until the calculated reflectivities fit all three reflectivity profiles at the different isotopic

Table 3. Coverages (mg m^{-2}) and Thicknesses (Å) (in Parentheses) Obtained from the Best Fits of a Single Uniform Layer to Neutron Reflectivities from Poly(DMAEMA-*b*-dMMA) (80%) in Null Reflecting Water

	pH 2.5		pH 6.5		pH 7.5		pH 8.5	
concn/wt %	no salt	$c_{NaCl} = 0.1$ M	no salt	$c_{NaCl} = 0.1$ M	no salt	$c_{NaCl} = 0.1$ M	no salt	$c_{NaCl} = 0.1$ M
0.005							0.7 (10)	
0.008							2.0 (19)	
0.01							1.9 (19)	
0.02			0.9 (20)	2.4 (20)	2.7 (20)	3.0 (19)	2.1 (17)	3.4 (22)
0.03							4.3 (25)	
0.04			1.6 (20)	2.8 (20)	3.5 (25)	3.3 (20)	4.3 (24)	3.5 (23)
0.07			2.3 (20)	2.9 (20)	4.3 (27)	3.4 (21)		3.5 (24)
0.1	0.9 (30)		2.4 (20)	2.9 (20)	4.4 (30)	3.3 (25)	4.4 (32)	3.8 (29)
0.2			4.2 (24)	3.0 (22)	4.6 (36[a])	3.5 (25)	4.2 (35)	4.2 (33)
0.5	1.9 (16)						4.9 (35[a])	
1.0	2.2 (25)	2.6 (22)						

[a] Approximate values because the single uniform layer does not fit the data well.

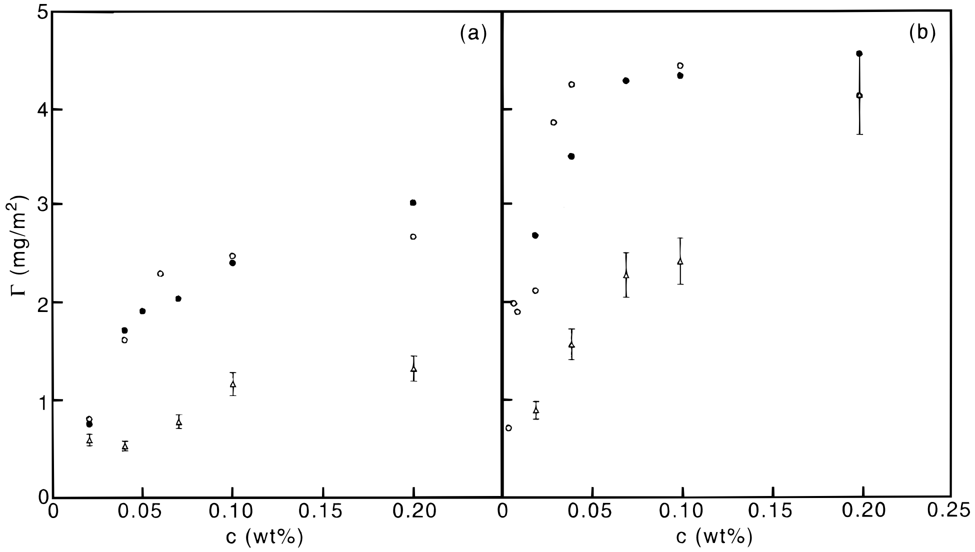

Figure 4. Surface coverage of diblock copolymers containing (a) 70% and (b) 80% DMAEMA as a function of copolymer concentration at pH (○) 8.5, (●) 7.5, and (△) 6.5.

compositions. Each layer is characterized by its scattering length density, given by

$$\rho = \sum n_i b_i \tag{4}$$

where n_i is the number density of atomic species i and b_i its empirically determined scattering length. The scattering length density of any component layer can be expressed in terms of the volume fraction, ϕ_i, of the species constituting that layer

$$\rho = \phi_M \rho_M + \phi_D \rho_D + \phi_W \rho_W \tag{5}$$

where M denotes the MMA block, D the DMAEMA block, and W denotes water. The data were fitted by trial and error using structural models that both preserve the stoichiometry of the polymer and conform to space-filling constraints in any layer containing water. The method for doing this has been discussed in the previous papers, and we do not reproduce the procedure here. There is some uncertainty in the values of the specific volumes; this and possible small isotopic differences can contribute errors or make it very difficult to fit one chemical structure to the set of reflectivities from the different isotopes. The derived structures of the surface layers are summarized in Tables 4 and 5. In comparison with the 70% copolymer, the stratified structure exists at much lower concentrations at pH 7.5 and 8.5 and at lower pH. Thus in the absence of added electrolyte there is no stratification of the structure for the 70% copolymer at pH 6.5, whereas for the 80% copolymer the stratified structure is observed at 0.2 wt % although not at 0.04 wt %. The main characteristic of the stratified structure is that the upper layer largely consists of DMAEMA residues with the MMA block in a second lower layer with very little water. As in the previous paper we have used the stoichiometry of the copolymer as a constraint in the fitting procedure. This leads to the need to include a lowest layer containing a relatively low density of DMAEMA residues. This contributes little, if any, signal to the reflectivity and we attribute no significance to the structural parameters of this layer, although it is included for completeness in the Tables.

II. Effects of Molecular Weight on the 70% DMAEMA Copolymer. The effect of increasing the molecular weight of the 70% DMAEMA copolymer from 10K to 20K is generally to lower its surface activity substantially. In the absence of electrolyte the surface tension of the 20K copolymer is always higher than that of the 10K copolymer, as shown in Figure 7, and the surface coverage is too small to be measured, except at a pH of 8.5. In the presence of electrolyte the differences between the two copolymers are less marked, the surface tension of the 20K copolymer dropping substantially on addition of electrolyte (Figure 8a) and the coverage increasing substantially (Figure 8b).

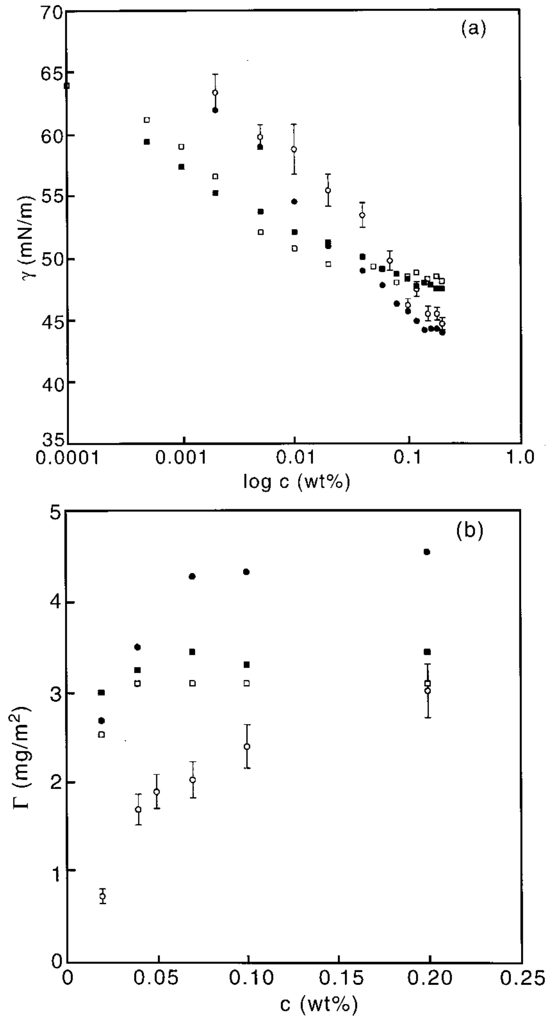

Figure 5. (a) Surface tension of copolymers containing 70% (open symbols) and 80% (closed symbols) DMAEMA residues as a function of copolymer concentration at pH 7.5 (○) and in the presence of 0.1 M NaCl (□). (b) The surface coverages corresponding to part a.

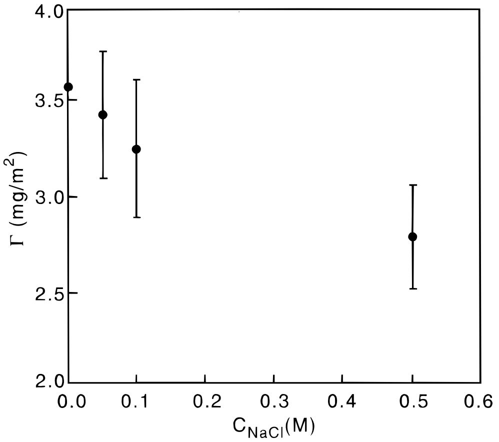

Figure 6. Variation of surface coverage of the 80% DMAEMA copolymer with concentration of NaCl at a pH of 7.5 for a solution containing 0.04 wt % copolymer.

Table 4. Composition of Poly(DMAEMA-*b*-MMA) Layers (80%) at the Air/Water Interface at Different pH Values

			pH 6.5		pH 7.5		pH 8.5	
layer		1 wt %	0.04 wt %	0.2 wt %	0.04 wt %	0.2 wt %	0.04 wt %	0.2 wt %
1st	τ/Å	16	7	15	17	22	18	20
	$\phi_{\rm MMA}$	0.0	0.10	0.03	0.05	0.04	0.04	0.04
	$\phi_{\rm DMAEMA}$	0.63	0.63	0.85	0.86	0.88	0.90	0.90
	$\phi_{\rm water}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2nd	τ/Å	4	13	5	9	10	9	8
	$\phi_{\rm MMA}$	0.25	0.10	0.20	0.35	0.37	0.45	0.38
	$\phi_{\rm DMAEMA}$	0.32	0.63	0.70	0.50	0.47	0.44	0.46
	$\phi_{\rm water}$	0.0	0.27	0.0	0.15	0.16	0.11	0.16
3rd	τ/Å	6		9	26	15	10	15
	$\phi_{\rm MMA}$	0.25		0.45	0.0	0.11	0.12	0.15
	$\phi_{\rm DMAEMA}$	0.32		0.40	0.20	0.19	0.20	0.22
	$\phi_{\rm water}$	0.43		0.15	0.80	0.70	0.68	0.63
4th	τ/Å	30		45		24	15	25
	$\phi_{\rm MMA}$	0.0		0.0		0.0	0.0	0.0
	$\phi_{\rm DMAEMA}$	0.10		0.1		0.10	0.13	0.17
	$\phi_{\rm water}$	0.90		0.9		0.90	0.87	0.83

Table 5. Composition of Poly(DMAEMA-*b*-MMA) Layers (80%) at the Air/Water Interface at Different pH Values at an Ionic Strength of 0.1 M

		pH 6.5		pH 7.5		pH 8.5	
layer		0.04 wt %	0.2 wt %	0.04 wt %	0.2 wt %	0.04 wt %	0.2 wt %
1st	τ/Å	16	16	15	16	20	20
	$\phi_{\rm MMA}$	0.0	0.02	0.03	0.03	0.04	0.04
	$\phi_{\rm DMAEMA}$	0.88	0.91	0.84	0.84	0.83	0.83
	$\phi_{\rm water}$	0.0	0.0	0.0	0.0	0.0	0.0
2nd	τ/Å	8	8	8	8	8	8
	$\phi_{\rm MMA}$	0.44	0.45	0.36	0.36	0.50	0.37
	$\phi_{\rm DMAEMA}$	0.45	0.44	0.47	0.47	0.40	0.47
	$\phi_{\rm water}$	0.11	0.11	0.17	0.17	0.10	0.16
3rd	τ/Å	50	50	8	10	25	15
	$\phi_{\rm MMA}$	0.0	0.0	0.12	0.12	0.0	0.12
	$\phi_{\rm DMAEMA}$	0.10	0.10	0.28	0.28	0.10	0.18
	$\phi_{\rm water}$	0.90	0.90	0.60	0.60	0.90	0.70
4th	τ/Å			40	40		28
	$\phi_{\rm MMA}$			0.0	0.0		0.0
	$\phi_{\rm DMAEMA}$			0.10	0.10		0.10
	$\phi_{\rm water}$			0.90	0.90		0.90

There is an apparent discrepancy between the surface tension and surface coverage measurements for this copolymer. Figure 7 shows that the copolymer is surface active at pH 7.5 in that it lowers the surface tension, but no adsorption could be detected using neutron reflection. The most likely explanation is that the higher molecular weight copolymer forms a thicker more diffuse layer, and unless measurements are extended to lower values of momentum transfer than we normally use, the sensitivity of neutrons to the signal from partially deuterated copolymer (hDMAEMA−dMMA) drops significantly in comparison with the thinner layers characteristic of the other two diblock copolymers. The lower limit of sensitivity is probably about 0.3 mg m^{-2}. Nevertheless, it still seems surprising that the significant lowering of surface tension observed at pH 7.5 and a copolymer concentration of 0.1 wt % should be caused by adsorption of less than about 0.3 mg m^{-2}.

Finally, the structure of the adsorbed layer of the 20K polymer was determined using the same three isotopic compositions as for the other copolymers, i.e., hDMAEMA−dMMA in NRW and in D_2O and hDMAEMA−hMMA in D_2O and the results are given in Table 7. For this 20K 70% DMAEMA copolymer only the stratified structure described earlier was observed. Thus, this copolymer does not appear to form a layer with the relatively simple structure of the type observed at lower coverages or higher copolymer charge density (low pH) for its 10K counterpart.

Discussion

Since there is a transition in the surface activity of these copolymers that seems to be associated with the

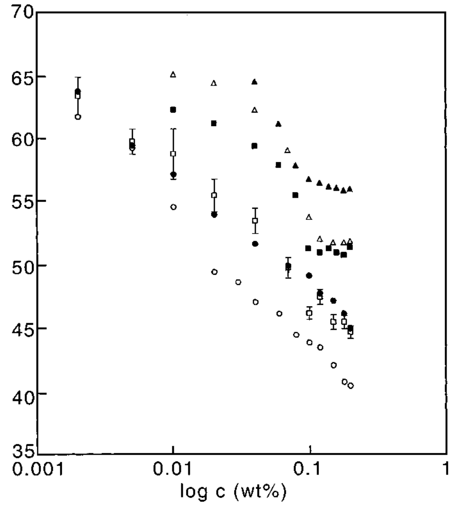

Figure 7. Surface tension of the 70% DMAEMA-10K (open symbols) and 70% DMAEMA-20K (closed symbols) copolymers as a function of copolymer concentration at pH 8.5 (○), pH 7.5 (□) and pH 6.5 (△).

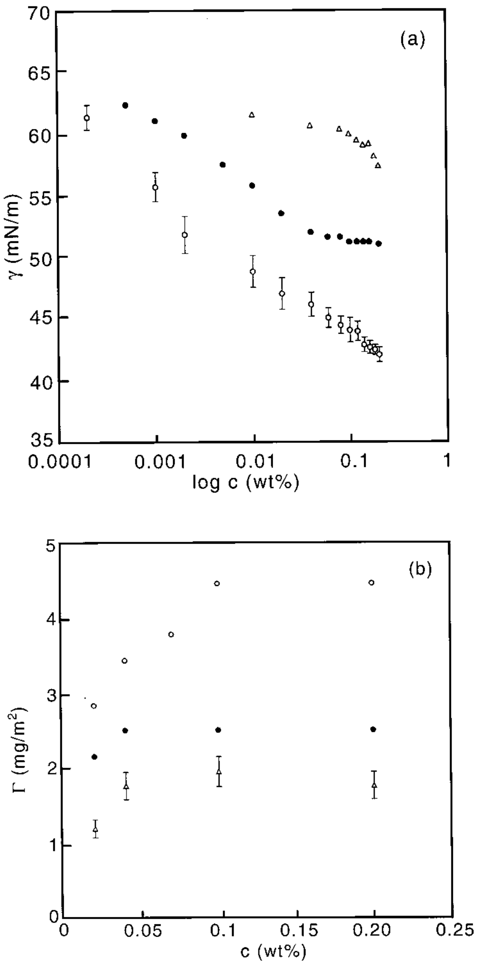

Figure 8. (a) Surface tension of 70%−DMAEMA-20K copolymer in the presence of 0.1 M NaCl as a function of copolymer concentration at pH 8.5 (○), pH 7.5 (●) and pH 6.5 (△). (b) The surface coverages corresponding to (a) at pH 8.5 (○), pH 7.5 (●) and pH 6.5 (△).

Table 6. Coverages (mg m^{-2}) and Thicknesses (Å) (in Parentheses) Obtained from the Best Fits of a Single Uniform Layer to Neutron Reflectivities from Poly(DMAEMA-*b*-dMMA) (70%, 20K) in Null Reflecting Water

			pH 8.5	
concn/wt %	c_{NaCl} = 0.1 M	c_{NaCl} = 0.1 M	no salt	c_{NaCl} = 0.1 M
0.02	1.3 (50)	2.2 (58)		2.9 (52)
0.04	1.8 (45)	2.5 (56)	0.3 (13)	3.5 (55)
0.07			0.7 (40)	3.8 (56)
0.1	1.9 (50)	2.5 (58)	0.5 (30)	4.5 (60)
0.2	1.8 (45)	2.5 (58)	3.5 (60)	4.5 (60)
0.5			4.1 (58[a])	
1.0			5.0 (62[a])	

[a] Approximate values because the single uniform layer does not fit the data well.

Table 7. Composition of Poly(DMAEMA-*b*-MMA) Layers (20K) at the Air/Water Interface at Different pH Values with and without Salt (0.1 M)

		pH 6.5		pH 7.5		pH 8.5		pH 8.5 (no salt)	
layer		0.04 wt %	0.2 wt %	0.04 wt %	0.2 wt %	0.04 wt %	0.2 wt %	0.04 wt %	0.2 wt %
1st	τ/Å	18	18	20	20	25	25	10	25
	ϕ_{MMA}	0.05	0.05	0.03	0.03	0.05	0.03	0.07	0.06
	ϕ_{DMAEMA}	0.31	0.31	0.46	0.46	0.56	0.71	0.24	0.48
	ϕ_{water}	0.0	0.0	0.0	0.0	0.0	0.0	0.70	0.0
2nd	τ/Å	10	10	10	10	12	15		15
	ϕ_{MMA}	0.10	0.10	0.13	0.13	0.23	0.23		0.18
	ϕ_{DMAEMA}	0.38	0.38	0.34	0.34	0.24	0.25		0.30
	ϕ_{water}	0.52	0.52	0.53	0.53	0.53	0.52		0.51
3rd	τ/Å	20	20	20	20	30	30		30
	ϕ_{MMA}	0.08	0.08	0.08	0.08	0.08	0.13		0.07
	ϕ_{DMAEMA}	0.10	0.10	0.10	0.10	0.07	0.08		0.13
	ϕ_{water}	0.82	0.82	0.82	0.82	0.85	0.79		0.80
4th	τ/Å			15	15	30	30		30
	ϕ_{MMA}			0.06	0.06	0.0	0.0		0.0
	ϕ_{DMAEMA}			0.05	0.05	0.05	0.10		0.10
	ϕ_{water}			0.89	0.89	0.95	0.90		0.90

formation of micelles in the bulk, it is convenient to review features of micelle formation in these systems. As already observed by Baines et al. the cmc of the poly(DMAEMA-*b*-MMA) copolymers decreases on increasing the fraction of polyelectrolyte in the copolymer.[3] Our copolymers are sufficiently similar that it can be concluded from their results that the cmc of the 80%−10K copolymer should be about half that of the 70%−10K copolymer. This observation agrees with the systematic study of poly(styrene-*b*-sodium acrylate) copolymers by Astafieva et al.,[9] who found that the cmc passes through a maximum as the polyelectrolyte block size increases. For a short polyelectrolyte block the solubility of the copolymer will increase with the length of this polyelectrolyte block, and hence the cmc should increase. Astafieva et al. refer to this as the short ionic block regime. At large polyelectrolyte block sizes, which Astafieva et al. refer to as the long ionic block regime, the cmc decreases with increasing polyelectrolyte block length, which they attribute to the greater screening of the electrolyte block in the vicinity of the micelle core, leading to a lower solubility. Neutral diblock copolymers consisting of an insoluble block (anchor) and a soluble block (buoy) also exhibit maxima in their adsorption behavior (see, e.g., refs 10 and 11), but the maximum then has its origin in size differences of the two blocks at the interface and occurs at low fractions of the buoy because the buoy is swollen by solvent and the anchor is not. This is quite different from the present observations. For poly(DMAEMA-*b*-MMA) the behavior of the cmc with molecular weight is composition dependent and for these copolymers the cmc of the 70%−10K copolymer is about half that of the 70%−20K when measured in weight percent but about the same in molar units. The micelle aggregation numbers at the cmc increase by about 50% on going from 70%−10K to 80%−10K and the effect of increasing the molecular weight from 10K to 20K at 70% DMAEMA is to decrease the aggregation number to maintain a constant micelle size, i.e., the number of copolymer chains forming in the micelle is approximately cut in half.

All the results we have obtained on this copolymer system, in this paper and the two previous ones, show that there are two regimes of adsorption. One is the simple monolayer structure where the mean distribution of the two monomers along the surface normal is relatively uniform and where the layer is about half-immersed in the underlying aqueous phase. This simple monolayer structure occurs below the cmc, and adsorption in this regime is not large, although it may lower the surface tension significantly. The surprising feature of this adsorption is that it does not conform to the expected picture of an anchor−buoy system where the insoluble block forms a layer on the surface and the soluble block extends into the solution. The amount of material adsorbed does, however, correlate well with the surface activity, as assessed from the value of the cmc. Thus, at points where this pattern of adsorption can be compared, the 80%−10K copolymer is most strongly adsorbed and then the 70%−10K, and the 70%−20K copolymer is hardly adsorbed at all (less than can be detected by neutron reflection). Actual values at pH 6.5 and 0.02 wt % are 0.9, 0.6, and 0 mg m^{-2}, respectively, for the three copolymers, at pH 7.5 and 0.02 wt % the values are 2.7, 0.8, and 0 mg m^{-2}, and at pH 8.5 and 0.02 wt % they are 2.1, 0.8, and 0 mg m^{-2}. These values of the surface coverage have exactly the same trends as the surface tension in the corresponding conditions. Overall, the surface activity seems to depend on the same feature that determines the cmc in these copolymers.

Astafieva et al. have explained the decrease of the cmc with electrolyte block length in the long ionic block regime in terms of the theoretical model of Ronis.[12] They argue that the crowding of polyelectrolyte around the micellar core leads to locally high polyelectrolyte and counterion concentrations which screen the charge on the polyelectrolyte and that increasing the length of the polyelectrolyte block will enhance this screening. Since the screening is known to reduce the solvent quality of water for polyelectrolytes it leads to a decreased solubility of the polyelectrolyte chain and will therefore lower the cmc. Since the increased surface activity of our copolymers correlates with a lower cmc we might expect a similar mechanism to operate at the air/water interface. However, the structure of the layer in the low concentration regime does not seem consistent with such a picture. Bearing in mind that neutron specular reflection gives no information about the lateral distribution in the monolayer, there are two possible structures of the monolayer in the low coverage regime; MMA and DMAEMA blocks may mix uniformly or the MMA block may form islands surrounded by DMAEMA. In either case the observations require that each block is approximately half immersed in the underlying aqueous phase. Neither structure conforms with the mechanism that lowers the cmc suggested by Astafieva et al.

The DMAEMA block itself is expected to be surface active.[13] When uncharged it is not very soluble in water, and this alone will make DMAEMA homopolymer surface active unless it is more or less completely ionized. Furthermore, even the isolated monomer residue is expected to be amphiphilic when charged. Thus, it is not surprising that, at low coverage, both MMA and DMAEMA fragments are adsorbed in a relatively thin layer at the surface rather than adopting the anchor−buoy structure. One apparently awkward aspect of the structure is that a significant number of DMAEMA residues are out of the water, and yet they should be significantly ionized. Any ionized residues out of the water would have to be in the form of ion pairs because of the low dielectric constant of air. Such a structure has also been observed by Li et al.[14] for a layer of spread copolymer. Israels et al.[15] have shown that for weak grafted polyelectrolyes the high potential that would occur if the whole polyelectrolyte fragment were ionized leads to progressive suppression of ionization on moving through the layer to the grafting point. Since the MMA and un-ionized DMAEMA would be expected to be miscible, this would mean that the outer layer (next to air) should be a mixed layer of MMA and un-ionized DMAEMA residues with the residual partially ionized DMAEMA block forming a diffuse layer extending into the aqueous subphase. The balance of stability between an anchor−buoy structure and the present one of a partially collapsed polyelectrolyte block may also be sensitive to the factors identified by Khokhlov and Kramarenko,[16] which cause “supercollapse” of polyelectrolyte gels, where the dehydrated phase of the polyelectrolyte becomes more stable when the mean dielectric constant of the medium (average of water and polymer) is no longer able to sustain separated charges as the charge density increases. Neither of these factors explains why the layer is so uniform (in terms of MMA and DMAEMA distributions) nor why the copolymer with the smallest number of MMA units is the most surface active (the approximate number of MMA: DMAEMA residues in the three copolymers is 12:48, 23:48, and 44:100 in order of decreasing surface activity).

We now turn to the higher concentration regime with the layered surface structure. As before, we note that the neutron experiment is not sensitive to lateral inhomogeneity so the MMA block in the structured layer may or may not be uniform across the surface. The resemblance of the cross section of the layered structure to a flattened micelle suggests that the MMA-rich layer consists of MMA cores separated by DMAEMA-rich regions. In our previous results on the 70%−10K copolymer the transition between the simple monolayer and the layered structure appeared to be sharp and to be suppressed if the charge density on the DMAEMA became too high, unless this was compensated by the screening produced by adding electrolyte. These conclusions are not changed significantly by the results on the present two copolymers except that the lower cmc of the 80%−10K copolymer is paralleled by a greater tendency of the layered structure to form at the surface. Thus, in this case, the layered structure is formed not only at a pH of 6.5, at which the 70%−10K copolymer does not form a micellar layer, but even at a pH of 2.5 where the DMAEMA would be expected to be fully ionized.[6,7] The enhancement of the stability of the layered structure with added electrolyte is most marked for the 70%−20K copolymer where significant adsorption only seems to occur for the layered structure and, apart from pH 8.5, only when salt is present.

There are trends in the effects of pH and ionic strength on the structure of the layer that support a mechanism involving suppression of ionization as predicted by Israels et al. associated with miscibility of unionized DMAEMA and MMA blocks. Thus, at high concentrations, the pH hardly affects adsorption of the 80%−10K copolymer and, at a bulk concentration of 0.2 wt %, similar surface coverages are obtained at pH 8.5, 7.5, and 6.5, but the structure of the layer changes. This can be seen from the main MMA-containing layers. At pH 7.5 and 8.5, there are two significant contributions, one about 8−10 Å thick containing volume fractions of about 0.4 MMA, 0.45 DMAEMA, and 0.15 water (note that lateral inhomogeneity may mean that the water and MMA are not in the same region) and the other is about 15 Å thick and contains 0.10 to 0.15 MMA with 0.2 DMAEMA and 0.6−0.7 water (see Table 4). However, at pH 6.5 the MMA is best fitted by two layers, of total thickness 14 Å with a mean fraction of 0.36 MMA, 0.51 DMAEMA, and only 0.10 water. This is a more compact and dehydrated adsorbed layer; i.e., the DMAEMA and MMA blocks seem to be better segregated. At pH 2.5, although the total amount adsorbed is less, the segregation is also much clearer. A similar pattern is observed for the 70%−10K copolymer, although the effects are less clear because the amount adsorbed varies more strongly with pH. In comparison with the 80%−10K copolymer the MMA core of the 70%−10K copolymer is slightly narrower in distribution, although the effect must be comparable with the fitting errors. For the 70%−20K copolymer the large width of the MMA distribution along the surface normal direction suggests that mixing of the MMA and DMAEMA is an important factor in the behavior of the system.

The addition of electrolyte has quite different effects on the three copolymers. If there is significant charge density on the DMAEMA block, addition of electrolyte should lower the cmc and enhance the surface adsorption because of the additional screening of the charges on the DMAEMA block. This effect is clear for the 70%−10K copolymer at low concentrations, where the amount adsorbed increases markedly and the layered surface structure occurs at copolymer concentrations where previously only simple monolayer adsorption occurred. Similar effects are observed for the 70%−20K copolymer, which only adsorbs significantly in the presence of electrolyte, and for the 80%−10K copolymer. However, when electrolyte is added to a solution that is above the cmc the effects are different for each copolymer. Thus, for the 80%−10K copolymer addition of electrolyte increases the surface tension and decreases the surface excess. This effect is particularly striking for the 0.2 wt % solutions at pH 6.5 and 7.5 where addition of 0.1 M NaCl increases the surface tension (Figure 1) and decreases the adsorbed amount by 20−25% (Table 3). This is quite unlike any effects of added electrolyte on small molecule surfactants. On the other hand, addition of electrolyte to the 70%−10K copolymer affects the system differently according to the pH; at pH 7.5 it increases the surface tension but actually decreases the surface excess. For the 70%−20K copolymer, addition of electrolyte always increases the surface excess. Israels et al.[15] have predicted that addition of electrolyte may, in some circumstances, enhance the ionization of a weak polyelectrolyte block because the electrostatic screening reduces the surface potential. Thus, there are two effects that could act in opposite directions, but it is difficult to understand why the balance of these effects, or any others, should be so sensitive to composition and type of surface structure. A further interesting comparison is of the structure of the three copolymer layers at concentration 0.2 wt %, pH 7.5, and 0.1 M NaCl, where the surface coverages are similar for the three copolymers and are 65−75% of the highest coverages observed (Figure 3b). The similar coverage shows that addition of electrolyte at this copolymer concentration tends to equalize the surface activity, which is what would be expected if addition of electrolyte screens the charged interactions. The thicknesses of the three layers under these conditions are in the ranges 19−25, 25−35, and 55−60 Å respectively for the 80%−10K, 70%−10K, and 70%−20K copolymers and examination of the layer structures shows that the diffuseness of the adsorbed layer is closely paralleled by the diffuseness of the MMA distribution in the layer, showing that the two blocks become less distinct as the electrolyte screening becomes more effective.

There are several features of the surface behavior of the poly(DMAEMA-*b*-MMA) diblock copolymers which are quite different from small molecule surfactants, notably the formation of a layered structure, with the hydrophobic block not forming the outer layer, and the effect of electrolyte on adsorption of this layered structure. This apparently anomalous behavior and the highly collapsed state of the copolymer in the adsorbed micelle regime raise the question as to whether the surface layer in this regime is a true equilibrium structure. This cannot be answered with certainty. As noted earlier, the surface tension changes with time over the first few minutes of a measurement and all the values shown in this and the two previous papers were taken after 20 min. At this point the surface tension is moderately stable and reproducible (±0.5 mN m^{-1}). Minor fluctuations do occur, and it must be remembered that the ring method of measuring surface tension involves dynamic phenomena to which copolymer surface tension measurements may be sensitive. Overall the surface tension behavior indicates that the surface is at equilibrium whether at low or high concentrations. The neutron reflection measurements were found to be reproducible to a high level of accuracy and to be totally independent of time over periods ranging from about 10 min to several hours. Nonequilibrium behavior is often associated with lack of reproducibility and fluctuations over long time scales. Since neither of these effects was observed in the neutron experiment, it seems probable, though not certain, that all of the structures presented in this and the previous two papers are equilibrium structures. Recent work by Creutz et al.[17] on the exchange rate of copolymers between micelles and bulk solution using poly(DMAEMA-*b*-sodium acrylate), where DMAEMA is the hydrophobic block, find that it is much slower than for small molecule micelles with an exchange rate of the order of 10^{-3} s^{-1}. This corresponds to one polymer molecule exchanging per micelle every 17 min and a typical micelle contains 10−20 polymer molecules. This should be sufficient to allow equilibrium to be established in the neutron experiments.

There may be be several patterns of behavior concealed in the extensive number of measurements we have made on this diblock copolymer. However, although there has been a recent surge of theoretical models relating to the aggregation of polyelectrolytes and diblocks containing polyelectrolyte (e.g. refs 12, 15, 16, 18−23), not only are there some major experimental features still unexplained but also little attention has been given to the nature of the adsorbed layer structure at a planar interface. In particular, there seems to be no current model that explains our central observation that layered structures are adsorbed at copolymer concentrations above the cmc.

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