Alternating Multiblock Amphiphilic Copolymers of PEG and Tyrosine-Derived Diphenols. 2. Self-Assembly in Aqueous Solution and at Hydrophobic Surfaces

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ABSTRACT: We present an initial study of the surfactant behavior of a new family of strictly alternating multiblock polyethers referred to as poly(DTR-PEG ether)s. These polymers consist of blocks of poly(ethylene glycol) (PEG) and desaminotyrosyl-tyrosine alkyl esters (DTR, where R = ethyl, hexyl, dodecyl). The PEG and DTR units are linked through an ether bond, resulting in a polymer with an amphiphilic backbone and regularly spaced, hydrophobic hydrocarbon pendent chains. The associative behavior of poly(DTR-PEG ether)s in dilute aqueous solutions was investigated spectrophotometrically by the benzoylacetoanilide enolization method and by static light scattering. The critical aggregation concentration for all investigated polymers was found to be lower than the detection limit of the spectrophotometric method used (estimated at 10^{-5} M of PEG-DTR blocks). The aggregation numbers measured by static light scattering were dependent on polymer composition. The adsorption of two polymers on a model graphite surface from aqueous solution was evaluated by X-ray photoelectron spectroscopy. The shape of the adsorption isotherms was dependent on the ability of the polymer to form multichain aggregates in solution.

Introduction

Surfactant behavior is generally related to the ability of an amphiphilic molecule to form micellar aggregates in solution and to adsorb at surfaces. Both of these aspects are relevant to numerous applications such as cleaning, wetting, emulsifying, dispersing, and foaming.[1−3] Amphiphilic copolymers play an important role in the stabilization of colloidal particles in inks, paints, coatings, and magnetic storage materials.[4] PEG-based nonionic surfactants, such as Pluronics, PEG−ε-caprolactone amphiphilic block copolymers, and PEG−alkyl mono- and diethers and esters have been studied from a physicochemical point of view, and their interactions with biological systems have been explored.[5]

The phase behavior of poly(ethylene glycol)-*b*-poly(ethylethylene)[6] and poly(ethylene glycol)-*b*-polybutadiene[7] copolymers in water has been studied extensively. These studies showed that the distribution and the spacing of the hydrophobes along the chain play a role in the inter- and intramolecular aggregation of polymeric surfactants.[8] In continuation of these studies, alternating copolymers of PEG and L-lysine derivatives with long hydrophobic pendent chains have been synthesized in this laboratory, and their solution behavior has been studied in detail.[9] As expected, they exhibit a low critical aggregation concentration (cac) and have the ability to provide a hydrophobic environment for poorly water-soluble molecules. In a continuing effort to explore novel biocompatible surfactants with high structural versatility, we designed a template for a polymeric surfactant based on PEG and the diphenolic tyrosine derivatives DTR (Figure 1). These new polymers are referred to as poly(DTR-PEG ether)s, and their synthesis and characterization have been described previously (see part 1 of this series of publications).[10] The poly(DTR-PEG ether)s included in this study have alkyl pendent chains comprising 2−12 carbons and PEG blocks of molecular weight 2000−8000. We report the results of an initial study of the surfactant behavior of poly(DTR-PEG ether)s. In particular, we assess the ability of these polymers to aggregate in dilute aqueous solutions and to adsorb at hydrophobic interfaces. This investigation provides the basis for more detailed structural studies focusing, for instance, on aggregate size and shape and on adsorbate self-organization.

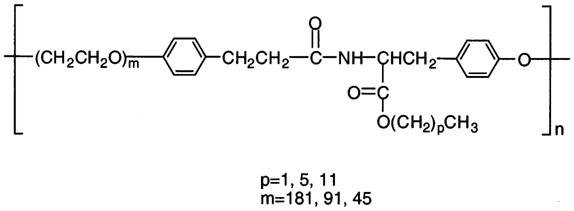

Figure 1. Structure of poly(DTR-PEG ether)s. DTR = desaminotyrosyl-tyrosine alkyl ester (see also Special Note on Nomenclature).

Special Note on Nomenclature

We use three-digit abbreviations to designate the various polymer compositions. The first letter of this three-digit code indicates the alkyl pendent chain "R" linked to the DTR unit, where DTR stands for desaminotyrosyl-tyrosine alkyl ester (Figure 1). The three pendent chains "R" used are E = ethyl, H = hexyl, and D = dodecyl. The second digit is a number indicating the molecular weight of the PEG units, and the third digit is always the letter "K" to indicate that the molecular weight of the PEG units is measured in kDa (i.e., 2K = PEG_{2000}). Therefore, E2K stands for poly($DTE-PEG_{2000}$ ether).

Materials and Methods

Synthesis and Structural Characterization of Poly(DTR-PEG ether)s. The synthesis of poly(DTR-PEG ether)s

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Table 1. Molecular Masses and Root-Mean-Square Radii of Gyration (R_g) of Poly(DTR-PEG ether)s by GPC and Light Scattering

polymer	M_w (Da) GPC in DMF/LiBr	M_w (Da) light scattering	chains per aggregate	N_R[a]	R_g[b] (nm) light scattering	R_g[c] (nm) max	R_g[d] (nm) min
E2K	21 000	20 300	1	8.6	<10	71	19
H2K	33 000	69 000	2	28.5	60 ± 6	94	20
D2K	22 500	302 200	13	121	55 ± 2	77	21
D4K	31 000	214 700	7	48	45 ± 3	89	29
D8K	65 000	426 600	6.5	50	58 ± 11	106	42
E8K	88 000	87 100	1	10	21 ± 5	109	42

[a] N_R = number of hydrophobes/aggregate. Estimated from the light scattering M_w. [b] Root-mean-square radii of gyration determined by light scattering. [c] Root-mean-square radii of gyration predicted through eq 2 for random-coiled PEGs with same M_w as the GPC M_w of the copolymer. [d] Root-mean-square radii of gyration calculated for flowerlike micelles. Core radius is given by eq 4. Corona thickness is calculated through eq 2 for PEGs of same molecular weight as the blocks in the copolymer.

and their characterization, including the determination of molecular weights by GPC, have been reported in part 1 of this series of publications.[10]

Static Light Scattering. Static light scattering measurements were performed on a miniDawn apparatus (Wyatt Technology Corp., Santa Barbara, CA) operated in batch mode, with a laser wavelength of 690 nm and detectors at 41°, 90°, and 139°. The refractive index increment was determined on a Waters 410 refractometer operating at 930 nm. Refractive index increments reported in the literature[11] for PEGs in water show less than 3% variation with wavelength. Since the molar mass determination in batch mode is a function of the second power of the refractive index increment, the difference in operating wavelength of the light scattering apparatus and the refractometer results in less than 6% error. Weight-average molecular weights and root-mean-square radii were calculated using the Zimm equation. Each refractive index and light scattering determination was performed with five concentrations between 10^{-4} and 10^{-3} g/mL. Refractive index increments of 0.133−0.135 were found for all poly(DTR-PEG ether)s, so that an average value of 0.134 was used in the Zimm equation for all polymers. This value is in close agreement with literature values for PEG[11] and for poly(PEG-lysine stearylamide).[9]

Solubilization of Benzoylacetoanilide. The enolization of benzoylacetoanilide in aqueous poly(DTR-PEG ether)s solutions was observed spectrophotometrically by measuring its absorption at 320 nm.[12] A 10 mg/L solution of benzoylacetoanilide (99+%, Acros Organics) was prepared by dissolving the compound in water of 18.0−18.3 MΩ/cm resistivity (Nanopure Infinity ultrafiltration apparatus from Barnstead/Thermolyne Corp.). Dissolution was complete after stirring at room temperature for 72 h. A 2% (w/w) stock solution of each polymer was prepared in the benzoylacetoanilide solution with gentle shaking overnight. A weighed amount of benzoylacetoanilide solution was loaded into a 1 cm quartz UV cell. The cell was inserted in the spectrophotometer (Perkin-Elmer Lambda 3B UV−vis spectrophotometer), and 5−20 μL aliquots of polymer stock solution were added successively, taking a reading of the absorption at 320 nm after equilibration after each addition (maximum 2 min). The reference cell was loaded with benzoylacetoanilide solution. No phase separation was observed at the polymer concentration ranges used in the experiment.

X-ray Photoelectron Spectroscopy (XPS). Sample Preparation. Graphite foil of 0.5 mm thickness (Alpha Aesar, MA) was used as the substrate. Disks of 10 mm diameter were cut and soaked in polymer solution for 2 h at room temperature with gentle shaking. Polymer solutions of 10^{-4}−0.3% (w/w) were prepared in Nanopure water of about 18 MΩ/cm resistivity. Larger volumes of solution were used for higher dilutions, so as to ensure the presence of an excess polymer at all concentration levels. 250 mL was prepared at the 10^{-4}% (w/w) concentration level by dissolving 1−2.5 mg of polymer in water. 30 mL solutions of 10^{-3}% (w/w) polymer concentration and 3 mL at the 0.1% (w/w) level were prepared gravimetrically. The solutions were shaken at room temperature for at least 3 h prior to use. After the disks were soaked in the polymer solution, they were rinsed four times in 3 mL of Nanopure water with gentle stirring and then dried for 2 days at 0.1 mmHg and room temperature prior to XPS analysis.

XPS analysis was performed on a Kratos XSAM-800 spectrometer equipped with a nonmonochromatized Mg Kα X-ray source (1253.6 eV) operating at an anode voltage and an emission current of 12 kV and 8 mA, respectively. For core-level measurement, a pass energy of 20 eV was used. These parameters resulted in an instrumental resolution of about 0.8 eV. The base pressure in the analysis chamber was about 10^{-9} Torr. Spectra were recorded at a 90° takeoff angle.

Results and Discussion

Static Light Scattering. Static light scattering was used to determine the weight-average molecular weights and root-mean-square radii of poly(DTR-PEG ether)s in water. The molecular weight of nonassociated chains relative to PEG standards was determined by GPC.[10] The light scattering molecular weight also reflects interchain aggregation since higher values than the ones obtained by GPC indicate the formation of multimolecular aggregates. The average number of hydrophobes per aggregate N_R, reported in Table 1, was estimated under the strong assumption that all aggregates contain the same number of hydrophobes. Thus, N_R is given by

$$N_R = M_w(\mathrm{ls})/M_r \quad (1)$$

where M_w(ls) is the weight-average molecular weight determined by light scattering and M_r is the molecular weight of one PEG-DTR block.

No significant difference was observed between the light scattering and GPC molecular weights of E2K and E8K, indicating that the chains are nonassociated in both water and DMF/LiBr. Intermolecular association, on the other hand, was observed for all other polymers, with a remarkably large N_R of 121 for D2K. This value is much larger than the N_R reported for poly(PEG-lysine stearylamide) ($N_R = 12-14$),[9] hydrophobically modified ethoxylated urethanes ($N_R = 20$),[13] and $C_{12}-EO_{200}-C_{12}$ ($N_R = 31$).[14] An increase in molecular weight of PEG within the DTD copolymers series leads to a decrease in N_R. The root-mean-square radii of gyration of the poly(DTR-PEG ether)s in water are listed in Table 1. No concentration dependence of the root-mean-square radii was observed (data not shown), in contrast to what was previously reported for the PEG−lysine-stearylamide copolymers.[9] The values of the root-mean-square radii of gyration can be used in order to obtain information on the structure of the aggregates in water. PEG exhibits an unusually large size in water compared to other linear polymers in good solvents, such as polystyrene in toluene.[15] This is because random-coiled PEG is highly swollen by tightly packed water of hydration. A correlation has been established[15] between the radius of gyration of random-coiled PEG (determined by static light scattering) and its molecular weight:

$$R_g = 0.215 M_w^{0.583} \qquad (2)$$

The micelles formed by a PEG-containing polymeric surfactant are usually represented as a compact hydrophobic core surrounded by a PEG corona.[8] The PEG loops crowd each other in the vicinity of the micellar core, so that they stretch outward, resulting in a larger coronal thickness compared to the dimensions of the unperturbed chain. If the assumption is made that the volumes of the hydrophobic cores for the poly(DTR-PEG ether)s are only determined by the length of the alkyl pendent chains, their values can be estimated through the Tanford equation[16]

$$V_C = N_R(27.4 + 26.9n) \times 10^{-3} \quad \text{nm}^3 \qquad (3)$$

and the radii are calculated on the basis of the estimated volumes:

$$R_C = \sqrt[3]{3V_C/4\pi} \qquad (4)$$

On the basis of eqs 2−4, we can set an upper and lower limit for the radii of gyration of the poly(DTR-PEG ether)s. The upper limit is the radius of a random-coiled PEG of same molecular weight as the poly(DTR-PEG ether) (column 7 in Table 1). The lower limit is the sum of the radius of the hydrophobic core and of a random-coiled PEG of same molecular weight as the PEG blocks in the copolymer (column 8 in Table 1). The observed radii (column 6 in Table 1) are significantly smaller than predicted for random-coiled, hydrated PEGs, and their values do not increase with overall molecular weight. It can therefore be concluded that poly(DTR-PEG ether)s are not random coils and that they assume a compact conformation in water. In the case of E2K and E8K, the observed radii of gyration are even smaller than predicted for a flowerlike micelle with a random-coiled PEG corona. In fact, the radius of gyration of E2K could not be determined because the polymer is an isotropic scatterer (<10 nm). It is possible that DTE copolymers, which have a very short pendent chain, behave as backbone amphiphiles, rather than comb structures, and that the hydrophobic domains formed by self-organization of the backbone contain a large amount of dehydrated PEG. The release of water of hydration provides a strong entropic advantage to the micellization process and could account for the small sizes observed by light scattering. On the other hand, the radii of gyration of all the other polymers are larger than the values predicted for a flowerlike micelle with a random-coiled corona. These large values may result from the stretching of PEG due to crowding effects in the corona in the vicinity of the hydrophobic core.[8] Crowding effects also account for the lower N_R values of D4K (N_R = 48) and D8K (N_R = 50) with respect to D2K (N_R = 121).[8]

Solubilization of Benzoylacetoanilide. The keto−enolic equilibrium of benzoylacetoanilide is strongly sensitive to solvent polarity.[17] Only the ketonic form is present in water, with a λ_{max} of 250 nm. The equilibrium is shifted toward the enolic form (λ_{max} = 320 nm) in less polar solvents or in the hydrophobic core of the micelles formed by nonionic surfactants in water.[12] Figure 2 shows the absorbance at 320 nm, which is proportional to the concentration of enolic benzoylacetoanilide, as a function of the molar concentration of hydrophobic DTR units. This choice of units allows for a direct comparison of polymers with different molecular weights of the PEG-DTR block. A steeper increase in absorbance at 320 nm indicates a faster increase in hydrophobic environment for the probe, as the polymer is added. Low molecular weight surfactants exhibit a break in the curve at a concentration that corresponds to the critical micellar concentration.[12] Such a discontinuity was not observed for the poly(DTR-PEG ether)s, suggesting a cac below the detection limit of this spectrophotometric method (0.01 absorbance), estimated at 10^{-5} M for D4K. The concentration of enolic benzoylacetoanilide increases linearly with polymer concentration at a rate that depends not only on polymer composition but also on the number of hydrophobes per chain. The curve obtained with D2K is about 3 times steeper than that of MeO-PEG2000-DTD. In fact, D2K, which contains several hydrophobes/chain, can provide a micellar environment through aggregation of fewer chains than its monofunctional equivalent. The length of the hydrophobic pendent chain in the PEG2000 copolymer series (Figure 2a) has the greatest influence on the rate of increase in benzoylacetoanilide enolization with polymer concentration. Smaller differences are observed between DTE, DTH, and DTD copolymers with PEG4000 and PEG8000. Interestingly, the PEG4000 series exhibits a smaller slope than both the PEG2000 and the PEG8000 series. This observation indicates that simple considerations of hydrophobic−hydrophilic balance are not sufficient in order to explain the associative behavior of the poly(DTR-PEG ether)s. Light scattering data

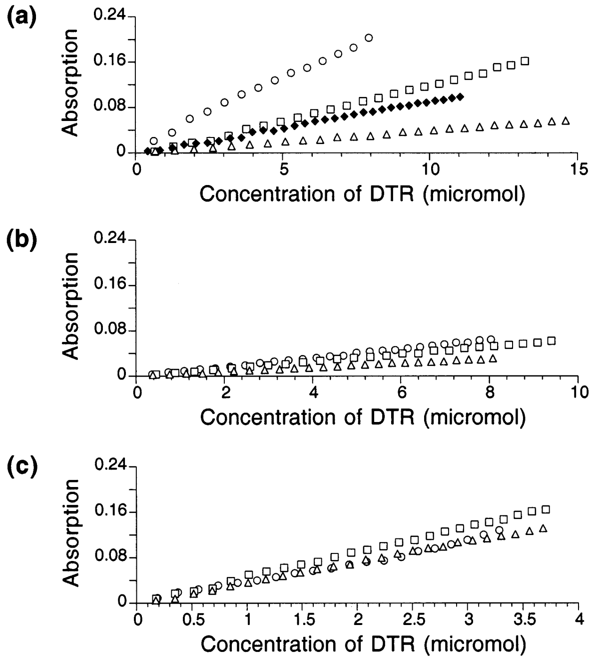

Figure 2. Adsorption at 320 nm of solutions of benzoylacetoanilide and poly(DTR-PEG ether)s. The signal is proportional to the concentration of enolic benzoylacetoanilide. (a) Copolymers containing blocks of PEG2000: D2K (○), H2K (□), E2K (△). For comparison, data for a model representing a single repeat unit of D2K (MeO-PEG2000-DTD) are also included (◆). (b) Copolymers containing blocks of PEG4000: D4K (○), H4K (□), E4K (△). (c) Copolymers containing blocks of PEG8000: D8K (○), H8K (□), E8K (△).

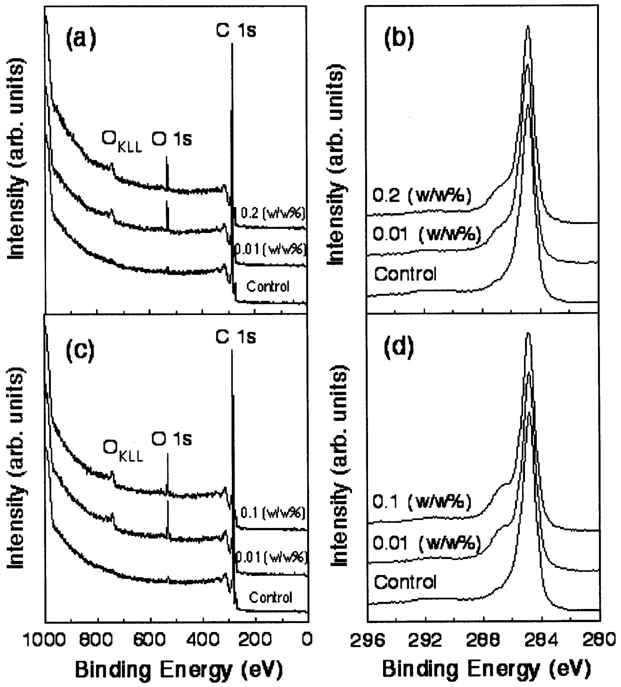

Figure 3. XPS traces of graphite treated with D2K and E8K polymer solutions at different concentrations and with water (control). D2K-treated graphite at 0.01% and 0.2% (w/w): survey scan (a) and C 1s peak (b). E8K-treated graphite at 0.01% and 0.1% (w/w): survey scan (c) and C 1s peak (d).

Table 2. Surface Composition of Graphite Substrates Following Adsorption Experiments as a Function of Polymer Concentration

sample	polymer concn (w/w%)	polymer concn (mM)	O (at. %)	O/C (at. ratio)
D2K	3.0×10^{-1}	1.2	6.24	0.067
	5.0×10^{-2}	2.0×10^{-1}	6.41	0.069
	1.0×10^{-2}	4.0×10^{-2}	5.87	0.063
	8.3×10^{-3}	3.3×10^{-2}	4.73	0.050
	7.0×10^{-3}	2.8×10^{-2}	4.87	0.051
	3.3×10^{-3}	1.3×10^{-2}	5.11	0.054
	6.4×10^{-4}	2.6×10^{-3}	3.35	0.035
	4.8×10^{-4}	1.9×10^{-3}	4.99	0.053
E8K	1.0×10^{-1}	1.2×10^{-1}	6.32	0.067
	3.0×10^{-2}	3.6×10^{-2}	6.54	0.070
	1.0×10^{-2}	1.2×10^{-2}	6.24	0.067
	1.2×10^{-3}	1.4×10^{-3}	4.81	0.051
	7.8×10^{-4}	3.3×10^{-4}	3.45	0.036
	4.0×10^{-4}	4.8×10^{-4}	3.21	0.033
no polymer	0	0	1.60	0.016

(Table 1), discussed in the previous section, indicate that differences in polymer composition influence the number of hydrophobes per aggregate and possibly the presence of dehydrated PEG in the hydrophobic core, such as in the case of E2K and E8K. In fact, the estimated N_R of D8K is about 50 times smaller than that of D2K. This can be explained in terms of an altogether different aggregate structure (cylindrical or bicontinuous as opposed to flowerlike) or by assuming that the contacts between alkyl chains in D8K are looser than in D2K, so that a large part of the hydrophobic core consists of dehydrated PEG. The latter interpretation is also consistent with the very similar slopes (Figure 2c) obtained for copolymers of PEG8000. In short, the plots in Figure 2 show the net effect of aggregation, and a more detailed study of aggregate structure is needed to provide a full interpretation of these results.

Adsorption on Graphite. While D2K is the most hydrophobic member of the series of poly(DTR-PEG ether)s considered in this study, E8K is the least hydrophobic. These two polymers were therefore selected as models to study the adsorption behavior on a hydrophobic graphite surface. Light scattering data discussed above showed that these two polymers differ in their ability to self-assemble into micellar aggregates in aqueous solution. Specifically, D2K exhibits a tendency to form multimolecular aggregates, while E8K chains are isolated in water. Figure 3 shows the XPS survey scans of D2K and E8K at 0.01% and 0.2% (w/w) concentration of polymer in solution. Controls consist of graphite disks treated with pure water. The XPS spectra were normalized to the intensity of the C 1s peak at 285 eV. Even though oxygen is theoretically absent in graphite, an oxygen peak (corresponding to 1.5% atomic) was observed on the control sample. Surface contamination by oxygen is common for carbon-based materials such as carbon fibers and graphite,[18−20] and our experience suggests that oxygen is still detected even after pumping overnight under high vacuum at 150 °C. The appearance of a shoulder in the C 1s peak at the high binding energy side of the main peak (Figure 3) confirms the adsorption of the polymer on the graphite surface. This shoulder is only present in the spectra of samples treated with poly(DTR-PEG ether) solutions and is attributed to the large number of C−O bonds in the polymer. Table 2 summarizes the atomic concentration in oxygen and C/O ratio derived from XPS analysis. It is worth noting that the intensity of the N 1s peak is too low for accurate quantitation, due to the small number of nitrogen atoms per molecule.

The following form of the Langmuir equation[21] was used to fit the data and construct the adsorption isotherms:

$$\frac{C}{\Gamma} = \frac{1}{\Gamma_m b} + \frac{C}{\Gamma_m} \qquad (5)$$

where C is the polymer concentration in solution, Γ is the polymer concentration at the graphite surface, Γ_m is the amount of polymer at the surface in the completed monolayer, and b is a constant. Since D2K and E8K have different molecular weights, and the molecular weights of their blocks also differ, it is convenient to express C in millimoles of PEG-DTR blocks per liter. XPS allows the determination of relative elemental concentrations over a thickness of ≈60 Å from the sample surface, and therefore the absolute values of Γ and Γ_m cannot be measured by XPS. In the present work, the assumption is made that the surface concentration of polymer at the surface (Γ) is proportional to the relative atomic concentration of oxygen (column 4 in Table 2). The Γ_m values obtained through fitting the XPS data with eq 5 can only be used to compare the maximum coverage of a substrate with different solutes.[22] The PEG blocks in E2K and D2K crystallize in the dry state[10] so that the structure of the surface layer after drying can be assumed to be independent of the degree of coverage. On the basis of this assumption, it is acceptable to consider that the measured C/O ratios are proportional to the degree of surface coverage.

The values for $1/\Gamma_m$ and b were determined by linear regression of C/Γ vs C according to eq 5, using the data in Table 2. The plots are shown in Figure 4. The same value of $1/\Gamma_m$ was obtained for both D2K (0.156) and E8K (0.157). It can therefore be concluded that the amount of PEG at monolayer saturation is the same for

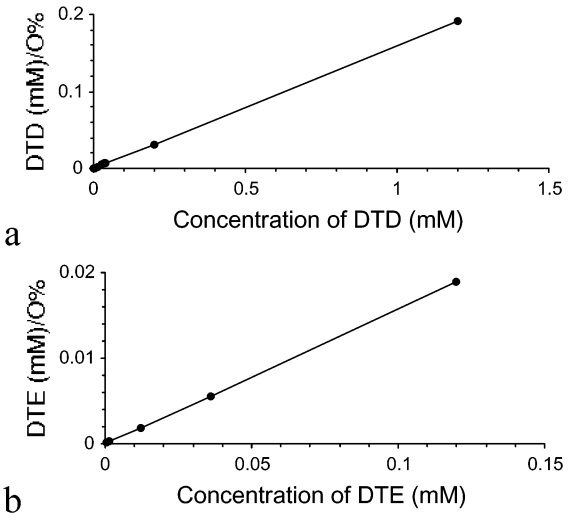

Figure 4. Plots of polymer concentration in solution/surface concentration vs polymer concentration in solution for D2K (a) and E8K (b). Polymer concentration in solution is expressed in millimoles of PEG-DTR blocks per liter. Surface concentration of polymer is expressed as oxygen atomic percent composition. By extrapolation according to eq 5, the intercept yields the value of $1/\Gamma_m$, and b is then obtained from the slope. D2K: $1/\Gamma_m = 0.156$, $b = 312$. E8K: $1/\Gamma_m = 0.157$; $b = 3935$.

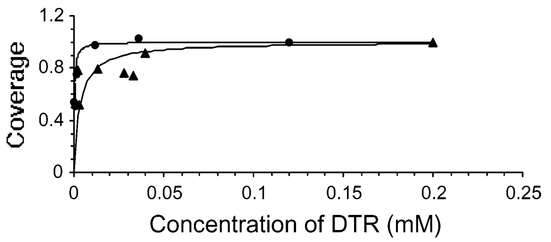

Figure 5. Experimental and calculated adsorption isotherms of D2K (▲) and E8K (●). Coverage is calculated as Γ/Γ_m. Data points for D2K at higher concentrations have been omitted in order to expand the low concentration region. The curves have been calculated from eq 5 using the values of b obtained from the slopes of Figure 4.

D2K and E8K and is determined by PEG packing. On the other hand, the surface concentration of DTR blocks is approximately 4 times higher for D2K than for E8K, since the molecular weight of PEG in D2K is 4 times lower than in E8K.

Figure 5 shows a comparison between the coverage (Γ/Γ_m) calculated from experimental O% atomic (Γ) and the Langmuir isotherm calculated by substituting the extrapolated values of b and Γ_m into eq 5. The very good agreement for E8K between the experimental data and the calculated curve shows that adsorbate–adsorbate interactions are negligible with respect to substrate–adsorbate interactions.[23] For D2K, the experimental data exhibit two plateaus, the first occurring in the range of 2.55–13.2 μM in terms of PEG-DTD blocks. This deviation from the calculated curve has been observed with aggregating nonionic surfactants.[24] When a critical concentration value is reached, the growth of the aggregates in solution becomes competitive with surface adsorption, and no increase in surface coverage is observed. Coverage increases again upon further increase of solution concentration, until monolayer saturation is reached. Adsorbate–adsorbate interactions cannot be ruled out in the case of D2K, although we cannot provide direct evidence to support or contradict this possibility. In fact, the XPS technique forced us to observe dry, semicrystalline samples,[10] where some aspects of adsorption (e.g., adsorbate–adsorbate self-association during adsorption) are possibly erased by crystallization in the dry state.

Conclusions

The surfactant behavior of the amphiphilic polymers poly(DTR-PEG ether)s has been characterized with respect to the ability of these polymers to form aggregates in aqueous solution, to provide a hydrophobic environment to a hydrophobic probe, and to adsorb on a hydrophobic graphite surface. Static light scattering measurements indicate that poly(DTE-PEG ether)s with a short ethyl pendent chain do not form multichain aggregates in water. They rather assume a compact conformation, possibly with partial dehydration of the PEG component. Poly(DTR-PEG ether)s bearing longer pendent chains, on the other hand, form multichain aggregates with aggregation numbers that are strongly dependent on polymer composition. An unusually large N_R or 121 has been estimated for D2K, the most hydrophobic polymer of the series. All polymers were shown to provide a hydrophobic environment to the benzoylacetoanilide probe. The most hydrophobic (D2K) and the most hydrophilic (E8K) polymers of the series have been studied with respect to their adsorption behavior on the model surface graphite. It has been shown that E8K, which does not form multichain aggregates in water, exhibits a simple Langmuir-type adsorption isotherm. D2K, on the other hand, exhibits two plateaus in its adsorption isotherm. The first plateau can be ascribed to the competition between aggregate growth in solution and surface adsorption. The second plateau of D2K, corresponding to monolayer saturation, overlaps with the plateau of E8K. It is postulated that the surface coverage at monolayer saturation is determined by PEG packing only and that the density of adsorbed hydrophobes increases with decreasing molecular weight of the PEG block.

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References and Notes

(1) Schick, M. J. In *Surfactants Science Series*; Marcel Dekker: New York, 1987; Vol. 23.
(2) Sharma, R. In *ACS Symposium Series*; American Chemical Society: Washington, DC, 1995.
(3) Parfitt, G. D.; Rochester, C. H. *Adsorption from Solution at the Solid/Liquid Interface*; Academic Press: London, 1983.
(4) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: London, 1983.
(5) Harris, J. M. *Poly(ethylene glycol) Chemistry, Biotechnical and Biomedical Applications*; Plenum Press: New York, 1992.
(6) Hajduk, D. A.; Kossuth, M. B.; Hillmyer, M. A.; Bates, F. S. *J. Phys. Chem. B* **1998**, *102*, 4269–4276.
(7) Zheng, Y.; Won, Y.-Y.; Bates, F. S.; Davis, H. T.; Scriven, L. E.; Talmon, Y. *J. Phys. Chem. B* **1999**, *103*, 10331–10334.
(8) Borisov, O. V.; Halperin, A. *Langmuir* **1995**, *11*, 2911–2919.
(9) Heitz, C.; Pendharkar, S.; Prud'homme, R. K.; Kohn, J. *Macromolecules* **1999**, *32*, 6652–6657.
(10) d'Acunzo, F.; Kohn, J. *Macromolecules* **2002**, *35*, 9360–9365.
(11) Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*; John Wiley and Sons: New York, 1999.

(12) Shoji, N.; Ueno, M.; Meguro, K. *J. Am. Oil Chem. Soc.* **1978**, *55*, 297−299.

(13) Yekta, A.; Xu, B.; Duhamel, J.; Adiwidjaja, H.; Winnik, M. *Macromolecules* **1995**, *28*, 956−966.

(14) Persson, K.; Bales, B. L. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2863−2870.

(15) Devanand, K.; Selser, J. C. *Macromolecules* **1991**, *24*, 5943−5947.

(16) Tanford, C. *The Hydrophobic Effect*; Wiley: New York, 1973.

(17) Naoum, M. M.; Saad, G. R. *J. Solution Chem.* **1988**, *17*, 67−76.

(18) Wang, Y.-Q.; Zhang, F.-Q.; Sherwood, P. M. A. *Chem. Mater.* **1999**, *11*, 2573−2583.

(19) Kinoshita, H.; Umeno, M.; Tagawa, M.; Ohmae, N. *Surf. Sci.* **1999**, *440*, 49−59.

(20) Diaz, J.; Anders, S.; Zhou, X.; Moler, E. J.; Kella, S. A.; Hussain, Z. *J. Electron Spectrosc. Relat. Phenom.* **1999**, 101−103.

(21) Baillie, C. A.; Watts, J. F.; Castle, J. E. *J. Mater. Chem.* **1992**, *2*, 939−944.

(22) Watts, J. F.; Leadley, S. R.; Castle, J. E.; Blomfield, C. J. *Langmuir* **2000**, *16*, 2292−2300.

(23) Giles, C. H.; Smith, D.; Huitson, A. *J. Colloid Interface Sci.* **1974**, *47*, 755−765.

(24) Clunie, J. S.; Ingram, B. T. In *Adsorption from Solution at the Solid/Liquid Interface*; Rochester, C. H., Ed.; Academic Press: London, 1983; pp 105−152.

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