

Influence of Ionic Surfactants on the Aggregation of Poly(Ethylene Oxide)–Poly(Propylene Oxide)–Poly(Ethylene Oxide) Block Copolymers Studied by Differential Scanning and Isothermal Titration Calorimetry

Rodrigo Cardoso da Silva,^{†,‡} Gerd Olofsson,^{*,†} Karin Schillén,^{†,§} and Watson Loh[‡]

Physical Chemistry I, Center for Chemistry and Chemical Engineering, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden, and Instituto de Química, Universidade Estadual de Campinas, Caixa Postal: 6154, CEP: 13083-970, Campinas, SP, Brazil

Received: July 16, 2001; In Final Form: November 1, 2001

The interaction between three triblock copolymers of poly(ethylene oxide) and poly(propylene oxide), $\text{EO}_n\text{PO}_m\text{EO}_n$, and the ionic surfactants sodium dodecyl sulfate, SDS, and hexadecyltrimethylammonium chloride, CTAC, has been studied in dilute aqueous solution using differential scanning calorimetry, DSC, and isothermal titration calorimetry. The length of the PPO block was the same in all three copolymers (68–69 PO units), and the lengths of the PEO groups varied from 5, 20 and 97 EO units. The copolymers are denoted L121, P123, and F127 in order of increasing PEO block size. In dilute aqueous solution P123 and F127 aggregate to form micelles, while the most hydrophobic polymer, L121, forms aggregates which, eventually, separate to give a liquid crystalline phase. Differential scanning calorimetry was used to follow the effect on the copolymer aggregates upon addition of ionic surfactants. Addition of SDS to P123 and L121 increased the temperature for aggregation, but polymer aggregates still formed in 6.2 mmol/L SDS. The effect is different on F127 where after an initial decrease in the aggregation temperature, the peak in the DSC curve flattens out and disappears at low SDS concentration, as has been observed previously. The addition of CTAC to solutions of the three polymers does not change significantly the aggregation temperature, but the transition peak decreases and eventually disappears in 2–3 mmol/L CTAC. The prominent feature of calorimetric titration curves at 40 °C from consecutive additions of surfactant to polymer solution is a well-defined exothermic peak that stems from the disruption of the polymer micelles/aggregates and accompanying hydration of the PPO block. The beginning of the peak indicates the start of binding of the surfactant to the polymer aggregates, and after the end of the peak, the titration curves indicate binding to polymer unimers. At 40 °C, about 20 SDS molecules per polymer chain are required to disarrange the P123 micelles and L121 aggregates, while about 10 suffice to disrupt the F127 micelles. The same amount of CTAC, about 10 molecules per polymer chain, destroys the aggregates of all three polymers.

Introduction

Water-soluble poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), PEO–PPO–PEO, triblock copolymers are nonionic surfactants with a wide range of applications. In aqueous solutions, the copolymers show a complex solubility and aggregation behavior that has been the topic of many fundamental studies (see, e.g., ref 1). Many PEO–PPO–PEO copolymers form micelles above a critical micelle concentration, CMC. A notable feature is the strong temperature effect on the self-association in that a small temperature increase may result in a dramatic decrease in CMC. This temperature, the critical micellar temperature CMT, is a useful micellar parameter. The self-aggregation arises from the limited and temperature dependent solubility of the PPO block, which gives aggregates with a hydrophobic, essentially water-free, core surrounded by the more hydrophilic and hydrated PEO blocks. In many applications of the triblock copolymers, ionic surfactants are present, which is likely to influence the properties of the

polymers. The surfactants will preferentially bind to the PPO block and will interfere with the polymer aggregation already at low concentrations. The interaction between nonionic, linear homopolymers, and ionic surfactants in aqueous solution has been extensively studied.^{2–6} Among more recent papers of relevance for the present work are refs 7 and 8. Systems containing micelle-forming block copolymers and ionic surfactants are less studied. The interaction between sodium dodecyl sulfate, SDS, and two PEO–PPO–PEO triblock copolymers with on the average 30 PO units and 26 and 156 EO units, respectively, was studied by NMR shift and fluorescence decay measurements.⁹ This study dealt primarily with the self-association of SDS in the presence of PEO–PPO–PEO unimers up to the saturation of the polymer by surfactant. The basic features of the interaction of SDS with the block copolymers were the same as those with homopolymers. The influence of the ionic surfactants SDS and DTAB (dodecyltrimethylammonium bromide) on the self-aggregation of F127 ($\text{EO}_{97}\text{--PO}_{69}\text{--EO}_{97}$) has been studied by Hecht et al. using differential scanning calorimetry, static light and small-angle neutron scattering, and temperature jump measurements.^{10–12} A detailed study of the F127–SDS system at low concentrations has been carried out recently by Li et al.^{13,14} This study included

* To whom correspondence should be addressed. E-mail: Gerd.Olofsson@fkem1.lu.se.

[†] Lund University.

[‡] Universidade Estadual de Campinas.

[§] E-mail: Karin.Schillen@fkem1.lu.se.

electromotive force (emf) measurements of the surfactant ion activity leading to binding isotherms both below and above the CMT.

We have extended the study of the effect of ionic surfactants on the self-aggregation of PEO–PPO–PEO triblock copolymers to include three copolymers with the same length of the PPO block, 68–69 PO units, but with varying PEO block length, 5, 20, and 97 EO units, and using one anionic, SDS, and one cationic surfactant, CTAC (hexadecyltrimethylammonium chloride). We have used differential scanning calorimetry to follow changes in the aggregation of the copolymers with the addition of ionic surfactants and isothermal titration calorimetry to get information about the copolymer–surfactant interaction. Detailed information about the binding of surfactant to polymer can be obtained from isothermal titration calorimetric measurements.^{7,8} We observe distinct differences in the effect of the surfactants on the aggregates of the different PEO–PPO–PEO copolymers, indicating a subtle interplay between properties of the triblock copolymers and the surfactants on the copolymer aggregation.

Experimental Section

Materials and Sample Preparation. Three block copolymers of the average compositions EO₅PO₆₈EO₅, EO₂₀PO₆₉EO₂₀, and EO₉₇PO₆₈EO₉₇, denoted L121, P123, and F127, were gifts from BASF and used without further treatment. The nominal molar masses are 4400, 5750, and 12 600 g/mol, and the cloud point of 1 wt % solution is 14, 90, and >100 °C, respectively.¹⁵ Sodium dodecyl sulfate, SDS, (BDH, Analar Biochemical quality), and hexadecyltrimethylammonium chloride, CTAC (Tokyo Chemical Industries, 95%), were used as received. At 25 °C, the CMC of SDS is 8.4 mmol/L, and the enthalpy of micelle formation ΔH_{mic} (at the CMC) is -0.20 kJ/mol.¹⁶ ΔH_{mic} for SDS is 4.7 kJ/mol at 15 °C and -7.5 kJ/mol at 40 °C.¹⁶ The CMC of CTAC is 1.25 mmol/L and $\Delta H_{\text{mic}} = -1.7$ kJ/mol at 25 °C, and ΔH_{mic} is estimated to be -15.5 kJ/mol at 40 °C.¹⁷ Stock solutions of 1 wt % of polymers and 10 wt % of surfactants were prepared by weight using analytical grade water from a Millipore Milli-Q filtration system. The polymer solutions were prepared 24 h before use and stored in a refrigerator.

Differential Scanning Calorimetry, DSC. Measurements were made using a MicroCal MC-2 high-sensitivity differential scanning calorimeter (MicroCal, Northampton, MA.) in the temperature range 5–80 °C with a scanning rate of 54 °C/h. It uses 1.2 mL total-fill cells with the sample solution in one cell and water in the reference cell. The cold polymer solutions were quickly transferred to the DSC cell kept at 5 °C that was the starting temperature. The samples were kept in the cell at 5 °C for 20 min before the temperature scan was started. After the scan was finished at 80 °C (or at 60 °C for the pure L121 samples), the temperature was decreased to 5 °C and the sample left to equilibrate for 20 min before a second scan was made. The second scan gave for all samples a curve that was identical to the curve for the first scan. Origin (Version 2.9) Software for DSC Data Collection and Analysis supplied by the manufacturer was used for instrument control, data acquisition, and analysis. We have used the temperature for the peak maxima T_m to characterize the transitions. T_m is between 2 and 3 °C higher than the onset temperature that represents more closely the critical micellization temperature CMT.¹⁴

Isothermal Titration Calorimetry. The titration calorimetric measurements were made using the 2277 TAM Thermal Activity Monitor system (Thermometric AB, Järfälla, Sweden).

The experiments consisted of series of consecutive additions of concentrated surfactant solution to the calorimeter vessel initially containing 2.7 g of polymer solution or pure water. The liquid samples were added in portions of 2–10 μL from a gastight Hamilton syringe through a thin stainless steel capillary tube. A microprocessor-controlled motor-driven syringe drive was used for the injections. The fast titration procedure was used with six minutes between each injection.¹⁸ All experiments were repeated twice and the reproducibility was good.

Results and Discussion

To characterize the aggregation of the PEO–PPO–PEO triblock copolymers, we have made DSC measurements on solutions with polymer content varying between 0.05 and 1.00 wt % and evaluated the transition temperatures and enthalpies. All systems show a well-defined endothermic transition peak. The effect of SDS and CTAC on the aggregation in 0.1 wt % P123 and L121 solutions and in a 1.00 wt % solution of F127 was studied by DSC. Isothermal titration calorimetric measurements were made of addition of concentrated surfactant solution to polymer solutions at 40 °C where the copolymers are in aggregated form. Measurements have also been made at 15 and 25 °C.

DSC of Pure Polymer Solutions. The results of DSC measurements on solutions of P123 with varying polymer content are summarized in Figure 1a. The curves are normalized to a common start at 10 °C and are shown on a common scale of the ordinate axis. The peaks at low polymer content were enlarged for the area determinations, which give the transition enthalpies. Values for the transition temperature T_m , represented by the temperature at the peak maxima and enthalpy change ΔH_{tr} are shown in Table 1. The transition temperature decreases with increasing polymer content in accordance with the endothermic enthalpy change. Results for F127 in the same concentration range are shown in Figure 1b and in Table 1. The DSC traces for the two micelle-forming copolymers look similar but the transition temperature of F127 is slightly higher and the transition enthalpy significantly lower than those for P123. DSC measurements on F127 were extended to 10 wt % solutions, and the enthalpy of micelle formation ΔH_{tr} was derived from the variation of CMT with polymer concentration c :¹⁹

$$\Delta H_{\text{tr}} = R \frac{d \ln c}{d(1/\ln \text{CMT})} \quad (1)$$

Values of CMT were calculated as the temperature at the intersection of the extrapolated linear ascent of the peak and the baseline. A least-squares fit of the values in the range 0.050–10.00 wt % gave an enthalpy value of 348 ± 20 kJ/mol. Values of CMT varied between 20.91 and 37.61 °C and the derived value of ΔH_{tr} refers to the mean temperature in the interval. This value is in full agreement with values derived from the DSC measurements and shows that the micelle formation process is the same over the whole concentration range. The sample used by Hecht and Hoffmann¹⁰ gave a significantly higher micelle formation enthalpy of 459 kJ/mol, while a much lower value of 253 kJ/mol was derived for an unpurified sample by Alexandridis et al.²⁰ Also for other PEO–PPO–PEO block copolymers varying values of micellization enthalpies are found in the literature.^{21,22} Our results indicate that it may be not so much the method but the composition of the samples used that gives the variation.

The transition for L121 is more complex, as the shoulder on the left-hand side of the peaks in Figure 1c indicate. Traces at

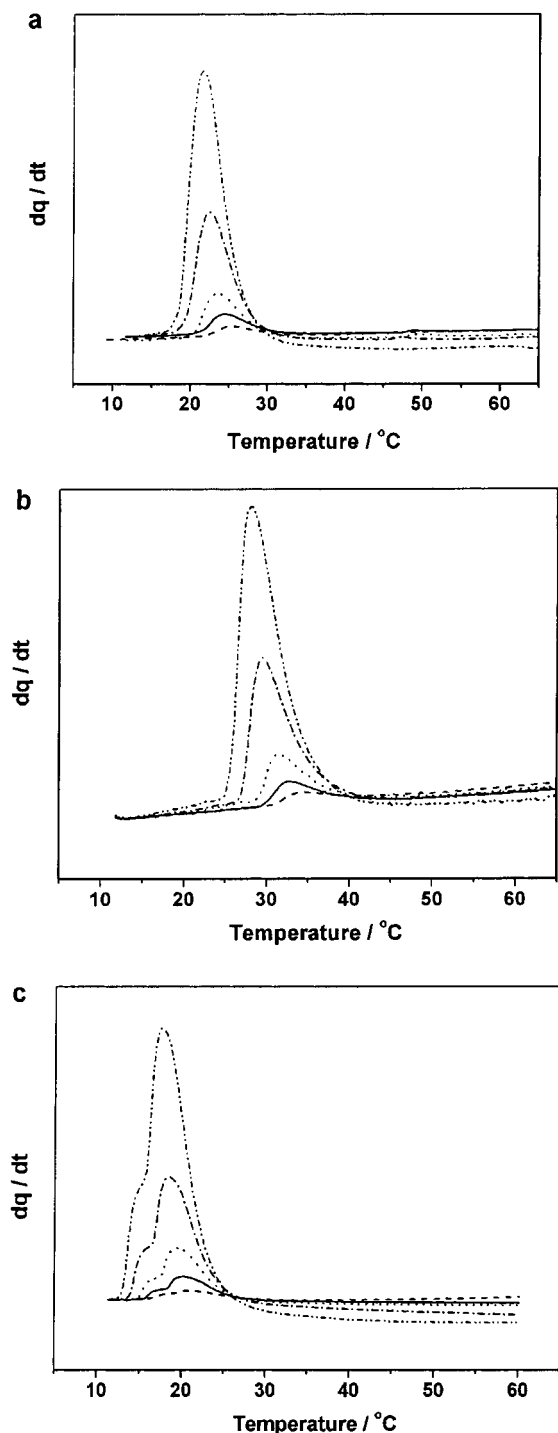


Figure 1. DSC curves for (a) P123, (b) F127, and (c) L121 in pure water: ---- 0.05 wt %, — 0.1 wt %, 0.2 wt %, -.-.- 0.5 wt %, and - - - - - 1.0 wt %.

lower scanning rate looked the same. The solutions became cloudy at the transition temperature as L121 phase separates to give a dispersion of liquid crystalline aggregates in the unimer solution.²³ The dilute dispersions are fairly stable; for instance, the 0.1 wt % used in the titration calorimetric experiments could stand at room temperature for a couple of days without any sign of macroscopic phase separation. The composite peak in the DSC traces of L121 indicates that the aggregation to give the dispersion of the liquid crystalline phase proceeds in at least two steps. However, the enthalpy change for the aggregation process is the same as for the formation of the P123 micelles, which indicates that the change in hydration of the PPO block

TABLE 1: Enthalpy of Transition ΔH_{tr} and Transition Temperature T_m for the Aqueous Copolymers P123, F127, and L121

W_p (wt %)	P123		F127		L121	
	ΔH_{tr} (kJ mol ⁻¹)	T_m (°C)	ΔH_{tr} (kJ mol ⁻¹)	T_m (°C)	ΔH_{tr} (kJ mol ⁻¹)	T_m (°C)
0.050	400	25.4	357	29.1	420	20.8
0.100	419	24.4	354	27.7	461	20.2
0.200	451	23.7	359	26.5	493	19.4
0.500	466	22.5	360	24.1	460	18.4
1.000	477	21.6	366	28.0	491	17.7

accompanying aggregation gives the dominant enthalpy contribution. From calorimetric measurements, the enthalpy of solution of liquid PPO 400 in water at 25 °C was determined to -164 ± 4 J/g.²⁴ This will give an enthalpy of solution of a PPO block containing 68 units of -650 kJ/mol. Thus, it appears reasonable to assume that change in hydration from hydrated PPO blocks in the unimers to give aggregates where the PO units have lost most of the hydration water gives the large endothermic aggregation enthalpies.

EO_nPO_mEO_n and SDS. The interaction between the block copolymers and SDS has been studied at one polymer concentration namely 0.100 wt % for P123 and L121 and 1.00 wt % for F127. We choose the higher concentration for F127 because a detailed study on more dilute solutions has recently been reported.^{13,14} The results of DSC measurements on 0.1 wt % solutions of P123 containing between 0.100 and 6.20 mmol/L of SDS are shown in Figure 2a. Measurements were made at four intermediate concentrations, but for the sake of clarity, the curves are not included in the figure. The curve for P123 in pure water is included for comparison. The peaks shifted to higher temperature as the SDS concentration increased, and they became skewed, but there was only a moderate decrease of the area. Micelle formation of P123 takes place even in the presence of 6.2 mmol/L SDS, but the temperature is increased to 62 °C. Thus, the interaction with SDS appears to make the copolymer more hydrophilic and increase the micelle formation temperature.

We have made titration calorimetric measurements at 40 °C, where the polymer will be in the form of micelles at the start of the titration (see Figure 2a). Figure 2b shows the results of addition of 10 μ L portions of 10 wt % SDS solution to the P123 solution. Included in the figure is the curve observed when starting with pure water. The insert shows the curve observed when the additions were decreased to 2.5 μ L SDS solution. The first three small injections gave endothermic enthalpy changes of about 6.5 kJ(mol SDS)⁻¹, which is close to the expected enthalpy of demicellization of SDS and indicates that the added SDS micelles break up to give monomers in solution. At about 1 mmol/L SDS, a large exothermic peak started that extended to about 5 mmol/L SDS. From Figure 2a, we can conclude that at this SDS concentration the P123 micelles are completely dispersed. The exothermic peak can be ascribed to the break up of the P123 micelles and the accompanying hydration of PO units. Upon further addition of SDS, the observed enthalpies decreased slowly to join the dilution curve in water at about 18 mmol/L. We consider this to be the saturation concentration, and above this concentration, added SDS micelles are only diluted. A closely similar behavior was observed for the SDS—polyNIPAM microgel system.²⁵ At 40 °C, the microgel latex exists as compact particles containing only approximately two water molecules per isopropyl group. Addition of SDS to a microgel suspension gave a large exothermic peak in the titration curve where the microgel took up water and swelled. Addition

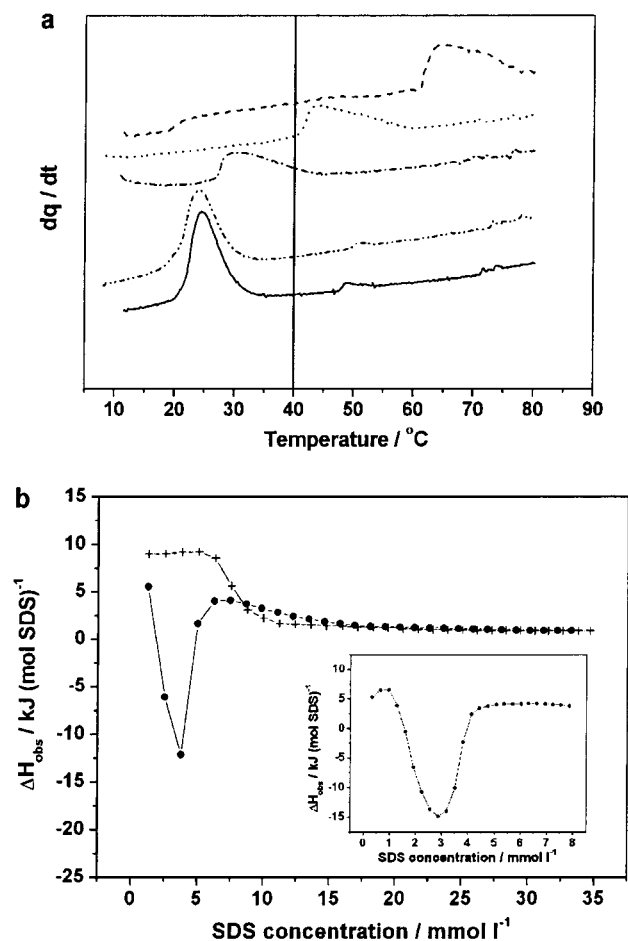


Figure 2. P123–SDS. (a) DSC curves for P123 (0.1 wt %) and SDS: — pure water, — · — · — 0.1 mmol/L, — · — · — 1.6 mmol/L, · · · · 3.1 mmol/L, — — — 6.2 mmol/L. (b) Calorimetric titration curves at 40 °C: 10 μ L portions of 10 wt % SDS in 2.70 mL of 0.1 wt % P123. Insert: 2.5 μ L portions of 10 wt % SDS in 2.70 mL of 0.1 wt % P123. • SDS–P123; + SDS in pure water.

of SDS to the swollen microgel at 25 °C where the polyNIPAM is fully hydrated showed a typical calorimetric titration curve for a hydrophobic polymer with an initial endothermic peak followed by a shallow exothermic hump before it joined the dilution curve in water. Thus, the hydration of the polyNIPAM is the likely cause for the exothermic effect seen in the curve at 40 °C.

Titration calorimetric experiments at 15 °C of addition of SDS solution to P123 solution (0.1 wt %) gave results closely similar to those observed by Li et al. from titration experiments of consecutive additions of SDS to solutions of F127 unimers.¹⁴ The calorimetric titration curves at 15 °C, where the copolymer is unassociated, show the typical features of a titration curve of a hydrophobic nonionic homopolymer with a pronounced endothermic peak at low SDS concentration followed by what appears to be a slight exothermic hump before merging with the dilution curve in water (see Figure 2a of ref 13 and Figure 6 of ref 14). The binding of SDS to P123 unimers started at about 0.3 mmol/L. SDS binds cooperatively to the PPO units,⁹ and we consider this value to represent also the critical aggregation concentration, CAC, of SDS in the presence of the PPO homopolymer. Due to the limited solubility, measurements on pure PPO have been made on short chain samples with an average molar mass of 1000, which will not behave as a true polymer.²⁶ For instance, CAC of SDS was observed to vary with PPO content so the CAC for longer chain samples can be expected to be significantly lower. It is noteworthy that the

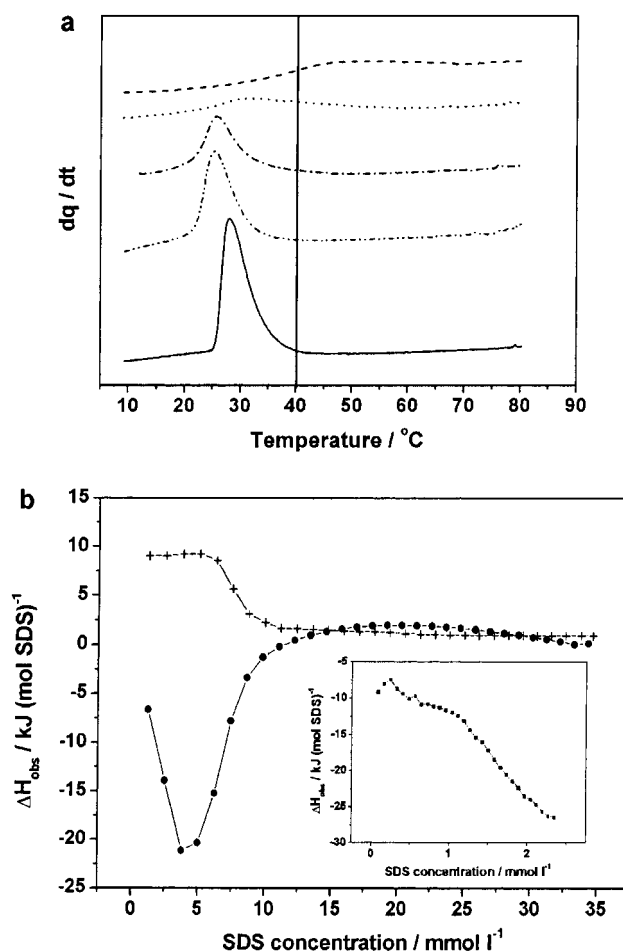


Figure 3. F127–SDS. (a) DSC curves for F127 (1.0 wt %) and SDS: — pure water, — · — · — 0.1 mmol/L, — · — · — 1.6 mmol/L, · · · · 3.1 mmol/L, — — — 6.2 mmol/L. (b) Calorimetric titration curves at 40 °C: 10 μ L portions of 10 wt % SDS in 2.70 mL of 1.0 wt % F127. Insert: 2.5 μ L portions of 2.5 wt % SDS in 2.70 mL of 1.0 wt % F127. • SDS–F127; + SDS in pure water.

binding of SDS to micellar P123 at 40 °C starts at about 1 mmol/L, which is significantly higher than that at 15 °C.

The effect of addition of SDS to a micellar solution of F127 differed from the effect on P123 as seen from Figure 3a, which shows DSC curves for F127 in 1.00 wt % solution at four different SDS concentrations and in water. In this system, T_m initially decreases and then moves upward, but at the same time, the peak flattens out, and at 6.2 mmol/L SDS, only a gentle shift in baseline remains. This behavior is not particular for our batch of polymer but closely reproduces the DSC curves observed by Hecht and Hoffmann, also for 1 wt % solution.¹⁰ The more dilute samples used by Li et al. showed the same behavior.^{13,14} The calorimetric titration curve from addition of SDS (10 wt %) to a 1.00 wt % F127 solution at 40 °C is shown in Figure 3b. The inserted curve was observed when 2.5 μ L portions of 2.5 wt % SDS solution was added. The polymer is in micellar form at the beginning of the titration. Although the concentration of SDS is below 0.10 mmol/L after the first small injection, the observed enthalpy change is exothermic, indicating that SDS binds to the polymer aggregates. Thus, binding to F127 aggregates starts at a much lower surfactant concentration than that for P123 (see Figure 2b). In other respects, the F127 curve is similar to the titration curve for P123 taking into account the difference in polymer content. The exothermic peak extended to about 10 mmol/L. Above this concentration, the polymer–SDS interaction continued but was not followed till the end. It

is noteworthy that the exothermic peak extended well above the SDS concentration where the peak in the DSC curve has vanished (see Figure 3a). However, only cooperative transitions can be observed by DSC, and the disappearance of the copolymer peak indicates that the cooperativity has decreased to the extent that the excess heat capacity from the transition is too low to be registered. The sample can still be in the form of aggregates but with a low aggregation number. We find that the binding of SDS to F127 at 40 °C leads to a rapid loss of cooperative copolymer aggregation as seen in Figure 3a, where only a small bump remains of the polymer peak in 3.1 mmol/L of SDS. However, we observed large exothermic enthalpies at this concentration that indicates that SDS binds to copolymer chains that are aggregated and not unimers. Not until above 10 mmol/L SDS did we observe enthalpies consistent with binding to unimers which indicates that the disintegration of the micelles is gradual.

Calorimetric titration curves of addition of SDS to F127 at 15 °C where the polymer is unassociated show the typical features of a titration of a hydrophobic nonionic homopolymer. We estimate the CAC of SDS to 0.3 mmol/L, in agreement with the value determined from emf measurements in 0.1 wt % solution.¹³ Similar titration curves were observed by Li et al., cf. Figure 2a of ref 13 and Figure 6 of ref 8. Thus, unimers of P123 and F127 show the same CAC, and we conclude that the PPO block determines the aggregation behavior of SDS.

Li et al. have studied the SDS–F127 system in detail using emf, light scattering, and DSC in addition to isothermal titration calorimetry.^{13,14} They determined the binding isotherm of SDS onto F127 at varying concentrations both below and above the micellization temperature. At 35 °C, binding was observed at the lowest measured concentration, 0.01 mmol/L, while at 15 °C, binding started at 0.35 mmol/L in a 0.5 wt % F127 solution; that is, SDS binds much stronger to the F127 micelle than to the unimers. Li et al. observed that small amounts of SDS induced micelle formation of the polymer in solutions close to the micellization temperature.¹⁴ Our results fully agree with their results and conclusions. However, it is interesting to note that P123 with the same length of the PPO block but substantially shorter PEO chains shows a different behavior in the presence of SDS. In pure water, micelles form at 24 °C in 0.100 wt % solution, and addition of SDS increased the micellization temperature regularly without any pronounced decrease in enthalpy. In 6.2 mmol/L SDS, P123 still forms micelles as seen in Figure 2a. In this system, it appears that the interaction with SDS increases the hydrophilicity of the polymer but cooperative aggregation still takes place. In the F127 system, the cooperative aggregation is lost at a much lower SDS concentration even in a 1.00 wt % solution.

Results of DSC measurements on 0.100 wt % solutions of L121 containing varying SDS concentrations are shown in Figure 4a. In this system, the transition peak is shifted upward with increasing SDS concentration like in the P123 system. There is still in 6.2 mmol/L SDS a significant peak starting at about 53 °C. The shoulder on the peak in pure water is resolved in 1.6 mmol/L SDS, and the trace shows two overlapping broad peaks. At higher SDS content, there is the broad skewed peak, as observed in the P123 system. We have made titration calorimetric measurements both at 25 and 40 °C of addition of SDS to L121 solution. According to the DSC curve, all L121 is in aggregated form at 40 °C, while at 25 °C, the transition is not complete. The titration curve at 25 °C is shown in Figure 4b and at 40 °C in Figure 4c. The inserts show the results of titrations with smaller injections. The results are similar when

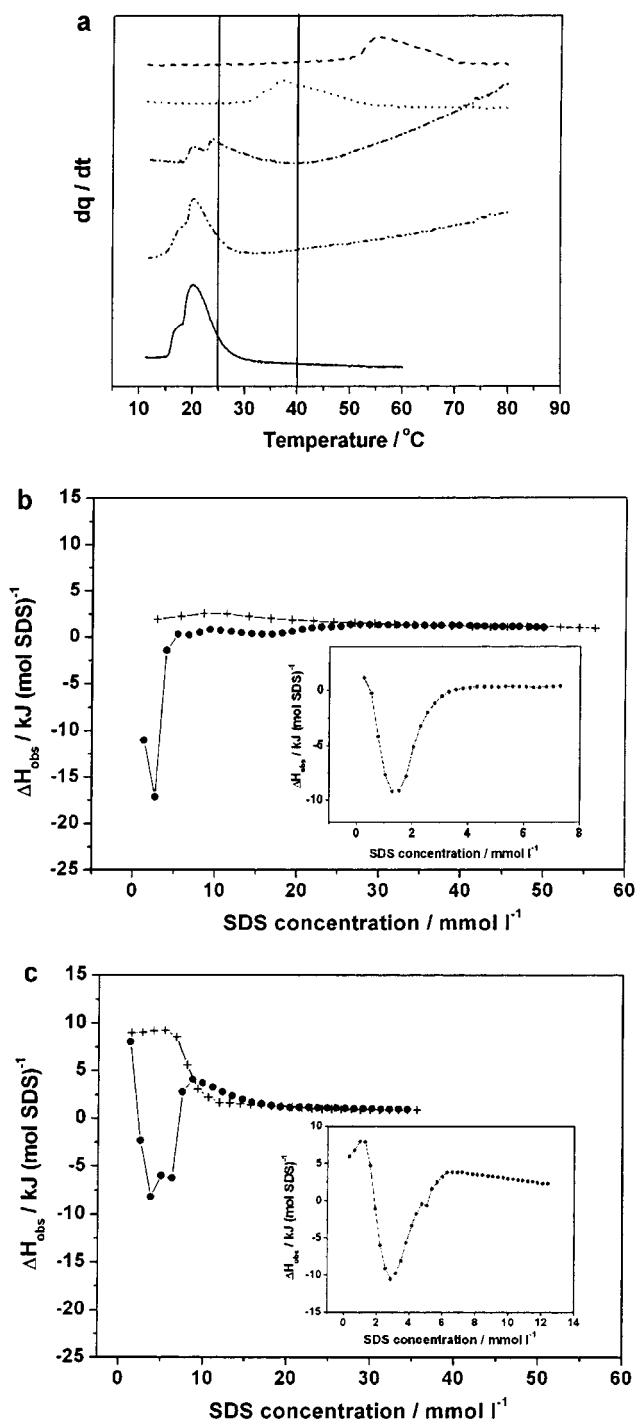


Figure 4. L121–SDS. (a) DSC curves for L121 (0.1 wt %) and SDS: — pure water, - - - - 0.1 mmol/L, - · - · 1.6 mmol/L, · · · 3.1 mmol/L, - - - - 6.2 mmol/L. Calorimetric titration curves at 25 °C (b) and at 40 °C (c): 10 μ L portions of 10 wt % SDS in 2.70 mL of 0.1 wt % L121. Inserts: 2.5 μ L portions of 10 wt % SDS in 2.70 mL of 0.1 wt % L121. • SDS–L121; + SDS in pure water.

taking into account the change in ΔH_{mic} for SDS from -0.2 kJ/mol at 25 °C to -7.5 kJ/mol at 40 °C. However, while at 25 °C the exothermic peaks started already from the first small injection (0.26 mmol/L), SDS did not start to interact with the aggregates at 40 °C until the concentration had reached 1.5 mmol/L. Thus, while SDS starts to bind to micelles of F127 at very low concentrations, below 0.01 mmol/L at 35 °C,^{13,14} SDS does not start to bind to aggregates of P123 and L121 until 1 to 1.5 mmol/L (at 40 °C). The reason for the much stronger binding

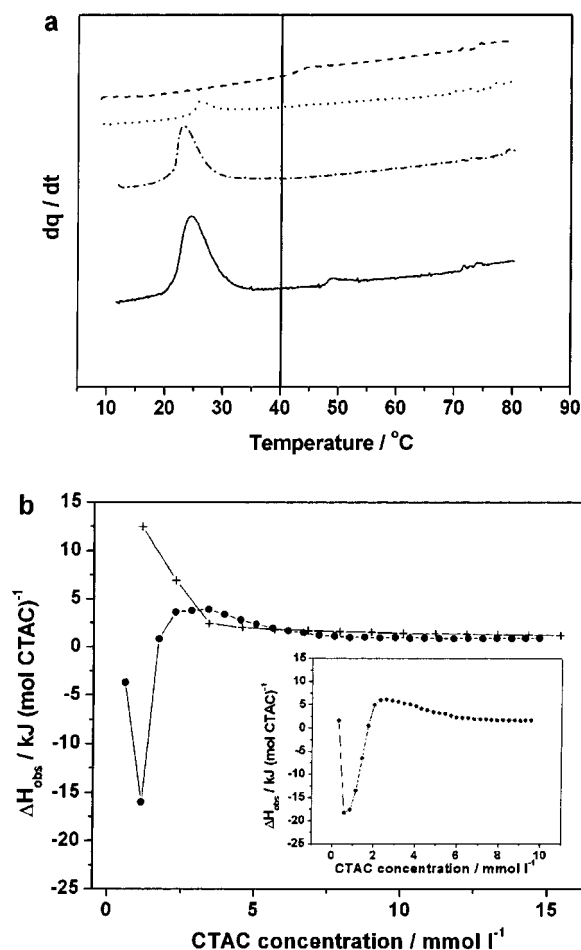


Figure 5. P123–CTAC. (a) DSC curves for P123 (0.1 wt %) and CTAC: — pure water, —•—•— 0.41 mmol/L, ••• 0.82 mmol/L, ---- 1.6 mmol/L. (b) Calorimetric titration curves at 40 °C: 10 μ L portions of 5.0 wt % CTAC in 2.70 mL of 0.1 wt % P123. Insert: 2.5 μ L portions of 10 wt % CTAC in 2.70 mL of 0.1 wt % P123. • CTAC–P123; + CTAC in pure water.

of SDS to F127 is obscure but is probably the reason for the effective disarrangement of the F127 micelles.

$\text{EO}_n\text{PO}_m\text{EO}_n$ and CTAC. The effect of addition of CTAC on the aggregation process of P123 differed from the effect of SDS as seen in Figure 5a, which shows DSC curves of P123 in 0.41, 0.82 and 1.60 mmol/L CTAC solutions. In fact, the response is similar to that of F127 to SDS addition (see Figure 3a). At the lowest concentrations, the peak stayed at about the same temperature but decreased in size, and in 1.60 mmol/L CTAC, only a shift in baseline is seen. The calorimetric titration curves in Figure 5b shows that CTAC start to interact at the lowest concentration of the measurements, 0.2 mmol/L, and the exothermic peak extended to about 2.2 mmol/L, where the disruption of the micelles is complete. At higher concentrations, CTAC continues to interact with the unimers. Addition of CTAC to F127 in solution gave similar effects, as seen in Figure 6a showing DSC traces and in 6b, which summarizes the titration experiments. Here the exothermic peak extends to about 10 mmol/L CTAC, which reflects the higher polymer concentration. The influence of CTAC on the aggregation of L121 showed in the DSC curves as a diminishing peak at constant temperature (see Figure 7a). The exothermic peak in the calorimetric titration curve at 40 °C started at about 0.5 mmol/L CTAC and ended at about 2.5 mmol/L (see Figure 7b). Thus, CTAC influences the aggregation of the three copolymers in the same way and disrupts the aggregates more effectively than SDS. The hydro-

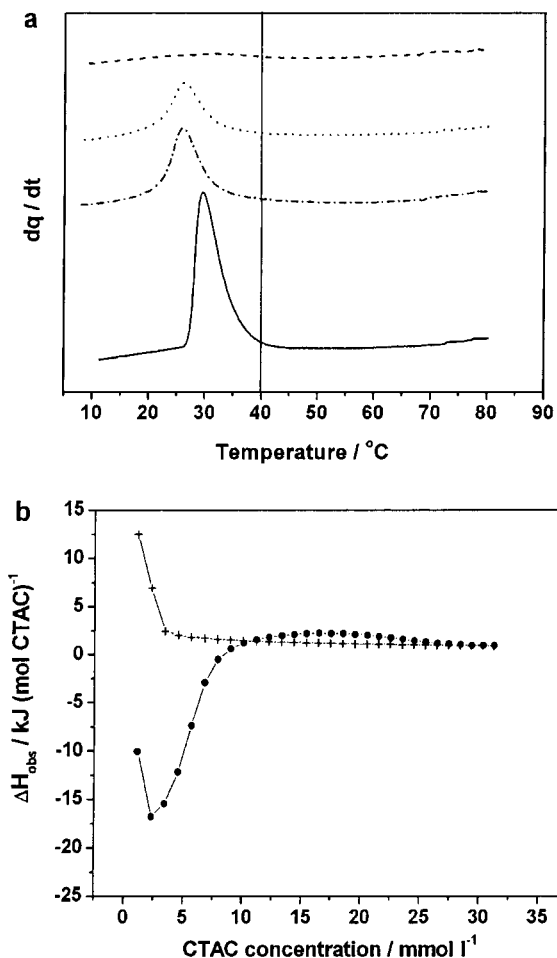


Figure 6. F127–CTAC. (a) DSC curves for F127 (1.0 wt %) and CTAC: — pure water, —•—•— 1.3 mmol/L, ••• 1.6 mmol/L, ---- 3.1 mmol/L. (b) Calorimetric titration curves at 40 °C: 10 μ L portions of 5.0 wt % CTAC in 2.70 mL of 1.0 wt % F127. • CTAC–F127; + CTAC in pure water.

carbon chain in CTAC contains four CH_2 groups more than SDS and, therefore, is significantly more hydrophobic, which may be the reason it is more efficient in destroying the polymer aggregates. It also has a larger headgroup, which may act in the same direction.

Evaluation of the Titration Calorimetric Peaks. The process measured in the calorimetric experiment is the reaction between surfactant micelles $S(\text{mic})$ and polymer aggregates $P(\text{agg})$ to form a surfactant–polymer complex $S\cdot P$:



Dilution of surfactant micelles in water gives monomeric surfactant as long as the total concentration is below the CMC:



Above the CMC, a small enthalpy of dilution of the micellar solution is observed.

In the beginning of a titration into a polymer solution, the surfactant concentration may be below the critical aggregation concentration of the surfactant, CAC, and in these experiments, the observed enthalpy will be close to the demicellization enthalpy.

We can derive an estimate of the reaction enthalpy ΔH_r from the integral under the exothermic peak in the titration calorimetric curves, that is, by summation of the measured ΔH_{obs} in

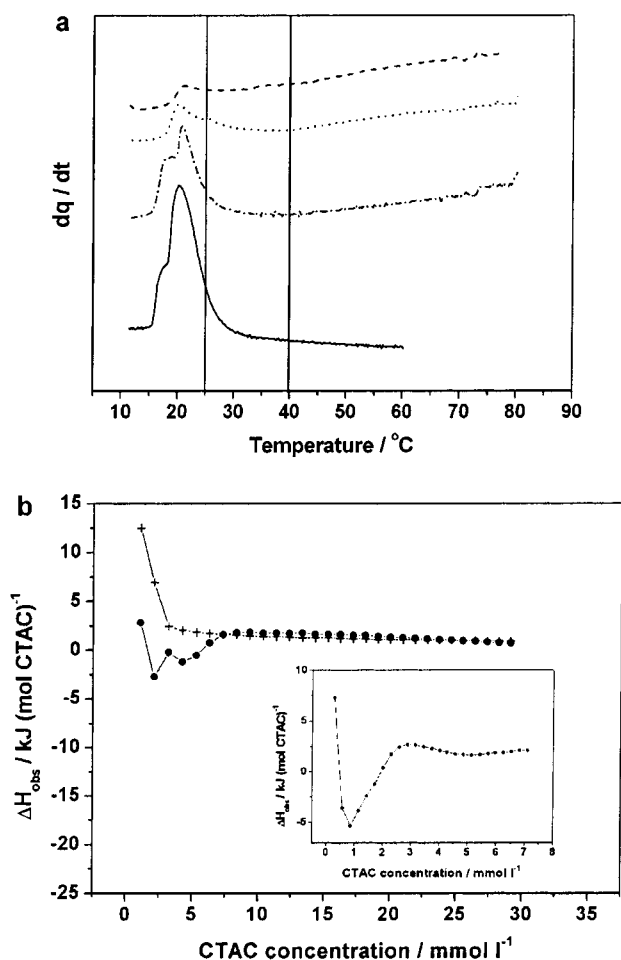


Figure 7. L121–CTAC. (a) DSC curves for L121 (0.1 wt %) and CTAC: — pure water, - - - 0.4 mmol/L, ···· 0.78 mmol/L, ---- 1.3 mmol/L. (b) Calorimetric titration curves at 40 °C: 10 μL portions of 5.0 wt % CTAC in 2.70 mL of 0.1 wt % L121. Insert: 2.5 μL of 10 wt % CTAC in 2.70 mL of 0.1 wt % L121. • CTAC–L121; + CTAC in pure water.

the concentration range of the peak. The peak was assumed to begin when ΔH_{obs} differed significantly from the demicellization enthalpy and end when the observed curve representing ΔH_{obs} leveled off. For instance, the peak in Figure 2b for P123 and SDS begins at 1.0 mmol/L and ends at 5.0 mmol/L. Above this concentration, we assume the polymer aggregates to be fully disintegrated. Results of the evaluation of the exothermic peaks in the experiments shown in Figures 2b–7b are summarized in Table 2. The first column gives the polymer, the second and third column give the amount of polymer and surfactant involved in the reaction, and column four gives the total enthalpy of reaction. The molar enthalpy of reaction, $\Delta H_{\text{r,m}}$, expressed per mole of polymer, is given in column five and per mole of surfactant in column six. Values of $\Delta H_{\text{r,m}}$ indicate the enthalpy changes for the formation of the surfactant-copolymer complexes. The deaggregation of the block copolymer and the interaction between surfactant and unimers give the major contributions to $\Delta H_{\text{r,m}}$. The deaggregation process is exothermic, while the initial interaction between surfactant and unimers is most probably endothermic and larger for CTAC than for SDS.²⁶

The molar ratio of surfactant to polymer at the end of the exothermic peak, that is, at the complete disruption of the polymer aggregates, is shown in column seven. The values for the molar ratio $N_{\text{S}}/N_{\text{P}}$ are surprisingly similar for P123 and L121. It is clear that while about 20 SDS monomers are required to

TABLE 2: Enthalpies of Interaction between Monomeric Surfactants and Aggregated Polymers $\Delta H_{\text{r,m}}$ Derived from Titration Calorimetric Measurements and the Surfactant to Polymer Molar Ratio $N_{\text{S}}/N_{\text{P}}$ at the Complete Break up of the Polymer Aggregates

polymer	N_{P} (μmol)	N_{S} (μmol)	ΔH_{obs} (mJ)	$\Delta H_{\text{r,m}}$ (kJ $\text{mol}^{-1} \text{P}^{-1}$)	$\Delta H_{\text{r,m}}$ (kJ $\text{mol}^{-1} \text{S}^{-1}$)	$N_{\text{S}}/N_{\text{P}}$
SDS						
P123	0.51	11.4	−51.2	−100	−4.5	22
F127	2.14	19.3	−287	−134	−15	9
L121	0.61	14.0	−35.1	−58	−2.5	23
CTAC						
P123	0.51	6.2	−29.5	−58	−4.8	12
F127	2.14	21.9	−219	−102	−10	10
L121	0.61	7.8	−2.0	−3.3	−0.2	13

break up the micelles/aggregates of these polymers at 40 °C, 13 CTAC molecules per polymer chain is enough. Toward micelles of F127, SDS, and CTAC are equally disruptive, and about 10 surfactant molecules per polymer chain are required to disintegrate the micelles. The stronger influence on the F127 micelles is also indicated by the much more exothermic interaction enthalpies that both surfactants exhibit. The results show that there is a delicate balance between the properties of the copolymer and the ionic surfactant that determines how the surfactant will influence the aggregation process leading to disintegration already at low surfactant concentrations or to an increase in the aggregation temperature.

Conclusion

At ambient temperature and in dilute aqueous solution, P123 and F127 aggregate to form micelles, while the most hydrophobic polymer, L121, forms aggregates which, eventually, separate to give a liquid crystalline phase. The copolymers have the same length of the PPO block and aggregate cooperatively at about the same temperature.

Addition of SDS to P123 and L121 increases the temperature for aggregation, but still in 6.2 mmol/L SDS, the copolymers aggregate cooperatively. The effect is different on F127, where already a low SDS content prevents the cooperative aggregation. The calorimetric titration curves at 40 °C from consecutive additions of SDS to the polymer solutions show a characteristic exothermic peak arising from the disintegration of the copolymer aggregates and concomitant hydration of PPO units. The start of the exothermic peak indicates the start of binding of surfactant to the polymer aggregates that occurred at 1 mmol/L of SDS for P123 and L121 but below 0.1 mmol/L for F127. The reason for the stronger binding of SDS to micellar F127 is unknown but probably related to the aggregate structure, as there is no difference in strength of binding to the unimers of P123 and F127 (at 15 °C).

The addition of CTAC to solutions of the three polymers does not change significantly the aggregation temperature, but the aggregates disappear already in 2–3 mmol/L CTAC. At 40 °C, about 20 SDS molecules per polymer chain are required to disarrange the P123 and L121 micelles/aggregates, while about 10 suffice to disrupt the F127 micelles. The same amount of CTAC, about 10 molecules per polymer chain, destroys the aggregates of all three polymers.

Acknowledgment. R. Cardoso da Silva thanks CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) for the fellowship supporting his stay in Lund. This work was supported by the Swedish Natural Science Research Council (NFR).

References and Notes

- (1) Alexandridis, P.; Hatton, T. A. *Colloids Surf. A* **1995**, 96, 1.
- (2) Robb, I. D. In *Anionic Surfactants - Physical Chemistry of Surfactant Action*; Lucassen-Reynders, E. H., Ed.; Surfactant Science Series 11; Marcel Dekker: New York, 1981; p 255.
- (3) Goddard, E. D. *Colloids Surf.* **1986**, 19, 255.
- (4) Saito, S. In *Nonionic Surfactants: Physical Chemistry*; Schick, M. J., Ed.; Surfactant Science Series 23; Marcel Dekker: New York, 1989; p 881.
- (5) Hayakawa, K.; Kwak, J. C. T. In *Cationic Surfactants: Physical: Physical Chemistry*; Rubingh, D. N.; Holland, P. M., Ed.; Surfactant Science Series 37; Marcel Dekker: New York, 1991; p 189.
- (6) Lindman, B.; Thalberg, K. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabhan, K. P., Ed.; CRC Press: Boca Raton, FL, 1993; p 203.
- (7) Olofsson, G.; Wang, G. In *Polymer - Surfactant Systems*; J. C. T. Kwak, Ed.; Surfactant Science Series 77; Marcel Dekker: New York, 1998; p 317.
- (8) Ghoreishi, S. M.; Fox, G. A.; Bloor, D. M.; Holzwarth, J. F.; Wyn-Jones, E. *Langmuir* **1999**, 15, 5474.
- (9) Almgren, M.; van Stam, J.; Lindblad, C.; Li, P.; Stilbs, P.; Bahadur, P. *J. Phys. Chem.* **1991**, 95, 5677.
- (10) Hecht, E.; Hoffmann, H. *Langmuir* **1994**, 10, 86.
- (11) Hecht, E.; Hoffmann, H. *Colloids Surf.* **1995**, 96, 181.
- (12) Hecht, E.; Mortensen, K.; Gradzielski, M.; Hoffmann, H. *J. Phys. Chem.* **1995**, 99, 4866.
- (13) Li, Y.; Xu, R.; Bloor, D. M.; Holzwarth, J. F.; Wyn-Jones, E. *Langmuir* **2000**, 16, 10515.
- (14) Li, Y.; Xu, R.; Couderc, S.; Bloor, D. M.; Wyn-Jones, E.; Holzwarth, J. F. *Langmuir* **2001**, 17, 183.
- (15) *BASF Manual*; 1989; p 25.
- (16) Johnson, I.; Olofsson, G.; Jönsson, B. *J. Chem. Soc., Faraday Trans. 1* **1987**, 83, 3331 and references therein.
- (17) Wang, G.; Olofsson, G. *J. Phys. Chem.* **1995**, 99, 5588 and references therein.
- (18) Bäckman, P.; Bastos, M.; Hallén, D.; Lönnbro, P.; Wadsö, I. *J. Biochem. Biophys. Methods* **1994**, 28, 85.
- (19) Ga-Er, Y.; Peng, Y.; Dalton, S.; Wang, Q.-G.; Attwood, D.; Prine, C.; Booth, C. *J. Chem. Soc., Faraday Trans.* **1992**, 88, 2537.
- (20) Alexandridis, P.; Holzwarth, J. F.; Hatton, T. A. *Macromolecules* **1994**, 27, 2414.
- (21) Beezer, A. E.; Loh, W.; Mitchell, J. C.; Royall, P. G.; Smith, D. O.; Tute, M. S.; Armstrong, J. K.; Chowdhry, B. Z.; Leharne, S. A.; Eagland, D.; Crowther, N. J. *Langmuir* **1994**, 10, 4001.
- (22) Wanka, G.; Hoffmann, H.; Ulbricht, W. *Macromolecules* **1994**, 27, 4145.
- (23) (a) Schillén, K.; Bryskhe, K.; Mel'nikova, Y. S. *Macromolecules* **1999**, 32, 6885. (b) Bryskhe, K.; Schillén, K.; Löfroth, J.-E.; Olsson, U. *Phys. Chem. Chem. Phys.* **2001**, 3, 1303.
- (24) Carlsson, M.; Hallén, D.; Linse, P. *J. Chem. Soc., Faraday Trans.* **1995**, 91, 2081.
- (25) Wang G.; Pelton R.; Zhang J. *Colloids Surf. A* **1999**, 153, 335
- (26) Wang, G.; Olofsson, G. *J. Phys. Chem. B* **1998**, 102, 9276.