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Polymer 41 (2000) 6741–6747

polymer

Surfactant characteristics of random block polyelectrolyte polyester emulsifier (SMTAPE) in aqueous solution and on polystyrene latex particles

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Received 15 April 1999; received in revised form 9 December 1999; accepted 24 December 1999

Abstract

The surfactant characteristics of novel random block polyelectrolyte polyester emulsifiers, SMTAPE, were investigated by analyzing the surface tension of a variety of SMTAPE with different molecular weights and different hydrophilicities in aqueous solution, and also by studying the change of surface tension of polystyrene (PS) latex with increasing SMTAPE emulsifier concentration. The SMTAPE emulsifier was found to lower the surface tension of water by about 15 mN/m at the CMC. All of the investigated SMTAPE emulsifiers show two CMC break points, which were attributed to their broad molecular weight distribution. A Langmuir type adsorption isotherm was observed in this system. The surface area occupied by an SMTAPE molecule on a PS latex particle at 25°C was found to be 187 Å^2 at saturation. The conformation of SMATAPE emulsifier molecule adsorbed on a PS latex particle is thought to be a hydrophobic segment "trains" anchored to the polymer surface. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: CMC; Polymeric emulsifier; Polyester

1. Introduction

Polymeric emulsifiers provide many significant benefits to industrial lattices, such as low foaming, good chemical and mechanical stability, rheology modification and improved quality of coatings [1–4]. Previous investigations have developed block or graft amphiphilic polymeric emulsifiers, polyelectrolytes and polysoap types of emulsifiers [4–11]. Among the various polymeric emulsifiers, polyester-based emulsifier is of paramount concern [2,3,8,12,13]. Previous studies have shown that polyester type emulsifiers possess excellent surface activity. In addition, it was concluded that a decrease of the polyethylene oxide (PEO) length of sulfopolyester emulsifier with polyethylene glycol (PEG), isophthalic acid (IPA) and 5-sulfoisophthalic acid dimethyl ester sodium salt (SSIPM) copolymer structure increases the surface active characteristics [3]. Moreover, the relationship between the CMC and the number of constitutional repeat units *m* of saturated emulsifying polyesters obeys the Shinoda equation [12], in which a high *m* value was found to result in a low CMC. The micellization of polymeric emulsifiers is inherently more complex than that of conventional low molecular weight emulsifiers. Two break points in the plot of surface tension vs emulsifier concentration are often observed [4,14–17]. This has been attributed to the molecular weight polydispersity with the transition region extending approximately one concentration decade [4,14], the quantity of unimers (individual copolymer molecules) [4], or the formation of unimolecular micelles [4,16].

Polymeric emulsifiers adsorb on solid surfaces by the anchoring of hydrophobic segment and leaving hydrophilic segments in water phase [4,18–22]. The conformation of emulsifier molecules adsorbing on a solid surface is thought to be effected by the concentration of emulsifier [4,19,20,23] and the microstructure of emulsifier molecule [21]. Further, it was found in the study of PEO–PPO–PEO block copolymer emulsifier, the whole extended molecule adsorbs on a solid surface at low concentration, and forms hydrophobic segment aggregated micelles at high concentration [4]. In addition, Balazs [22,24] computed the conformation of random or block polymeric emulsifiers absorbed on solid surfaces and showed a molecular conformation

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PII: S0032-3861(00)00013-6

with a hydrophilic “loop” or “hairpin” structure extending away from the solid surface, and the hydrophobic segment “trains” stuck to the surface wall. Random block types of polyelectrolytes, such as SSIPM modified tetra carboxylic acid terminated polyester (SMTAPE) emulsifier have been used to produce acrylic lattices [25–28] with good mechanic stability and low coagulum. The goal of the present work was to determine the relationship between the structure of SMTAPE emulsifiers and their CMC, and to study their adsorption on PS latex particle surfaces.

2. Experimental

2.1. Materials

Materials used in this study were styrene monomer (Acros), potassium persulfate (KPS) (Janssen), potassium hydroxide (KOH) (TEDIA), diethylene glycol (DEG) (TEDIA), isophthalic acid IPA (Lancaster) and 5-sulfo-isophthalic acid dimethyl ester sodium salt (SSIPM) (TIC). All of the chemicals were of reagent grade and used as received. The inhibitor was removed from the styrene by processing it through an aluminum oxide packed column. The water was deionized.

2.2. Synthesis of SMTAPE emulsifiers

The series of SMTAPE emulsifiers studied herein were the same as described by Chang and Lee [27]. They were prepared by condensation polymerization of diethylene glycol, isophthalic acid and specific amounts of 5-sulfo-isophthalic acid dimethyl ester sodium salt. The general structure of SMTAPE is shown in Fig. 1. The characteristics of various SMTAPE emulsifiers are summarized in Table 1.

2.3. Surface tension measurement

Surface tensions of SMTAPE in aqueous solutions and in PS lattices were determined by using CSC-Du Nouy Tensiometer at 25°C and l atm. SMTAPES were dissolved in water with potassium hydroxide in 100 ml volumetric flask with a magnetic stirrer at 70°C. The pH was then adjusted to 8.5 by adding 1 M potassium hydroxide aqueous solution. The surface tension were measured with a tensiometer.

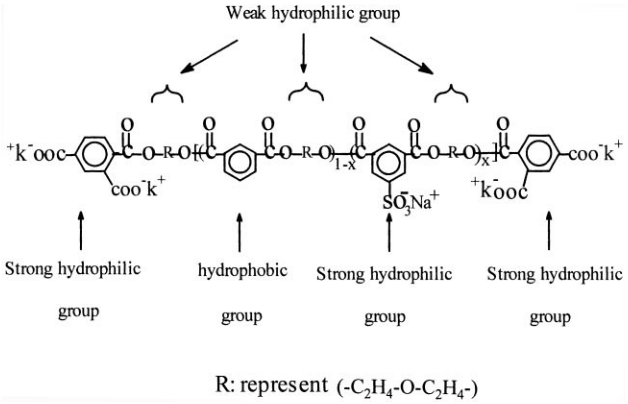


Fig. 1. General chemical structure of the salt form SMTAPE emulsifier.

2.4. PS latex for saturation absorption

The PS lattices used for the study of saturated adsorption were 12 wt% polymer solids content. The reaction procedure was the same as described by Chang et al [28]. Styrene, special amounts of A_4 emulsifier and 1 wt% of potassium persulfate were charged in reactor, then polymerized in batch reaction at temperature 70°C. The amounts of emulsifier and characteristics of lattices are summarized as Table 2. The lattices for the study of saturated adsorption of SMTAPE molecules were prepared by adjusting the pH of the PS lattices to 8.5, then adding equal amounts of various concentrations of A_4 or A_5 SMTAPE aqueous solutions. The PS solids contents in final samples were 6 wt% per cm^3 latex. A_4 and A_5 samples are described in Table 1.

2.5. Analysis of particle size

The particle size of SMTAPE micelles were determined by a Malvern 4700 Dynamic Light Scattering spectrophotometer. The latex particle sizes were determined by Quasi-Elastic Light Scattering (QELS) with a Coulter® Nanosizer™ at ambient conditions.

Table 1
The characteristics of SMTAPE and its micellar size in aqueous solution

Sample no.	A_3	A_4	A_5	A_6	A_9
$\bar{M}n$	5400	4700	5500	7100	1800
Hydrophobic section chain length m^a	8.5	6.5	4.0	9.0	4.8
Micellar size in aqueous solution (nm)	12.8	10.0	7.9	20.0	9.0
Ave. num. of strong hydrophilic group – $SO_3^-K^+$ or COO^-K^+ per SMTAPE chain[b]	3.5	3.8	6.0	4.0	2.4
Molecular chains per micelle	159	210	37	461	166

[a] Hydrophobic section chain length m = the number of repeat units between any two hydrophilic group (sulfonic or carboxylic).
[b] $-SO_3^-K^+$ incorporated in the molecular chain, COO^-K^+ attached on the chain ends.

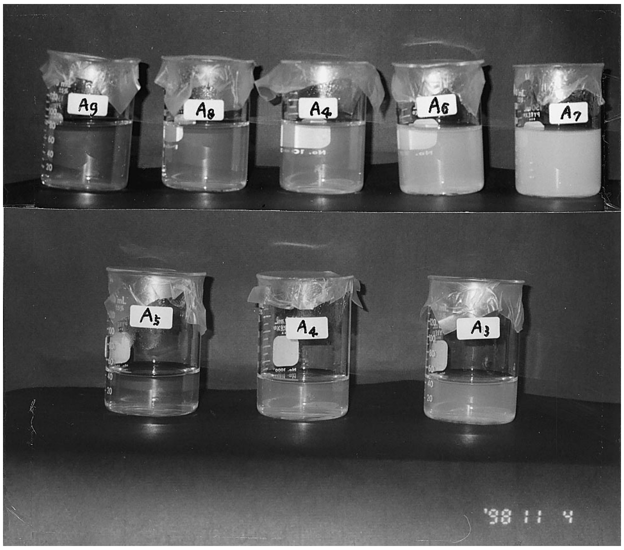


Fig. 2. Photos of SMTAPE emulsifiers in aqueous solution. (The samples A_7 and A_8 in the lower picture are difference series of samples, data regarding to those samples will be discussed in next paper.)

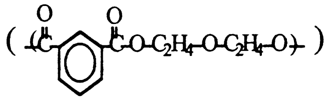
2.6. Molecular weight analysis

The number average molecular weights of the SMTAPE emulsifier were determined by chain-end –OH titration. The molecular weight polydispersities were determined by GPC (SP Thermo Separation Product). GPC samples were prepared by dissolving the polymer in a mixture of fifteen parts of DMF and 85 parts of THF, using THF as the elution solvent at 30°C.

3. Results and discussion

3.1. Molecular characteristics of SMTAPE

A variety of SMTAPE emulsifiers were prepared by condensation polymerization of diethylene glycol (DEG), isophthalic acid (IPA) and 5-sulfoisophthalic acid dimethyl ester sodium salt (SSIPM). The general chemical structure of the salt form SMTAPE is illustrated in Fig. 1. The salt form of SMTAPE contains strong hydrophilic portions with sulfonate groups (anionic) and carboxylate groups (anionic), and weak hydrophilic groups consisting of DEG (nonionic). The aromatic residuals are the hydrophobic portions. The average number of strong hydrophilic groups per SMTAPE used in the present study are 2.4–6.0 units. The hydrophobic groups are randomly arranged, depending on the SMTAPE molecular weight or/and different SSIPM amount in the molecule, as seen in Table 1. The average number "m" of hydrophobic repeat units



between any two strong hydrophilic groups (sulfonate or carboxylate) is 4.8–11.0. Due to the character of a batch condensation polymerization, the SSIPM groups are randomly distributed in the main chain. That means that the salt form of SMTAPE is a kind of random block polyelectrolyte polymeric emulsifier [5,22]. Further, the SMTAPE emulsifier had molecular weight polydispersity with $\bar{M}w/\bar{M}n$ around 2, as determined by GPC.

3.2. Characteristics of SMTAPE emulsifier in aqueous solution

Fig. 2 shows that all of the SMTAPE emulsifier aqueous solutions presented a bluish to blue-white color, indicating that they form fairly large micelles or clusters of micelles. The higher the molecular weight or the lower the hydrophilicity of the SMTAPE emulsifier the larger the micelles [27]. This translates into a greater number of emulsifier molecules aggregated in one micelle, as shown in Table 1.

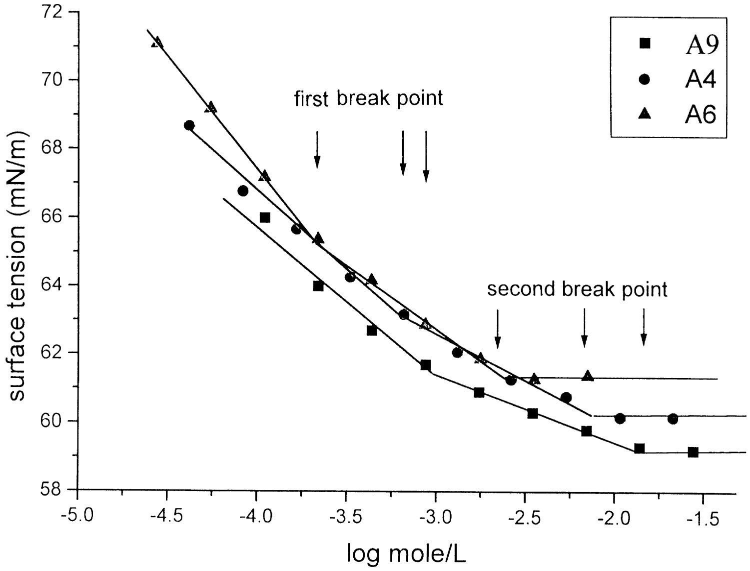


Fig. 3. Surface tension of the SMTAPE emulsifier aqueous solutions with different $\bar{M}n$.

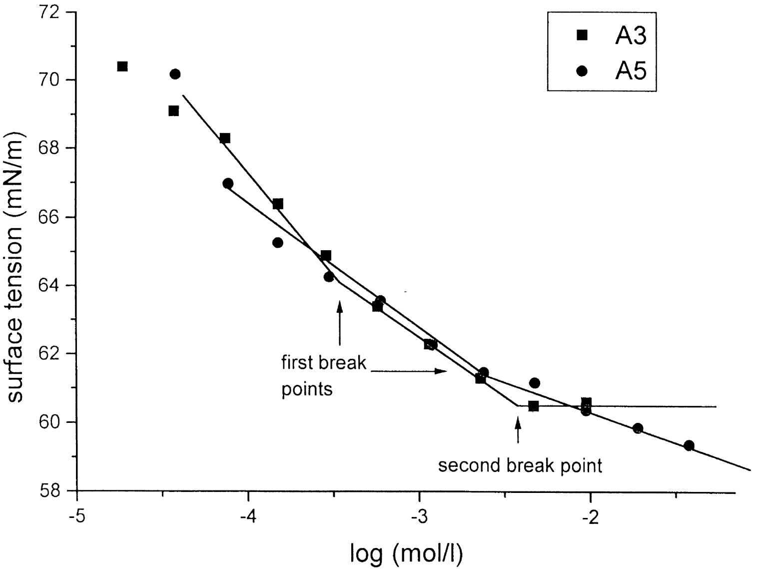


Fig. 4. Surface tension of various SMTAPE emulsifiers with different hydrophilicity depicting the first and second break points of the CMC range.

Fig. 3 shows the surface tensions of aqueous solutions of SMTAPE emulsifiers with different $\bar{M}n$, and Fig. 4 shows the same for SMTAPE emulsifiers with different hydrophilicity. The surface tension reduction is due to the emulsifier molecules absorbed on the air/water interface. The surface tension levels off round 60 mN/m at the CMC, which is about 15 mN/m lower than the surface tension of the deionized water used in this study. In all of the surface tension curves two break points were observed, with the transition region extending approximately one decade of concentration values. Also, the two break points, commonly seen in polymeric emulsifiers [4,14], are due to the molecular weight polydispersity of the SMTAPE emulsifier. In Fig. 3 it is shown that the higher the SMTAPE molecular weight, the lower both of the CMC values. This result is in agreement with the molecular weight dependency of the CMC of other saturated emulsifying polyesters (EPE) [12]. Fig. 4 shows that the higher the SMTAPE hydrophilicity, the lower both of the CMC values. This result is in agree with the previous study of Chen [3]. The concentration of the second break point for the A_5 sample appears to be higher than the concentration range used in this study and was not observed.

Shinoda has proposed a quantitative relation between the

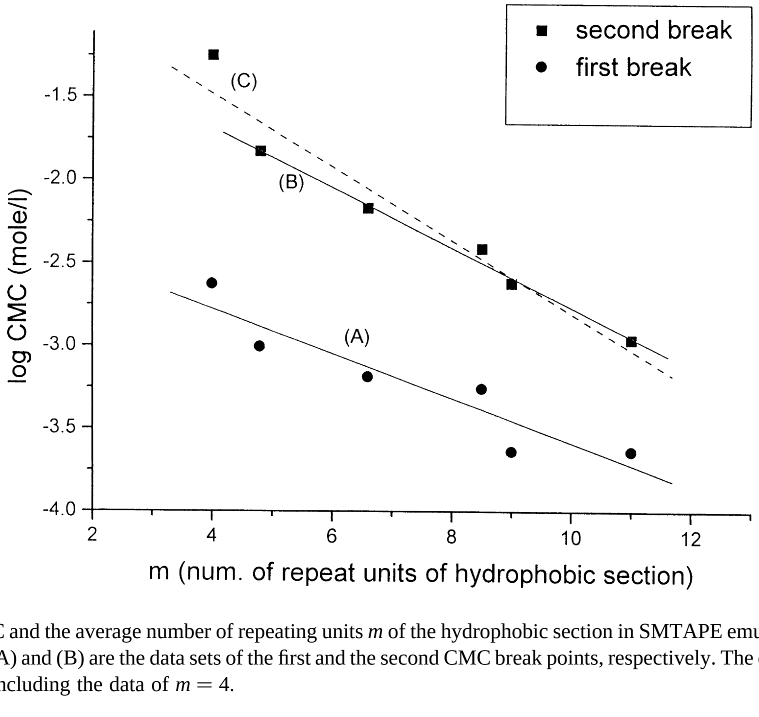


Fig. 5. Relationship between CMC and the average number of repeating units m of the hydrophobic section in SMTAPE emulsifiers according to the simplified Shinoda equation. Linear curves (A) and (B) are the data sets of the first and the second CMC break points, respectively. The dash linear curve (C) is the data set of the second CMC break point including the data of $m = 4$.

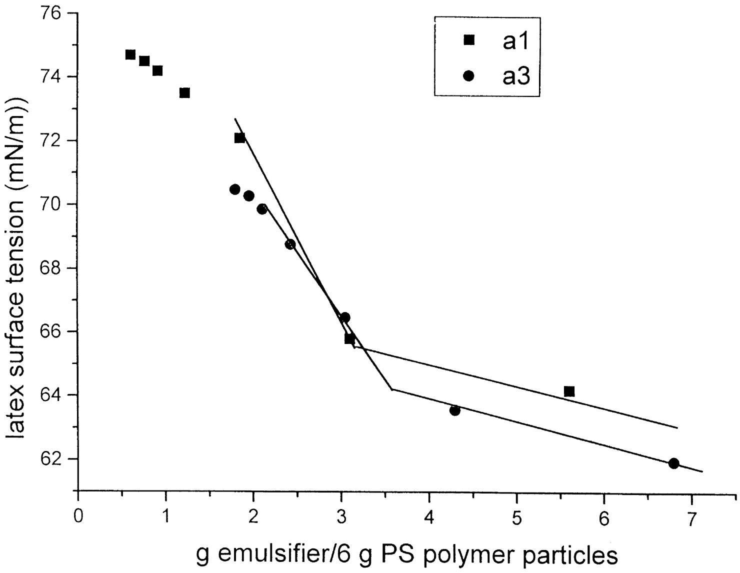


Fig. 6. The latex surface tension as function of the amount of A_4 SMTAPE emulsifier post-added to PS lattices synthesized using A_4 emulsifier at different initial concentrations (i.e. a_1 and a_3 of Table 2).

CMC and the hydrophobic chain length of normal emulsifiers. We used the following simplified form of the Shinoda equation [12],

$$\text{Log CMC} = A - B * m \tag{1}$$

where A and B are constants, and m is the average number of repeat units of the hydrophobic section in the emulsifier molecule. As seen in Fig. 5, our data for the dependency of both the first and second CMC points on the value of m are essentially in agreement with the linear characteristics of Eq. (1). The data point for the upper CMC (second break point) at $m = 4$ appears to be significantly away from the linear characteristic set by the values of $m > 4$, so we have drawn two possible curves through these data. Generally, the slopes of (A) and (B) that appear for the linear curves through both the lower and upper CMC data sets are relatively close, as we might expect from the homologous series of SMTAPE we studied. We postulate that the first break point is associated with high molecular weight portion of the emulsifier, and the second break point represents the lowest molecular weight portion. After the second CMC, the surface tension levels off, and essentially all of the emulsifier added after this point will form micelles. The concentration of the first CMC is 0.01–0.02 mol/l, which is about the same as that for sulfopolyester [3], but is higher than that of PEO–PPO–PEO emulsifier 0.0004 mol/l. The high

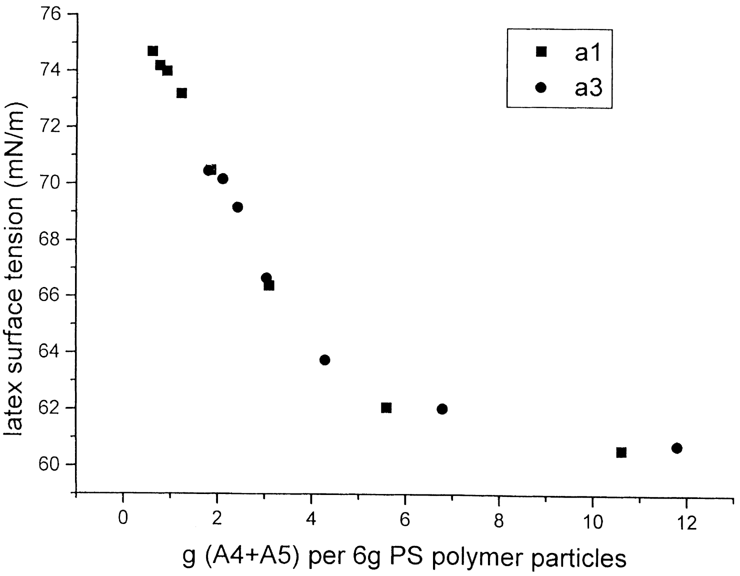


Fig. 7. The latex surface tension as function of the amount of A_5 SMTAPE emulsifier post-added to PS lattices synthesized using A_4 emulsifier (as in Table 2).

Table 2
The effect of A_4 SMTAPE emulsifier concentration on PS lattices properties

Emulsifier conc. (wt%)[a] (sample no.)	10 (a_1)	20 (a_2)	30 (a_3)
Coagulum (wt%)	0.8	0.2 <	0.2 <
Particle size (nm)	54.6	49.2	47.2
Surface tension (dynes/cm)	74.1	72.8	69.6

[a] Based on monomer.

concentrations at the CMC of SMTAPE is because of the relatively high hydrophilicity of SMTAPE emulsifiers.

3.3. Adsorption behavior of SMTAPE emulsifier on PS latex

A previous study [27] has shown, that among the SMTAPE emulsifiers studied here, A_4 was the most effective for the emulsion polymerization of acrylic lattices, resulting in lower coagulum and higher mechanic stability than the A_3,A_5,A_6,A_9 emulsifiers. Table 2 summarizes the characteristics of using various amounts of A_4 emulsifier in the synthesis of PS lattices. When emulsifier concentration based on styrene monomer was as low as 10 wt%, significant coagulum was formed and the surface tension of subsequent latex was essentially equivalent to that of deionized water used in this study. Our previous study of PBMA lattices containing 10 wt% of A_4 emulsifier showed poor Maron stability [27], while those containing 20 and 30 wt% A_4 emulsifier had good mechanic stability. Thus it appears that 10% (based on monomer) of A_4 emulsifier is the very least that can be used to produce a PS latex. Given that the surface tension of this latex is so high, it appears that nearly all of the emulsifier is adsorbed on the particle surface.

In this study, we monitored the surface tension of the PS lattices synthesized using 10 wt%(a_1) or 30 wt%(a_3) A_4 emulsifier as we added equal volumes of various concentrations of A_4 or A_5 aqueous solutions. Fig. 6 indicates that the first CMC break point is reached at about 3.2 g of A_4 emulsifier for latex a_1 (surface area of 6.70×10^{20} Å^2/cm^3 latex) and at about 3.5 g of A_4 for latex a_3 (surface area of 7.52×10^{20} Å^2/cm^3 latex). These adsorbed amounts scale directly as the surface areas of the particles indicating equilibrium adsorption points. Fig. 7 shows similar adsorption behavior for a mixture of A_4 (used in the latex preparation) and A_5 (used in the emulsifier titration) for both a_1 and a_3 lattices. This is consistent with the earlier finding [27] that A_4 and A_5 emulsifiers perform similarly.

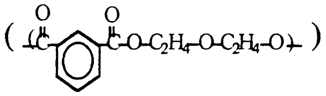
A_4 SMTAPE emulsifier contains 2.8 surface active sections, with each surface active section consisting of an hydrophobic section with average 6.5 repeat units of  and sulfonate or/and carboxylate groups at the end of each section. Using the data in Fig. 5 for the CMC of the first break point at m = 6.5 (A_4 emulsifier) and the data of Fig. 6 corresponding to the same condition (but with PS latex particles present), we have calculated that the saturated adsorption area of A_4 emulsifier is 187Å^2 per molecule.

Table 3 also shows that lattices a_1 and a_3 produce nearly equivalent numbers. Perhaps more useful, this saturation adsorption area per hydrophobic section of the molecule is 67 Å^2 (i.e. 187 Å^2 divided by 2.8). This value is only slightly higher than the value of 42–47 Å^2 per molecule of the low molecular weight SDS emulsifier on PS latex [29,30]. The latex particle size used in the calculation of saturated adsorption area for A_4 emulsifier was obtained by light scattering, which is not sensitive to small particles within a broad particle size distribution, as are the a_1 and a_3 lattices used here [28]. Consequently the adsorption area calculated here might be somewhat low.

Balazs [22,24] used a model to calculate the molecular conformation for a molecule like the SMTAPE adsorbed on a solid surface at saturated condition. In the present system it would correspond to the PS latex surface adsorbed with SMTAPE having a conformation where the hydrophilic carboxylated chain ends stretched out into the aqueous media and the sulfonated hydrophilic segments would from loops extending away from the PS surface. The flexible “weak” hydrophilic diethylene oxide segments will also be forced to extend into the surrounding aqueous media at saturated conditions, while the hydrophobic segments containing the aromatic groups would be anchored on the PS particle surface. The multi point adsorption of the SMTAPE molecules on the PS particle surface will improve the adsorption strength [5], which in turn might explain the high percent of SMTAPE coverage of the latex particles after polymerization.

Table 3
A_4 SMTAPE emulsifier adsorption area on PS lattices at 25°C

Sample no. from Table 2	Surface area (Å^2)[a]	Number of A_4 molecules adsorbed on latex particles at saturation[a]	Surface area occupied per molecule at saturation (Å^2)	Surface area occupied per surface active section at saturation (Å^2)
a_1	6.70×10^{20}	3.59×10^{18}	187	67
a_3	7.52×10^{20}	3.97×10^{18}	189	67

[a] Per cm^3 latex, 6 wt% solid content.

4. Conclusions

This study shows that the polyelectrolyte, random block type of polyester, SMTAPE, lower the surface tension of water by about 15 mN/m at room temperature. Such a polyester has a CMC dependency on molecular weight and chemical structure, which follows the Shinoda equation [12]. It also displays two distinct CMCs due to the breadth of the molecular weight distribution. Behaving like a polymeric emulsifier, A_4 SMTAPE adsorbs on the surface of PS latex particles with a saturation adsorption area is about 187 Å^2/molecule. It is proposed that the hydrophobic segment “trains” adsorb on the PS surface, and that the hydrophilic chain segments stretch into the aqueous media.

Acknowledgements

Y.H.C. would like to thank the members of the Polymer Research Group, University of New Hampshire, Durham, NH, USA for the many helpful discussions.

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