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Synthesis of core–shell composites using an *inverse surfmer*E. Armando Zaragoza-Contreras^{a,*}, Margarita Stockton-Leal^a, Claudia A. Hernández-Escobar^a, Yusuke Hoshina^b, Josué F. Guzmán-Lozano^b, Takaomi Kobayashi^b^a Centro de Investigación en Materiales Avanzados, S.C. Laboratorio Nacional de Nanotecnología. Miguel de Cervantes No. 120, Complejo Industrial Chihuahua, Chihuahua, Chih., Mexico^b Department of Materials Science and Technology, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Japan

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ABSTRACT

Anilinium dodecylsulfate was prepared from aniline and sodium dodecylsulfate. The critical micellar concentration of the salt was determined using electrical conductimetry, which revealed that the change of counteraction, sodium by anilinium, reduced the critical micellar concentration with respect to the conventional counterpart, sodium dodecylsulfate. The anilinium dodecylsulfate was used as the surfmer in the synthesis of polystyrene/polyaniline core–shell composites, first performing as the surfactant to stabilize the emulsion polymerization of styrene, and later as the monomer to synthesize polyaniline via oxidative polymerization. Here, the surfmer function was directed toward the external phase instead of to the internal phase, as with conventional surfmers with carbon–carbon double bonds. Consequently, the term *inverse surfmer* is proposed. Analyses of its composite microstructure using electron microscopy and thermogravimetric analysis confirmed the core–shell arrangement.

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1. Introduction

Perhaps the most studied surfactants with special functions are polymerizable surfactants, also known as surfmers. These compounds are especially attractive because, aside from acting as conventional emulsifiers, they can link covalently to a latex particle surface [1,2]. This feature avoids surfactant desorption from the polymer particles and improves resistance to freezing and to shearing of the latex [3]. Most surfmers are susceptible to homopolymerization and copolymerization [4]. However, maleic surfmers are only able to copolymerize [5,6]. Numerous reports have described state of the art over the years [3,7–10]. For this reason, their various aspects will not be detailed here.

Herein, we describe results of anilinium dodecylsulfate (DS-AN) used as a new concept of reactive surfactant. In this case, functionality lies on the anilinium group and not on a polymerizable carbon–carbon double bond. The reactive site is not located in the organic phase of the emulsion as found with traditional surfmers [11–17]. These features greatly distinguish DS-AN from the traditional surfmer concept. However, the intention is similar that DS-AN performs as a surfactant because it exhibits a critical micellar concentration and stabilizes emulsion polymerization, and it performs as a monomer because polyaniline is obtained from it

by oxidative polymerization. Therefore, DS-AN and other analog molecules can be regarded as a new approach to generating surfmers.

As described, because of its amphiphilic nature, DS-AN presents a number of potential applications. For instance, in the stabilization of emulsion polymerizations (macroemulsion, suspension, miniemulsion or microemulsion) and by combining the function as a monomer for the synthesis of electrically active polyaniline, DS-AN presents the possibility of obtaining electrically conductive polymer composites. Consequently, in this first approach, we applied DS-AN in the synthesis of polystyrene/polyaniline core–shell composites to demonstrate the feasibility and versatility of this class of reactive surfactants. It is noteworthy that several approaches to produce core–shell colloidal polymer composites of vinyl or acrylic polymers with polyaniline have been reported in the literature [18–25].

2. Experimental section

2.1. Materials

Aniline, sodium dodecylsulfate (SDS), ammonium persulfate (APS) and hydrochloric acid (Nacalai Tesque Inc.) were used as received. Styrene monomer (Nacalai Tesque Inc.) was distilled under vacuum. 2,2'-Azobis(2-methylpropionamide) dihydrochloride (WAKO pure Chemical Industries, Ltd.) was recrystallized from a saturated aqueous solution at 60 °C.

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2.2. Synthesis of anilinium dodecylsulfate (DS-AN)

DS-AN salt was synthesized as follows. First, the salt of anilinium hydrochloride was obtained by reacting aniline and hydrochloric acid in a 1:1 molar ratio. The amount of water sufficient to dissolve the salt was added. Next, an aqueous solution of sodium dodecylsulfate (SDS) corresponding to 1:1 molar ratio with respect to aniline was mixed with the salt of anilinium hydrochloride. The interchange of ions produced the precipitation of the sulfate salt of anilinium because of the much lower solubility of this salt in water at room temperature. Salt purification was performed by saturating an aqueous solution at ca. 50 °C. Then the solution was allowed to cool in laboratory conditions and then refrigerated at 4 °C for 12 h. The solid was recovered by filtration on a filter paper and dried under vacuum at 60 °C. ^1H RMN (400 MHz, δ , $(\text{CD}_3)_2\text{S}=\text{O}$) 0.85 (3H), 1.23 (18H), 1.26 (2H), 1.42 (2H), 3.65 (2H), 7.26 (2H), 7.44 (3H). FTIR (cm^{-1} , ATR) 3300–2850, 2940, 2850, 2920, 2620, 1500, 1623, 1600, 1478, 1470, 1374, 1200, 1214, 1056, 963, 950, 814, 740, 720. The critical micellar concentration (cmc) (mmol dm^{-3} , electrical conductimetry) was 2.99.

2.3. Determination of critical micellar concentration

The critical micellar concentration (cmc) of DS-AN and SDS was determined using electrical conductimetry. The procedure was the following. An aqueous concentrated solution of the salts was prepared in laboratory conditions. In a glass vessel, 100 ml of demineralized water, with electrical conductivity of $1.8 \mu\text{S cm}^{-1}$, was loaded and tempered at 35 °C. The cell of the conductivity meter was fixed 1 cm above the vessel bottom. Progressive additions of 1 ml each time of the solution were achieved. The evaluation consisted of measuring the increase of electrical conductivity as a function of the salt concentration. Gentle magnetic stirring was used to homogenize the solution.

2.4. Emulsion polymerization

Styrene emulsion polymerization, as the first step of the method, was performed as follows. First, an aqueous solution of DS-AN containing 10, 20 or 40 mmol dm^{-3} was loaded into the reactor and left to stabilize for 20 min at 70 °C. Then $0.00184 \text{ mol dm}^{-3}$ of 2,2'-azobis(2-methylpropionamide) dihydrochloride (V-50) was loaded into the reactor. The emulsion was prepared by injecting the monomer into the reactor. The relation of the monomer to water was 20/80 (wt/wt). Monomer addition was regarded as the initiation of the polymerization. Therefore, the first sample to determine polymerization kinetics was taken 3 min after monomer feeding. All polymerizations were performed at 70 °C, with stirring of 300 rpm and permanent flux of nitrogen. A series of samples were taken during the polymerization to determine the kinetics.

2.5. Oxidative polymerization

Polyaniline (PAni-DS) shell synthesis, as the second step, was conducted as follows. First, 50 ml of polystyrene latex was loaded into a glass vessel. In a separate container, an aqueous solution of DS-AN was prepared at 50 °C. Afterward, the solution and the latex were mixed together while maintaining gentle magnetic stirring and temperature for 4 h to allow the salt to absorb onto the polymer particles. After this time, the system was left to cool at room conditions. Then, an aqueous solution of ammonium persulfate (APS), corresponding to a molar ratio of 1.2:1 (DS-AN:APS), was poured dropwise to launch DS-AN polymerization. Once the initiator was fed, the reaction system was transferred to a refrigerator to complete oxidative polymerization at $-2 \text{ }^\circ\text{C}$ for 24 h.

2.6. Characterization

Proton nuclear magnetic resonance (^1H NMR) spectra of DS-AN and SDS were obtained using an FT-NMR (JNM GX400; JROL) in deuterated DMSO ($(\text{CD}_3)_2\text{S}=\text{O}$) at 60 °C. Infrared spectroscopy (FTIR) analyses were run in an IR Fourier Transform Spectrophotometer (IR Prestige-21 FTIR-8400s; Shimadzu Corp.). Before analyses, DS-AN was recrystallized from a saturated aqueous solution heated at 50 °C and then cooled to 4 °C.

Scanning electron microscopy in transmission mode (STEM) was performed in a field emission electron microscope (JSM-7401F; JEOL) at 30 kV. To prepare the samples, two drops of latex were dispersed using sonication for 5 min in 30 ml of tridistilled water. Subsequently, a drop of latex was placed and left to dry on a holey carbon copper grid. By this procedure, the latexes, the core-shell composites and samples of pure PAni-DS were analyzed.

3. Results and discussion

3.1. ^1H NMR and infrared spectroscopy

The ^1H NMR spectra of DS-AN and SDS, were run in deuterated DMSO ($(\text{CD}_3)_2\text{S}=\text{O}$; $\delta = 2.49 \text{ ppm}$). The most relevant difference between the spectra of DS-AN and SDS were the multiplets at $\delta = 7.44 \text{ ppm}$ and at $\delta = 7.28 \text{ ppm}$ corresponding to the protons of the anilinium cation. This difference indicated the presence of the anilinium group in DS-AN (Fig. S1).

The FTIR spectra of SDS presented the following bands (Fig. S2). The peaks at 2940 cm^{-1} and 2850 and 2920 cm^{-1} correspond to the symmetric stretching of the C–H bond of CH_3 groups and to the symmetric and asymmetric stretching bands of C–H bond of CH_2 groups, respectively. The bands at 1374 and 1478 cm^{-1} were assigned to bending vibration of C–H bonds of CH_3 groups. The peaks at 1200 and 1214 cm^{-1} and 1056 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations, respectively, of the S=O₂ bond. The peaks at 814 and 963 cm^{-1} , respectively, stand for the symmetric and asymmetric stretching of S–O bond. Finally, the band at 720 cm^{-1} corresponds to the rocking vibration of the C–H bond of CH_2 groups. On the other hand, the spectrum of DS-AN presented the same set of bands described for SDS. In addition, the following are also present (Fig. S2). A wide band at 2620 cm^{-1} corresponds to an overtone of the $^+\text{NH}_4$ group, whereas the bands at 1500 and 1600 cm^{-1} , respectively, correspond to the symmetrical and asymmetrical vibrations of N–H bonds of this group. The peak at 1623 cm^{-1} corresponds to the scissoring vibration of bond NH_2 of $^+\text{NH}_4$ group. The peaks at 1470 cm^{-1} , and 950 and 740 cm^{-1} , respectively, correspond to waving and out of plane bending vibrations of C–H bonds of the anilinium group. This set of bands confirms the presence of the counteranion in DS-AN. Literature is available to consult functional group frequencies [26–29].

3.2. Critical micellar concentration

The cmc of DS-AN was determined using electrical conductimetry. This technique is specially applied with ionic surfactants because the electrical conductivity of soluble ionic compounds in water depends directly on the concentration [30]. Some reports have described the surface activity of “aniline–organosulfonic acid” complexes (aniline–dodecylbenzenesulfonic acid), during polyaniline synthesis in aqueous or organic phase, or in emulsified systems [31–35]. However, the characterization and determination of the cmc of analog compounds to DS-AN have not been reported. The curves of electrical conductivity (k) ($\mu\text{S cm}^{-1}$) versus the surfactant concentration (mol dm^{-3}) of SDS and DS-AN are shown in

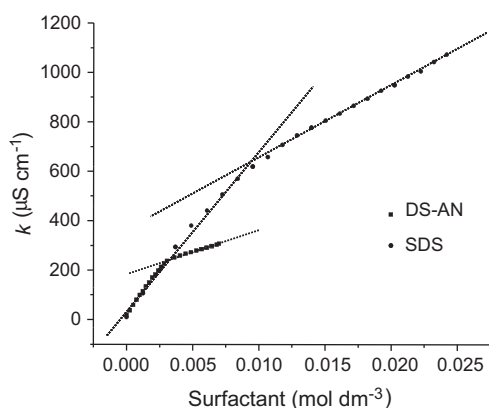


Fig. 1. Curves of electrical conductivity ($\mu\text{S cm}^{-1}$) versus surfactant concentration (mmol dm^{-3}) for sodium dodecylsulfate (SDS) and anilinium dodecylsulfate (DS-AN).

Fig. 1. The cmc for SDS was 7.9 mmol dm^{-3} . This value agreed well with those reported in the literature [36–39]. For DS-AN, the cmc was $2.99 \text{ mmol dm}^{-3}$, which is ca. 2.6 times lower than the cmc of SDS. This change indicates that the effect of changing counterion was extremely important.

The effect in conventional surfactants of changing an inorganic counterion to an organic counterion has been studied in detail. It has been reported that both reduction in the cmc and increment in the counterion binding were dependent on the hydrophobicity of the counterion. When the hydration size of the counterion increased, the cmc increased [40–49].

As found in cmc determination, the substitution of the inorganic by the organic counterion reduced this value considerably. Such a difference suggested that the area occupied by the molecule of DS-AN on the micellar aggregate changed with respect to SDS. As described in the literature, highly hydrophobic organic counterions fit into the chain palisade [44]. Consequently, the accommodation of the anilinium groups within the hydrocarbon micellar palisade is apparently the most feasible arrangement, causing the saturation of the water/micelle surface and the reduction of the cmc at lower concentrations. Simple molecular modeling of DS-AN and SDS allowed to visualize the molecular interaction between the anions and cations and the difference in the volume occupied at the water/micelle interface by molecule of each kind (Fig. S3). Thus, a formal study of chemical simulation should be considered. At this point, it is worth saying that the experimental study of the interfacial accommodation of some anilinium salts at the micellar interface has been reported by Im et al. [31,50] who determined, using NMR and electrical conductivity measurements, that the anilinium counterion was located at the interface water/micelle. Similarly, Bachofer and Simonis [51] found, also using NMR analysis, that in the case of tetradecyltrimethylammonium surfactants, with nitrobenzoate or salicylate counter-anions, the aromatic moiety of the counterion was located into the micellar palisade.

3.3. Emulsion polymerization (core synthesis)

In this work, emulsion polymerizations stabilized with DS-AN were used to produce the polystyrene core of the composites. Of course, some other conventional surfactants could be used in this stage. However, the intention of this study, evaluating DS-AN as a surfmer, must be recalled. Free radical initiator V-50 was selected to launch the polymerizations (constant concentration of $0.00184 \text{ mol dm}^{-3}$) because persulfate initiators can launch DS-AN polymerization via an oxidative mechanism. Fig. 2 (above) portrays the conversion (%) versus time (min) profiles for the systems containing

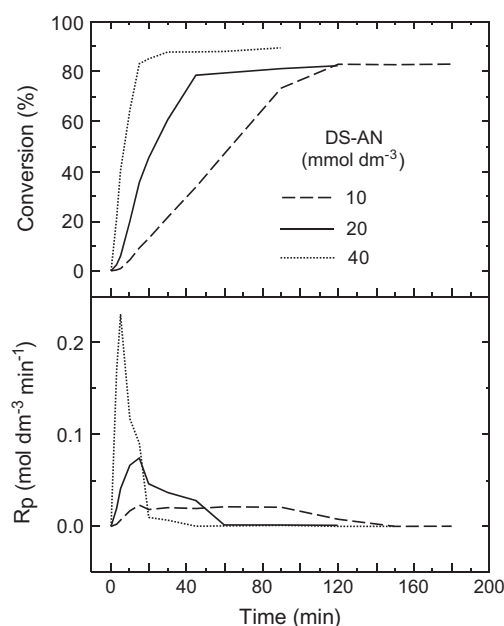


Fig. 2. Curves of conversion (%) versus time (min) (above), and curves of rate of polymerization (R_p) ($\text{mol dm}^{-3} \text{ min}^{-1}$) versus time (min) (below), for the emulsion polymerizations stabilized with 10, 20 or 40 mmol dm^{-3} of DS-AN.

different concentrations of DS-AN ($10, 20$ or 40 mmol dm^{-3}). Final latex conversions were in the range 80–90%. As observed, the kinetics was dependent on the surfmer concentration. This commonly reported behavior is related to the dependence of the total particle surface area with respect to the surfactant concentration. Consequently, at the very beginning of the polymerization, Interval I, the number of polymer particles formed (nucleation period) depends on the surfactant concentration. In this way, during the polymerization, the monomer was polymerized in a larger number of polymer particles for higher surfactant concentrations; consequently, higher rates of polymerization were observed [52,53].

Fig. 2 (below) shows the curves of the rate of polymerization ($\text{mol dm}^{-3} \text{ min}^{-1}$) versus time (min). As observed, the maximum values of the rate of polymerization depended on the concentration of DS-AN, as described above. These maximum values appeared during the first 15 min. It was also noted that the curves followed, at least to a certain degree, the behavior suggested by the Smith–Ewart model [54]. The curves for the polymerizations at 10 and 20 mmol dm^{-3} of DS-AN clearly presented the three Intervals of emulsion polymerization. At 40 mmol dm^{-3} of DS-AN, Interval II was poorly perceptible because of the high rate of polymerization at this concentration. Therefore, Interval II was very short, and Interval III was reached rapidly.

Fig. 3 portrays micrographs of the latexes obtained with DS-AN as the surfactant. The particle diameters were observed to depend on the surfactant concentration, with narrow evident polydispersities. As explained earlier, this effect is a consequence of the total micelle surface area. Depending on surfactant concentration, the amount of swollen micelles available for nucleation is greater for larger surfactant concentrations. Therefore, after the period of nucleation, the number of polymer particles is also greater for larger surfactant concentrations. Consequently, after the period of nucleation, the monomer has a greater number of loci for polymerization (compartmentalization). In turn, this is reflected as higher rates of polymerization. Narrow polydispersities are evidence of the nucleation period. This behavior indicates a predominant mechanism of nucleation. According to Smith–Ewart model, micellar nucleation is a quite probable mechanism under the present

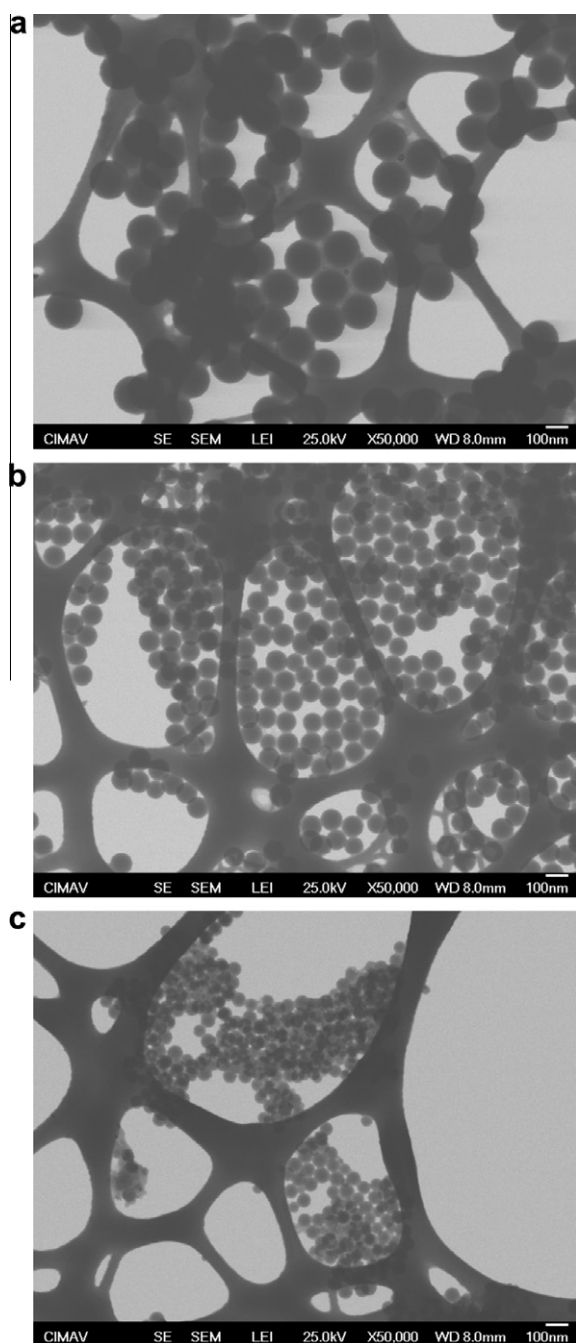


Fig. 3. STEM micrographs of the polystyrene latexes stabilized with DS-AN at (a) 10 mmol dm^{-3} , (b) 20 mmol dm^{-3} or (c) 40 mmol dm^{-3} .

conditions: surfactant concentration above cmc and low water-soluble monomer [54].

3.4. Oxidative polymerization (shell synthesis)

The second stage of the composite synthesis was performed via oxidative polymerization. In this stage, only the latex synthesized with 20 mmol dm^{-3} was considered. Consequently, more DS-AN was added as the monomer of PANi. Two composites corresponding to the theoretical proportions of 15 wt% and 30 wt% with respect to the content of polystyrene in the core were synthesized. Fig. 4 shows micrographs of the core-shell latexes with: (a) 15 and (b) 30 wt%. The pictures either show a lack of formation of

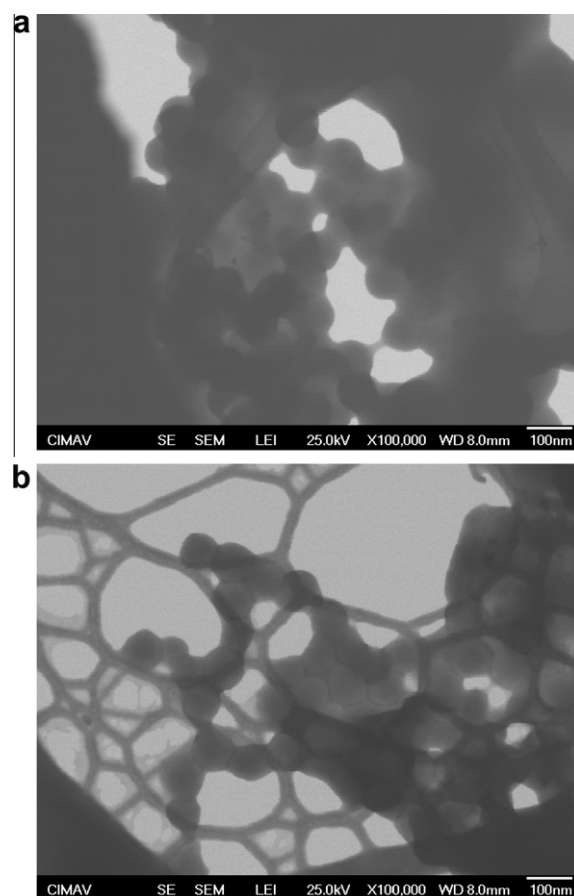


Fig. 4. STEM micrographs of the core-shell composites with PANi contents of (a) 15 wt% and (b) 30 wt%.

clots or separated phase of PANi, which indicated that most of the PANi polymerized on the polymer particles surface. However, comparison of morphology and texture of the particles in the images reveals physical changes that took place on the particles surface. Deformation of the particles was more prominent with the content of PANi, and the surface of the pristine polystyrene particles (Fig. 3a–c) is very clean in comparison with the composite particles.

To complement characterization, thermogravimetric analysis was performed. The traces of polystyrene obtained by emulsion polymerization using 20 mmol dm^{-3} of DS-AN, pure polyaniline obtained with DS-AN via oxidative polymerization and the different core-shell composites with 15 wt% and 30 wt% PANi are shown in Fig. 5. As shown, the core-shell composites present a clear combination of the profiles of the pristine polymers. In particular, the transition at ca. 350°C , associated to PANi backbone degradation [55], is perfectly observed in both composites (ca. 450°C), which also showed the proportion of PANi in the composite. By considering these transitions, it was possible to determine DS-AN conversion to PANi. In this way, the weight fraction in the range of $350\text{--}800^\circ\text{C}$, which corresponded to ca. 75 wt% of the total sample of pure PANi, was considered as a sample of PANi at 100% conversion. The composite with experimental 15 wt% of PANi indicated contents of ca. 11 wt% ($450\text{--}550^\circ\text{C}$), whereas the composite with experimental 30 wt% of PANi indicated contents of ca. 19 wt% ($450\text{--}550^\circ\text{C}$). Simple mathematical calculations indicated ca. 100% conversion for the composite with experimental 15 wt% of PANi and ca. 86% conversion for the composite with experimental 30 wt% of PANi.

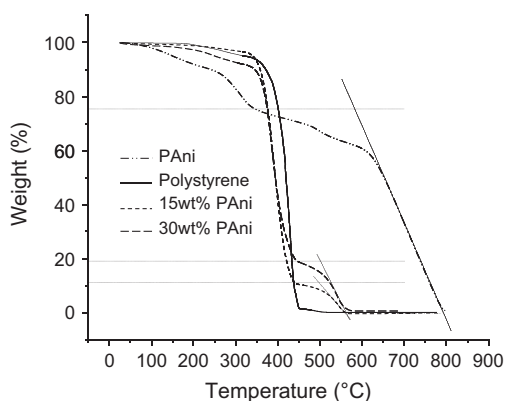


Fig. 5. TGA traces of PAni synthesized from DS-AN via oxidative polymerization, pristine polystyrene obtained with 20 mmol dm^{-3} of DS-AN, and the core-shell composites with PAni contents of 15 wt% and 30 wt%.

3.5. Core-shell composite

To elucidate interactions of the polystyrene core and the PAni shell, a sample of core-shell composite with 20 wt% of PAni was exposed to THF. The observed behavior showed no strong link between the polymeric materials, which was not surprising considering that the DS-AN as surfmer was only stabilizing the polymer particles and the interaction with the polystyrene core was merely physical. Fig. 6 portrays images of pure PAni and the solids of the core-shell composite recovered from the dissolution with THF. The following features can be highlighted. First, micrograph (a) shows the morphology of the pure PAni obtained with DS-AN; as observed, the polymer is in the form of tiny particles of ca. 30 nm. Second, micrograph (b) exhibits the PAni sample at lower magnifications: the polymer is observed as a large agglomeration of particles. Third, micrograph (c) depicts solids recovered from the dissolution with THF. The spherical polymer particles were not present. Instead, amorphous agglomerations were observed. Such agglomerations were similar to the observed in micrograph (b). Complementarily, infrared spectroscopy was performed on the pure PAni, the fraction of composite dissolved in THF and the recovered solids (Fig. S4). In summary, the spectrum of the recovered solids presented the same bands observed in the pure PAni. Consequently, the results clarified that the solids corresponded to the fraction of PAni in the composite (the shell) because polystyrene is soluble in the solvent. In this way, the individual shells of PAni collapsed once the polystyrene matrix was removed by solubilization. In this case, the egg-like arrangement, which is observed in some composites [56,25], was not observed. An important difference with these reports is that polyaniline was doped with hydrochloric acid. As known, the solubility of this kind of polyaniline in organic solvent or water is limited [57]. However, in the present case, the doping agent contains a large organic radical, which improves the interaction with organic solvents and water [58]. In fact, DS-AN is soluble in several organic solvents, including THF. As a result, shell's microstructure was destroyed by exposure to THF.

Based on the results and consideration of the theoretical scenario of a conventional surfmer in a water/oil system (inverse emulsion polymerization), it was possible to observe a similar performance to that shown by DS-AN: the reactive group is toward the continuous phase. Under this condition, in a first stage, a water-soluble monomer can be polymerized in the dispersed phase. In a second stage, an oily soluble monomer can be polymerized on the surface of the polar polymer particles. The result is expected to be a core-shell composite. With this in mind, it is possible to classify DS-AN as representative of a new group of surfmers: *inverse surfmers*.

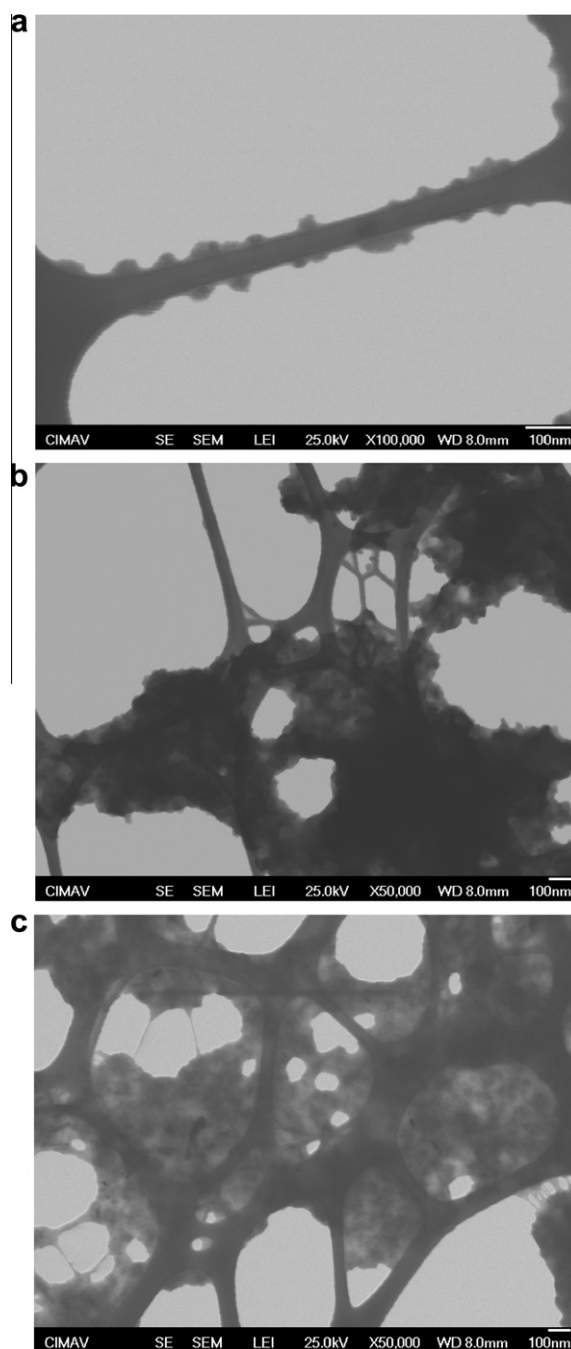


Fig. 6. STEM micrographs of: (a) pure PAni obtained by oxidative polymerization of DS-AN, (b) massive agglomeration of pure PAni, and (c) solids recovered from the dissolution of a core-shell composite in THF.

4. Conclusion

Polystyrene/polyaniline core-shell composites were successfully obtained using anilinium dodecylsulfate (DS-AN) as the surfmer [7–10]. In this study, electron microscopy, solubility tests and thermogravimetric analysis allowed us to validate composite microstructure [56,25]. By this novel procedure, we demonstrated the potential uses of DS-AN as a class of reactive surfactant or surfmer. Here, the polystyrene cores were obtained via conventional emulsion polymerization using DS-AN as the stabilizer, whereas the shell was obtained via oxidative polymerization using DS-AN as the monomer of polyaniline. This demonstrates the application of the double function surfactant-monomer. The differences of

DS-AN on both functionality and performance, with respect to the traditional surfmers, indicated DS-AN, and other analogue molecules can be considered as a new group of surfmers: *Inverse surfmers*. Significantly, this new concept contributes to the development of new reactive structures, and reactive surfactants for potential applications.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis.2012.03.047>.

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