ANILINIUM SALTS AS SURFMERS IN THE SYNTHESIS OF ELECTRICALLY CONDUCTING POLYANILINE BASED COMPOSITES

Elcin Coskun[1], Margarita Stockton-Leal[1], Claudia A. Hernández-Escobar[1], E. Armando Zaragoza-Contreras[1], Yusuke Hoshina[2], Josué F. Guzmán-Lozano[2], Takaomi Kobayashi[2]

(1) Centro de Investigación en Materiales Avanzados, S.C. Miguel de Cervantes No. 120, Complejo Industrial Chihuahua, Chihuahua, Chih., Mexico. E-mail: armando.zaragoza@cimav.edu.mx
(2) Department of Materials Science and Technology, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Japan

Abstract

Anilinium dodecyl sulfate (DS-AN) was obtained from aniline and sodium dodecyl sulfate (SDS). Critic micellar concentration (cmc) of the salt was determined by electrical conductimetry. This technique showed that the change of counterion, sodium by anilinium, induced the reduction of cmc with respect to their conventional counterpart, SDS. Afterwards, DS-AN was used as reactive surfactant (surfmer) in the synthesis of polystyrene / polyaniline core-shell conductive composites. The latexes obtained were stable, which indicated that DS-AN followed the mechanism implicated in traditional emulsion polymerization. Polyaniline synthesis was successfully performed by adding more DS-AN as the monomer and APS as the oxidizing agent, no acid addition was required in this procedure. The composite presented conductivities in the order of 10^{-4} to 10^{-3} S/cm.

Introduction

Polymerizable surfactants, also known as surfmers, are a special class of surfactants. These compounds are especially attractive because, besides of acting as conventional emulsifiers, they have the ability to link covalently to the surface of latex particles [1]. This feature avoids surfactant desorption from the polymer particles and improves resistance to freezing and high shearing of the latex [2]. Most surfmers are susceptible of homo and copolymerization [3]; however, maleic surfmers are only able to copolymerize [4].

In this work we are reporting results of anilinium dodecyl sulfate (DS-AN) salt used as surfmer in the synthesis of core-shell composites obtained in two steps. In this case, functionality lies on the anilinium group and not on a polymerizable carbon-carbon double bond as in traditional surfmers; neither its reactive activity develops within the oily phase of some emulsion system, as usually reported [5]. These features make a big difference of this anfifile with respect to the traditional concept of surfmer.

Experimental
DS-AN synthesis

DS-AN salt was synthesized as follows: First, the salt of anilinium hydrochloride was obtained by reacting aniline and hydrochloric in aqueous medium. Next, an aqueous solution of sodium dodecyl sulfate (SDS) was mixed with the salt of anilinium hydrochloride. Product purification was performed by saturating an aqueous solution at ~50 ℃.

Critic micellar concentration

Critic micellar concentration (cmc) of DS-AN was determined by electrical conductimetry. The procedure was as follows: An aqueous concentrated solution of the salts was prepared at laboratory conditions. 100 mL of demineralized water with electrical conductivity of ~1.8 S/cm was loaded in a glass vessel and tempered at 27 ℃. The cell of the conductivity meter was fixed 1 cm above the vessel bottom. Progressive additions of 1 mL each time of the salt solution were achieved. The evaluation consisted in measuring the increase of electrical conductivity as function of salt concentration. Gentle magnetic stirring was used to homogenize the solution.

Emulsion polymerization

Styrene emulsion polymerization, was performed as follows: First, aqueous solution of DS-AN was loaded into the reactor and let to stabilize for 20 min at 70 °C in the presence of nitrogen. Afterwards, initiator V-50 was loaded to the reactor and the solution was let for 5 min more. Next, the emulsion was prepared by injecting the styrene monomer into the reactor with vigorous stirring. The relationship monomer to water was 20 to 80 (wt/wt). All polymerizations were performed at 70 °C, stirring of 300 rpm and let for 180 min with permanent flux of nitrogen. Once polymerizations finished the latexes were let cool and kept into covered vessels. Series of samples were taken along the polymerization to determine kinetics.

Oxidative polymerization

PAni shell synthesis, as the second step, was carried out 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 and magnetic stirring. Afterwards, the solution and the latex were mixed together keeping magnetic stirring and temperature for 2 h in order to allow the salt to absorb onto the polymer particles surface. After this time, the system was let cool to room conditions. Finally, an aqueous solution of ammonium persulfate (APS) was poured to start PAni synthesis. Oxidative polymerization was carried out at laboratory conditions and allowed for 24 h.

Results and discussion
CMC

The curves of electrical conductivity (S/cm) versus surfactant concentration (mol/L) of SDS and DS-AN, are shown in Figure 1. The change in the slop for SDS was at 8.1 mmol/L. This value agreed well with literature, which also let us to validate our experimental procedure [6]. Of course, variations can be found in the values of the cmc depending, for example, on the surfactant purity. In special ionic impurities can promote changes in this value, since they can alter solution conductivity. In the case of DS-AN the slop changed at 3.1 mmol/L; that is, 2.6 times lower than the cmc of SDS. This change indicated that the effect of changing counter-cation was very important. The effect of changing inorganic counterion by organic counterion, in conventional surfactants, has been studied. As examples, we can comment that Li et al. [7] reported the effect of changing alkyl radical length of decylammonium dicarboxylate or monocarboxylate surfactants. They found that depending on the n-alkanoate radical the cmc reduced as function of length. However, the most important effect was observed with the monocarboxylated due to the easier incorporation of the alkyl chain into the micellar aggregate. Gamboa et al. [8] studied the effect of changing Cl- or Br- anions by Tosylate anion in cetyltimethylammonium surfactants. They reported the reduction of the cmc in water at 25 ℃, of 6.5 and 4.5 times, respectively.
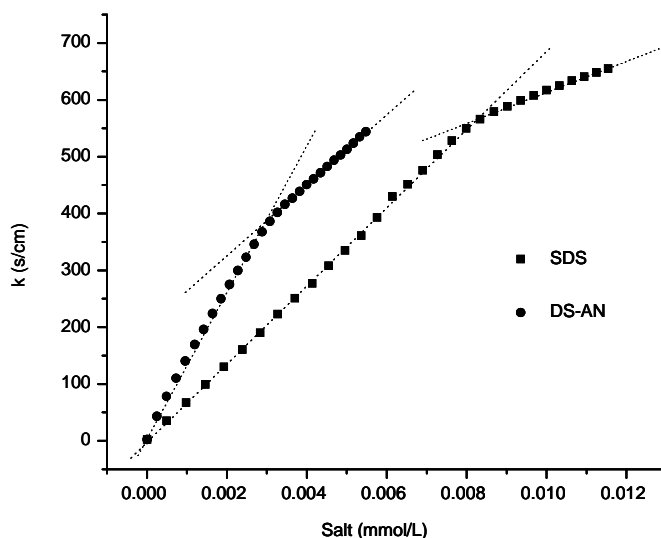
Figure 1. Curves of electrical conductivity (S/cm) versus surfactant concentration (mmol/L) for sodium dodecyl sulfate (SDS) and anilinium dodecyl sulfate (DS-AN)

Kinetics

Figure 2(a) illustrates conversion (%) versus time (min) profiles for the systems containing different concentrations of DS-AN. Final latexes conversions were in the range from 80 to 90 %. It is observed that the kinetic curves were dependent on surfmer concentration. This behavior is the commonly reported and is related to the dependence of the total particle surface area with respect to the surfactant concentration. These details of emulsion polymerization have been discussed deeply in literature [9]. Thus, at the very beginning of the polymerization, Interval I, the number of polymer particles formed (nucleation period) depends on the surfactant concentration. 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. Figure 2(b) shows the curves of rate of polymerization (mol/Lmin) versus time (min). As can be seen, the maximum values of the rate of polymerization were dependent on the concentration of surfactant, as mentioned above. These maximum values appeared during the first 15 min; it was also noticeable that the curves followed, at least in certain degree, the behavior suggested for the Smith-Ewart model [10]; i.e., the curves for the polymerizations at 10 and 20 mmol/L of DS-AN presented clearly the three Intervals of emulsion polymerization; however, with 40 mmol/L of DS-AN, Interval II was poorly perceptible. This was due to the high rate of polymerization at this concentration; in fact, as observed in Figure 2(a), the polymerization reached the maximum conversion during the first 20 min. So, the Interval II was very short and Interval III was reached rapidly.
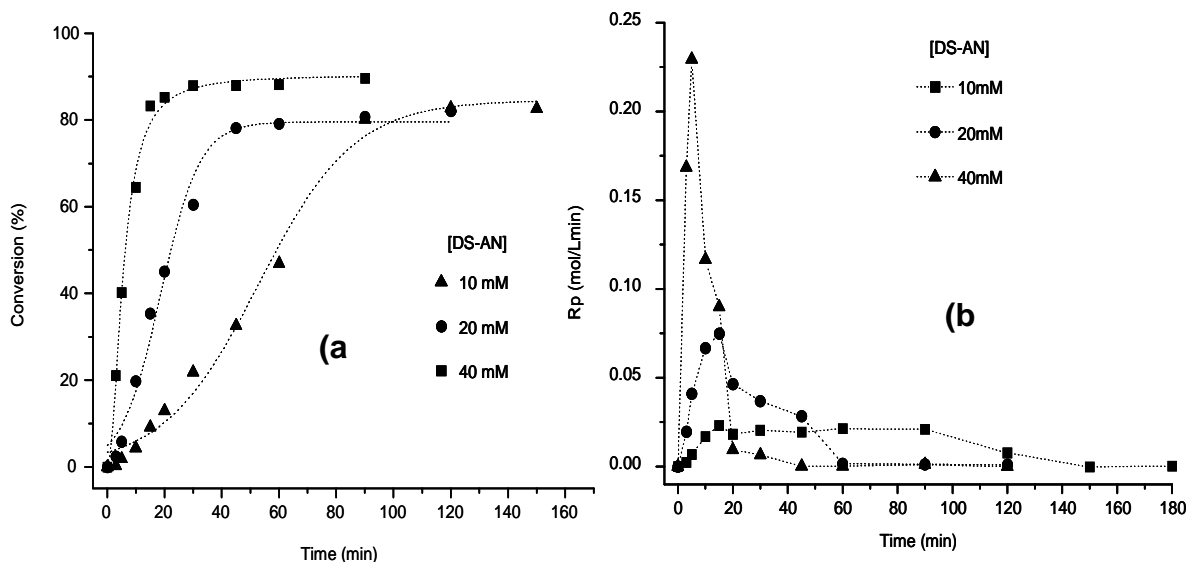
Figure 2. Curves of Conversion (%) versus time (min) (a) and curves of Rate of polymerization (mol/Lmin) versus time (min) (b) for the emulsion polymerizations stabilized with DS-AN at 10, 20 or 40 mmol/L

Shell synthesis

The second stage of the composite synthesis was performed via oxidative polymerization. With this technique the PANI shells were deposited. In this stage, only the latex with the highest content of surfmer was considered (40 mmol/L). Thus, more DS-AN was added as the monomers of PAni. The polymerizations were stable after 48 h and precipitation was not observed. In this stage, there were several changes in the appearance of the systems. At the very beginning of oxidative polymerization the latex was white; whereas that after ~10 min and ~15 min the latex turned pale yellow (leucoemeraldine) and dark blue (pernigraniline), respectively. Finally, after ~30 min the latexes acquired a dark green color (emeraldine salt), which varied very little thereafter. The observed changes in color were evidences of the different oxidative states of PAni. Figure 3 shows micrographs of the core-shell latexes; in the pictures it is clear that there was no formation of either clots or separated phase of PAni. This indicated that most of the PAni polymerized on the polymer particles surface. It is also important to emphasize that core-shell particles surface was rougher than in the pristine latex, showing the presence of the PAni shell. Besides, the particle diameters were in the order of 67 nm; that is, ~20% larger than the pristine latex (56 nm), which perfectly evidenced shell formation.

Conductivity

Conductivity measurements of the core-shell composites containing ~20 wt% of PAni were performed. For this, probes in the form of disk were prepared. The 4 pin probe procedure indicated conductivities (σ) of 10-4 and 10-3 S/cm for the composites; that is, in the range of semiconducting materials.
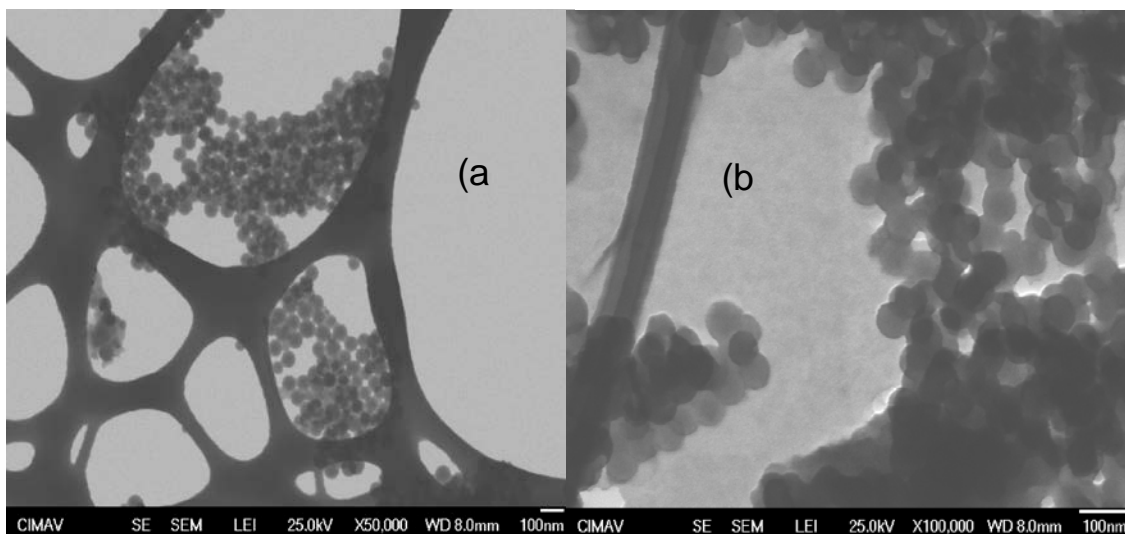
Figure 3. Micrographs of (a) latex particles of polystyrene (40 mmol/L) and (b) core-shell composite after oxidative polymerization.

Conclusions

The activity of anilinium dodecyl sulfate as surfmer was clearly evidenced in this work. Organic counterion manifested its presence by the reduction of the cmc with respect to the conventional salts. anilinium dodecyl sulfate was successfully employed as stabilizer in true emulsion polymerizations of styrene. Results suggested that this surfactant followed the mechanism of diffusion involved in emulsion polymerization. The function of anilinium dodecyl sulfate as surfmer was truly versatile, thus, the next features can be highlighted: (a) anilinium dodecyl sulfate allowed the synthesis the PAni shell via oxidative polymerization with no addition of acid and (b) no residuals of surfactant are needed to be eliminated, since each molecule of surfactant present in the system is potentially a monomer for PAni synthesis.

References

[1]. Guyot, A. Polymerizable surfactants. Curr. Op. Colloid Interf. Sci. 1996, 1, 580

[2]. Guyot, A. Adv. Colloid Interf. Sci. 2004, 108-109, 3

[3].Jiang, Z.; Du, Z. Colloid Polym. Sci. 2005, 283, 762

[4].Uzulina, I.; Zicmanis, A.S.; Graillat, C.; Claverie, J.; Guyot, A. J. Disp. Sci. Tech. 2002, 23, 799

[5].Lacroix-Desmazes, P.; Guyot A. Macromolecules 1996, 29, 4508

[6].Gracia, A.; Ghoulam, M.B.; Marion, G.; Lachaise, J. J. Phys. Chem. 1989, 93, 4167

[7].Li, P.; Jamson, M.; Bahadur, P.; Stilbs, P. J. Phys. Chem. 1989, 93, 6458

[8].Gamboa, C.; Rios, H. ; Sanchez, V. Langmuir 1994, 10, 2025

[9].Chern, C.S. Principles and Applications of Emulsion Polymerization. John Wiley and Sons, 2008

[10].Smith, W.V.; Ewart, R.H. J. Chem. Phys. 1948, 16, 592