Using an Inverse Surfmer in the Synthesis of Polystyrene / Polyaniline Core–Shell Composites. I. Kinetics and Morphology.

Claudia Hernández[1], *Alejandro Vega*[1], *Sergio Flores*[1], *Armando Zaragoza*[1]*.

1: Centro de Investigación en Materiales Avanzados, S.C. Chihuahua, Chih., México.

*armando.zaragoza@cimav.edu.mx

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 countercation, 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 towards 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. Analysis of composite microstructure, using electron microscopy and thermogravimetric analysis, confirmed the core–shell arrangement.

Keywords: Core–shell composite, Emulsion polymerization, Polyaniline, Surfmer.
Sesión: Nanocompuestos y materiales poliméricos compuestos.

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 (*Guyot, 1996*). This feature avoids surfactant desorption from the polymer particles and improves resistance to freezing and to shearing of the latex (*Guyot et al., 2004*). Most surfmers are susceptible to homopolymerization and copolymerization (*Jiang and Du, 2005*). However, maleic surfmers are only able to copolymerize (*Hevus et al., 2007*). Numerous reports have described state-of-the art over the years (*Asua and Schoonbrood, 1998*).

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 (*Âbele et al., 1997*). 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.

2 MATERIALS Y METHODS

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-methylpropionamidine) dihydrochloride (WAKO pure Chemical Industries, Ltd.) was recrystallized from a saturated aqueous solution at 60°C.

2.2 Methods

2.2.1 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 mol dm^{-3} of 2,2´-azobis(2-methylpropionamidine) 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.

2.2.2 Oxidative polymerization

The electrochemical performance was evaluated in a three-compartment cell equipped with the working electrode, an Ag/AgCl was used as the reference electrode, and a platinum wire was employed as the counter electrode.

The working electrode was prepared as follows: the composite suspension was dropped onto appropriated packed graphite-paste that was filled firmly into one end of a plastic tube, with a copper wire inserted through the opposite end to establish an electrical contact.

3 RESULTS AND DISCUSSION

3.1 Critical micellar concentration (cmc)

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 (*Mayers, 2006*). 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 (*Han et al., 2002; Yang et al., 2007*). However, the characterization and determi-nation of the cmc of analogue compounds to DS-AN have not been reported. The curves of electrical conductivity (*k*) (□S cm^{-1}) *versus* the surfactant concentration (mol dm^{-3}) of SDS and DS-AN, are shown in Fig. 1. The cmc for SDS was 7.9 mmol dm^{-3}. This value agreed well with those reported in the literature (*Gracia et al., 1989; Chang et al., 1998*). For DS-AN the cmc was 2.99 mmol dm^{-3}, which is ca. 2.6 times lower than the cmc of SDS. This change indicates that the effect of changing counter-cation was extremely important.

3.2 Emulsion polymerization kinetics

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 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 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 (*Chern, 2008*).

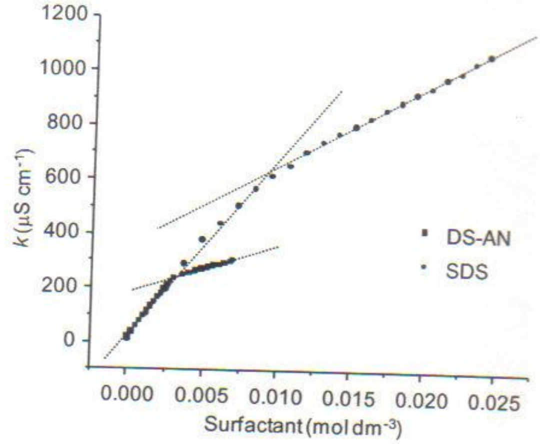

Fig. 1. Curves of electrical conductivity (μS cm^{-1}) *versus* surfactant concentration (mmol dm^{-3}) for sodium dodecylsulfate (SDS) and anilinium dodecylsulfate (DS-AN).

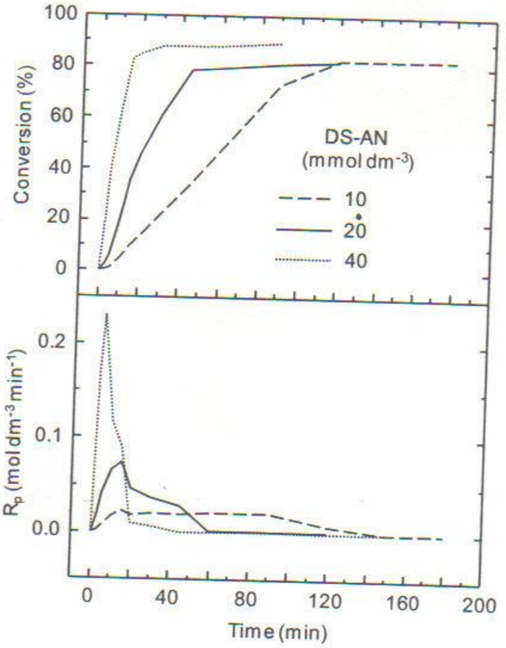

Fig. 2. Curves of conversion (%) *versus* time (min) (above), and curves of rate of polymerization (R_p) (mol dm^{-3} min^{-1}) *versus* time (min) (below), for the emulsion polymerizations stabilized with 10, 20, or 40 mmol dm^{-3} of DS-AN.