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Emulsion Polymerization of Styrene and Vinyl Acetate with Cationic Surfactant

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Summary: In this study, the emulsion homopolymerization system containing vinyl acetate and styrene, potassium persulfate, and a new cationic surfactant was studied in the classical glass emulsion polymerization reactor. The effects of new polymeric emulsifier on the physicochemical properties of obtained vinyl acetate and styrene latex properties were investigated depending on surfactant percentage in homopolymerizations.

Keywords: emulsion polymerization; lattices; stabilization; surfactants

Introduction

Conventional surfactants are typically characterized by a chemical structure that combines a hydrophilic group with one or two hydrophobic flexible alkyl chains of moderated length. In aqueous phase, small amounts of surfactant are enough to self-assemble into micellar microaggregates.

Important modifications on the micellar behavior have been observed by the total or partial substitution of the flexible alkyl chain by a rigid rodlike hydrophobic group.[1–2] For unconventional surfactants containing rigid hydrophobic groups it has been reported the formation of micellar microaggregates with a specific geometry.

Many studies have been carried out to analyze the effect of the type and amount of emulsifier in an emulsion polymerization, but in almost all cases anionic or anionic and nonionic mixed emulsifier systems are used.[3–9] However, the effect of the type and amount of cationic emulsifier in a cationic emulsion polymerization is reported in but a few cases.[10–14] Cationic latices have been presented in a few articles. In the majority of these studies, emulsifier-free emulsion polymerizations of cationic monomers with cationic initiators were investigated; conventional emulsion polymerizations and miniemulsions carried out with both cationic emulsifiers and initiators are reported in only few works.[10–14]

The search for new surfactants with improved emulsifying properties is also important for technical applications, since the common recipes still require large amounts of expensive materials.

The aim of this work was to study the effect of the concentration and type of cationic surfactant on the colloidal characteristics of a semi-continuous seeded cationic emulsion polymerization of styrene (St), and vinyl acetate (VAc).

Experimental Part

Materials

Vinyl acetate (VAc) and styrene (St) were used Merck purification. Stability of the latexes was achieved by cationic surfactant which chemical structure was given in Scheme 1. This substance was acted like a protective colloid because of given viscose solution even very low concentration, potassium persulfate (PPS) (Merck) was used as thermal initiator, and sodium bicarbonate

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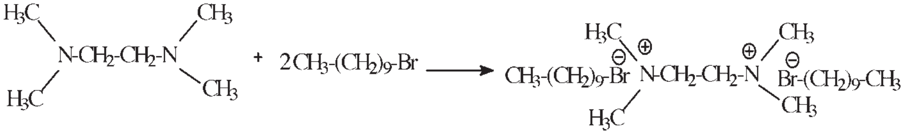

Scheme 1.
The production of the cationic surfactant.

(Merck) was used for adjusting the pH value of the polymerization media. All substances were used as received. Deionized water was used in all studies.

Preparation of the Cationic Surfactant

In this study, 10 ml of TMED (tetrametylene ethylenediamine) was added 20 ml of ether and 27.5 ml of decyl bromide was added to this solution. The reaction was preceded for 24 hour at room temperature. Precipitated solid product was filtered and was washed excess of ether. The product was dried under vacuum for 24 hour at room temperature. Reaction yield was found 33.3 g (90%).

Determination of the Critical Micelle Concentration (CMC)

For this purpose 0.513 g surfactant sample was dissolved in 20 ml water. This solution was placed in thermostat bath at 25 °C. 1 ml of water was added to polymer solution and the conductance was measured.

Emulsion Polymerization of Vinyl Acetate

The stability of the latexes was achieved by cationic surfactant. Semicontinuous emulsion polymerization was carried out in a 1 L three neck glass reactor equipped with a condenser, a dropping funnels and a mechanical stirrer having a constant speed of 400 rpm and a reflux condenser in a total batch period of 3 h. The polymerization was performed at 70 °C for different time depending of the surfactant value. PVAc was precipitated adding salt and the polymer was filtered and washed with excess of hot water to remove salt and surfactant.

Emulsion Polymerization of Styrene

Semicontinuous emulsion polymerization was carried out in a 1 L three neck glass reactor equipped with a condenser, a dropping funnels and a mechanical stirrer having a constant speed of 400 rpm and a reflux condenser in a total batch period of 3 h. Only 10% of the total monomer was introduced at the beginning of the reaction at 70 °C and the remaining monomer was added drop wise at 81 ± 2 °C from dropping funnels during the remaining time. Initiator was dissolved in a small amount of water and these freshly prepared initiator portions were added at 30 minute intervals throughout the reaction. Other procedures were repeated according to the procedure giving above.

According to the calculating results from solid contents as theoretical and practical, conversion changed between 99.3% and 99.8% for 3 hours polymerization time for both monomers.

Measurements

New synthesized polymeric surfactant was characterized by FT-IR and determining critic micelle concentration (CMC). Latexes were characterized by measuring Brookfield viscosity, viscosity average molecular weight (M_v), and surface tension of latexes to air.

Conversion was monitored gravimetrically. The original viscosities of the homopolymer latexes were determined by Brookfield Programmable DV-II model viscometer with spindle number 4 at 20 °C. M_vs of polymers were determined by capillary intrinsic viscometer using an Ubbelohde-type viscometer in an acetone solvent for polyvinyl acetate at 30 °C and a benzene solvent for polyvinyl acetate at 30 °C. Mark–Houwink constant values of VAc were used as $a = 0.72$ and $k = 1.02 \times 10^{-4}$ (dL/g)[15] and St were used as $a = 0.72$ and $k = 1.23 \times 10^{-4}$ (dL/g) in the calculations.[16] The surface tension measurements were performed on a Sigma 701 tensiometer (KSV instruments, Helsinki, Finland) equipped with a Pt du Nouy ring at 23.7 °C.

Results and Discussion

Preparation of the Cationic Surfactant

Cationic surfactant was prepared by the reaction between TMED and decyl bromide.

Characterization of the cationic surfactant was achieved mainly by FT-IR spectroscopy and critical micelle determination. The FT-IR spectrum of cationic emulsifier (Figure 1) was as expected, with bands for the alkyl group at 2900–2800 cm^{-1}. If FT-IR spectrum of surfactant was compared with TMED (Spectral Database for Organic Compounds, SDBS No: 2373) new bands were observed at 1170 cm^{-1} and 2992 cm^{-1} because of quaternization.

Determination of CMC of the Cationic Surfactant

Determination of CMC was performed by conductometrically at 25 °C. Critical micelle concentration of the cationic surfactant was determined as 2.14×10^{-4} g/mL from the Figure 2. Cationic surfactants are used in high limited in industrial emulsion polymerization, because of economical aspects. Studies concerning dimeric surfactants are focused on the relationship between surfactant structure and the critical micelle concentration by using the alkyl chain length and the chemical nature of the spacer as relevant parameters, on the effect of alkyl chain and spacer length on critical micelle concentration and micelle ionisation degree.[17]

The evolution of the Brookfield viscosity and viscosity average molecular weights of St and VAc polymer particles as a function of the surfactant concentration is shown in Table 1. In PVAc produces higher viscosity values than expected and this is clearly reflected in the stabilization of the already mentioned number of polymer particles (N_p), M_v, and particle size correlation. It should be mentioned that similar or even higher viscosity has been reported for the emulsion polymerization of styrene. One example is the correlation N_p and cationic surfactant reported by Vanderhoff et al.,[18]

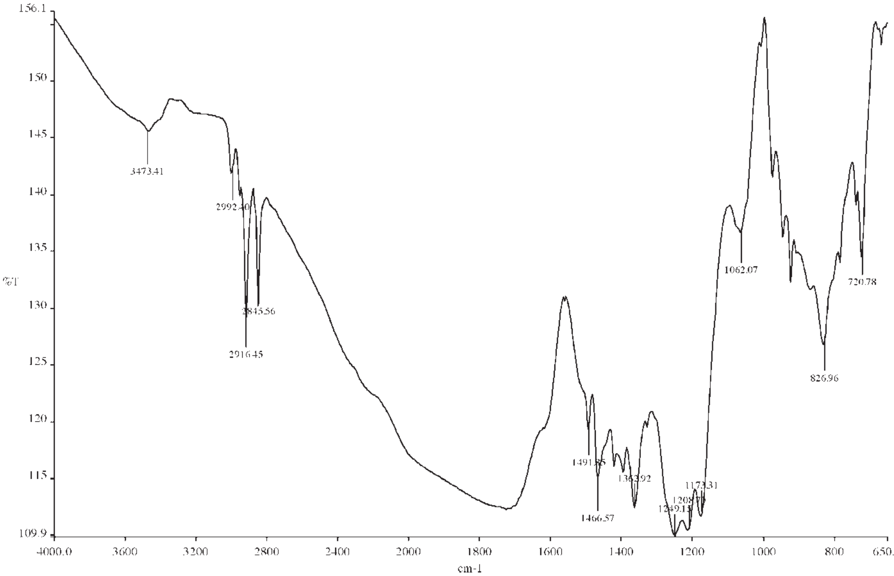

Figure 1.
FT-IR spectrum of cationic surfactant.

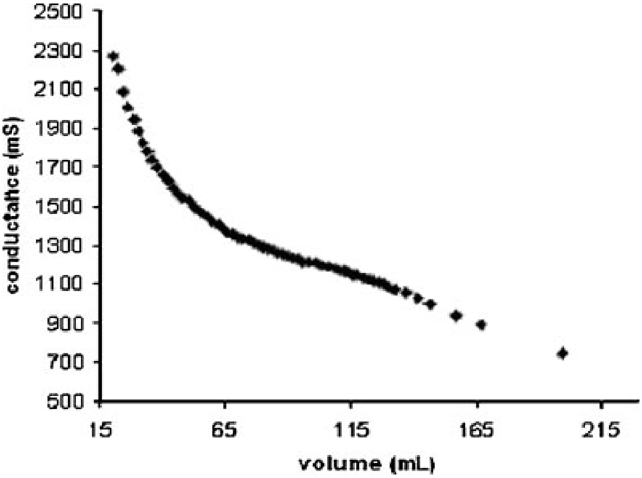

Figure 2.
Determination of critical micelle concentration of the new cationic surfactant.

Table 1.
The results from the experiments of the emulsion polymerization of styrene and vinyl acetate by using the cationic surfactant.

Polymer	Surfactant quantity (g)	Brookfield viscosity (cP)	Surface tension (mN/m)	M_v
PS (1.75 M)	0.4	0.78	31.107	$0.6 \cdot 10^6$
PVAc (2.2 M)	0.2	0.30	27.298	$0.8 \cdot 10^6$
PVAc (2.2 M)	0.4	0.95	39.776	$1.8 \cdot 10^6$

and Zaragoza-Contreras[19] for the emulsion polymerization of St using sulfonate type surface active agents as surfactants.

The surface tensions of polymer changed regularly with the increasing surfactant percentage in the VAc polymerization in Table 1. Surface tension depends on free emulsifier amounts in the latex, and the raising of this amount leads to the tendency of surface tension to increase. But emulsifier adsorption onto polymer particles cause to decrease free emulsifier concentration in latex, the increasing adsorption cause to increase surface tension of latexes. The increasing hydrophobic character into polymer causes to increasing emulsifier adsorption onto polymer particles. Thus the increasing of free emulsifier concentration in latex by blocking of emulsifier adsorption and the decreasing of polarity differences between interfaces cause to decrease the surface tension, especially for VAc latexes. These results are agreed well with Sarac et al.[20] data.

Conclusions

The features of the cationic polymerizations of styrene and vinyl acetate were analyzed by the consideration of the concentration of the emulsifier and the final viscosity of different latexes obtained from the polymerizations.

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