# Polymerizable and Nonpolymerizable Isophthalic Acid Derivatives as Surfactants in Emulsion Polymerization

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*Received January 26, 2000; Revised Manuscript Received July 11, 2000*

ABSTRACT: This article presents an initial study on the use of polymerizable and nonpolymerizable isophthalic acid derivatives as novel emulsifiers in emulsion polymerization. The polymerization process and the final latex properties are compared to latices made under the same conditions with commercial surfactants: sodium dodecyl sulfate (SDS) and potassium pentadecanoate (C15A). The use of the difunctional isophthalic acid appears to increase the stability of the polymer dispersion. This stabilization effect was further improved by introducing polymerizable derivatives. This kind of emulsion polymerization process is a new way of creating functional nanoparticles.

## Introduction

Emulsion polymerization is the most common process used in the production of dispersed polymers, called latices. These polymeric dispersions are used in a wide variety of applications such as adhesives, paints, coatings, diagnostic tests, drug delivery systems, thermoplastics, and synthetic rubbers.[1,2] A typical reaction mixture in emulsion polymerization consists of water, monomer, a water-soluble initiator, and an emulsifier. The role of the surfactant is fundamental in the stabilization of the starting emulsion as well as of the final latex.[3−7]

Conventional surfactants can freely adsorb or desorb from the latex particle in the final dispersion. This affects the stability of the polymeric dispersion, under certain conditions, such as shearing as well as during freezing−thawing cycles. During film formation when the polymer coalesces, the surfactant is able to migrate toward the surface of the film. This causes phase separation in the resulting film, so that one can find domains with a high surfactant[8,9] concentration. These film defects are the main cause of the water rebound in the film which is detrimental to the protection of the substrate against corrosion.[10]

In the process of polymer recovery via coagulation, the surfactants are wastewater pollutants and have a negative effect on the chemical oxygen demand (COD) and on the biological oxygen demand (BOD).[11]

In the past decade, methods have been proposed to improve the final latex stability. One of them is the covalent binding of the emulsifier to the polymer chain during the polymerization process. This can be achieved by using a polymerizable surfactant (surfmer),[12−18] which is a combination between a monomer and a surfactant. Recently, a number of articles have been published on the subject, showing the interest in reactive surfactants[19−22] as well as in reactive macroemulsifiers.[23,24]

Derivatives of isophthalic acid have been used as model compounds in the study of macroscopic supramolecular aggregates in various phases.[25,26] Some studies of water-soluble isophthalic acid derivatives have been made and indicate fiber formation from potassium 5-hexadecylisophthalate in water solutions,[27] but isophthalic acid derivatives have never been used as surfactants in emulsion polymerization.

It is possible to use the potassium salt of the isophthalic acid derivative as an anionic surfactant. The two carboxylate functions on each surfactant molecule would increase the surface charge of the final polymer particles. A higher charge on the particle surface improves the dispersion stability. This is explained with the high electrostatic repulsion of charged particles.[28] The stabilizing effect can be further improved with the use of polymerizable isophthalic acid derivatives, because these cannot desorb freely from the surface.

The main interest in the use of 5-alkoxyisophthalic acid derivatives as surfmers is the easy possibility to functionalize the final latex particle for different medical or biological applications, by functionalization of some of the carboxylate functions present at the particle surface. This aspect will be part of a further publication.

## Experimental Section

**Materials.** All solvents were distilled before use. Water was deionized and subsequently purified by a Milli-Q water purification system. Styrene, *n*-butyl acrylate, and *n*-butyl methacrylate were distilled from $CaH_2$ under reduced pressure and then stored at −20 °C under argon atmosphere. 1,10-Dibromodecane was distilled under reduced pressure before use. 5-Hydroxyisopthalic acid, 1-bromoalkanes (Aldrich), and *p*-chloromethylvinylbenzene (Polyscience) and all other chemicals are commercially available and were used without further purification.

**Analytical Methods.** The cmc's of the surfactants were measured with the conductometric titration method. The cmc's of SDS and C15A at 25 °C were $9.0 \times 10^{-3}$ and $3.3 \times 10^{-3}$ mol/L, respectively.[29] The particle size was determined with dynamic light scattering (Malvern Zetasizer 5000) or transmission electron microscopy (Zeiss EM 902).

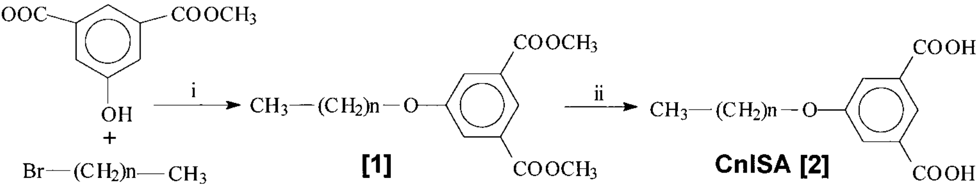
$^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker (300 MHz, 75 MHz) spectrometer.

For the measurement of the overall conversion of the monomer vs time samples of known weight were taken at given times from the polymerization vessel by a hypodermic syringe. The samples were discharged in a flask, chilled in a liquid nitrogen bath, to inhibit further polymerization and freeze-dried at room temperature under high vacuum (pressure ≤ 0.1 mbar). The conversion was then determined gravimetrically.

The conversion of the polymerizable surfactant was determined by the following procedure. The samples were weighted and afterward acidified by adding 1 mL of 1 N HCl solution. These probes were then immediately chilled in a liquid

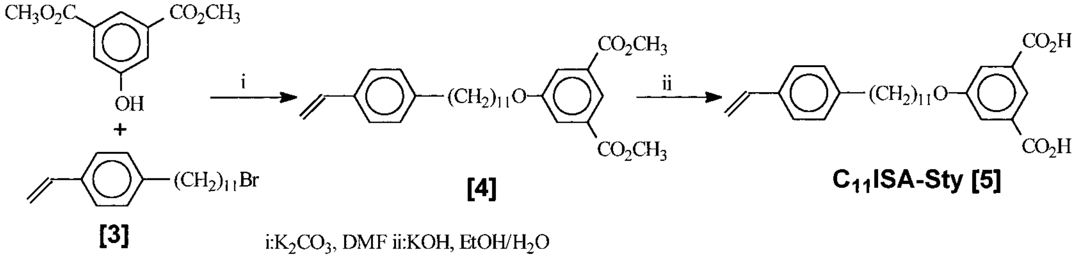
10.1021/ma000139u CCC: $19.00 © 2000 American Chemical Society
Published on Web 09/21/2000

**Scheme 1. Synthesis of the Isophthalic Acid Derivative (CnISA)**



i = $K_2CO_3$, DMF; ii = KOH, $EtOH/H_2O$

**Scheme 2. Synthesis of the Polymerizable Surfactant ($C_{11}$ISA-Sty)**



i:$K_2CO_3$, DMF ii:KOH, $EtOH/H_2O$

nitrogen bath, followed by lyophilization. Of the resulting dry copolymer powder 10 mg was dissolved in 2 mL of THF-$d_8$. The intensity of the triplet signal of the $-OCH_2$ group ($\delta$ = 4.01 ppm) in the surfactant (polymerized and nonpolymerized) was compared with that of the hydrogen doublet signal of the vinyl group ($\delta$ = 5.16 and 5.68 ppm).

The stability of the latices against electrolytes was studied by pouring 20 $\mu$L of latex into 10 mL of $CaCl_2$ or KCl solution of different concentration. The turbidity of these solutions was compared visually with samples diluted with pure water. For the latices made by copolymerization of the polymerizable surfactant with styrene, *n*-butyl acrylate, and *n*-butyl methacrylate, the increase of the particle size as a function of the KCl concentration was determined using a particle sizer (Malvern Zetasizer 5000).

**Surfactant Synthesis. a. 5-Alkoxyisopthalic Acid Nonpolymerizable Derivatives (2).** The synthesis of the 5-alkoxyisopthalic acid derivatives ($C_n$ISA, where *n* is the number of C atoms in the alkyl chain) **(2)** is described elsewhere[30] (Scheme 1). The synthesis involves the reaction between dimethyl 5-hydroxyisophthalate and *n*-alkyl-1-bromides ($C_nH_{2n+1}Br$) in the presence of $K_2CO_3$ in DMF, followed by the hydrolysis of the ester **(1)** performed in a solution of potassium hydroxide in ethanol and water.

**b. 5-Alkoxyisopthalic Acid Polymerizable Derivative (5).** The synthesis of 5-((4-styryl)undecyl)oxy)isophthalic acid ($C_{11}$ISA-Sty) **(5)** was performed in three steps (Scheme 2).

**c. 1-Brom-11-(4-styryl)undecane.** 1-Brom-11-(4-styryl)-undecane **(3)** was prepared by cross-coupling vinylbenzylmagnesium chloride with 1,10-dibromodecane using the workup described by Tomoi.[31,32] The distillation of the 1-brom-11-(4-styryl)undecane **(3)** was carried out at 145 °C/0.01 mbar. This gave a yield of only 30% before the residue polymerized. The further reactions between 1-brom-11-(4-styryl)undecane **(3)** and dimethyl-5-hydroxyisophthalate and the hydrolysis of the ester **(4)** occurred in analogy to the reactions mentioned in the Scheme 1 for the synthesis of $C_n$ISA **(2)**.

**d. 5-(11-(4-Styryl)undecyl)oxydimethyl Isophthalate (4).** Dimethyl-5-hydroxyisophthalate (22.2 mmol) and potassium carbonate (74 mmol) were stirred in 100 mL of dimethylformamide (DMF) for 1 h at 60 °C under an argon atmosphere. To this mixture was added a solution of 1-brom-11-(4-styryl)undecane **(3)** (14.8 mmol) in 20 mL of DMF. The mixture was stirred for 6 h. The solvent was evaporated, and the residue was mixed with water and extracted with dichloromethane (five times with each 100 mL). The combined organic layers were dried over magnesium sulfate and evaporated. The pure product was isolated by flash chromatography using dichloromethane as eluent.

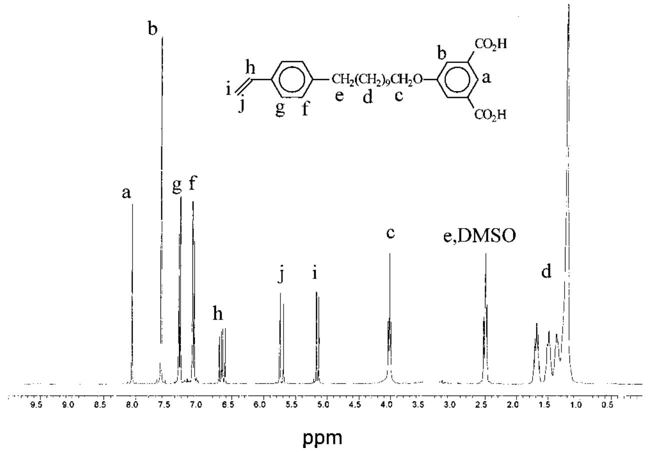


**Figure 1.** $^1H$ NMR spectrum of $C_{11}$ISA-Sty in DMSO-$d_6$ (300 MHz).

**e. 5-((4-Styryl)undecyl)oxy)isophthalic Acid (5).** To a solution of 5-(11-(4-styryl)undecyl)oxydimethyl isophthalate **(4)** (13.7 mmol) in 100 mL of ethanol/water = 8/2 was added potassium hydroxide (70 mmol). The mixture was stirred at 60 °C overnight. After cooling, the reaction mixture was concentrated and acidified with concentrated HCl to pH 2. The white solid obtained was filtered and dried under high vacuum. The crude acid, $C_{11}$ISA-Sty **(5)**, was recrystallized from methanol for an overall yield of 23%.

$C_{11}$ISA-Sty. $^1H$ NMR, 300 MHz (Figure 1) (DMSO-$d_6$): $\delta$ (ppm) = 1.2−1.55 (m, 14H, alkyls); 1.5−1.7 (m, 2H, alkyls); 1.83 (m, 2H, $-CH_2-CH_2-O-Ph$); 2.49 (t, 2H, $-CH_2-Ph$, $J_{H-H}$ = 7.6 Hz); 4.02 (t, 2H, $-CH_2-O-Ph$, $J_{H-H}$ = 6.5 Hz); 5.16 (d, 1H, Ph−CH=$CH_{trans}H_{cis}$, $J_{H-H}$ = 11.1 Hz); 5.72 (d, 1H, Ph−CH=$CH_{trans}H_{cis}$, $J_{H-H}$ = 17.6 Hz); 6.68 (dd, 1H, Ph−CH=$CH_{trans}H_{cis}$, $J_{H-H}$ = 11.1, 17.5 Hz); 7.11 (d, 2H, phenyl, $J_{H-H}$ = 8.0 Hz); 7.33 (d, 2H, phenyl, $J_{H-H}$ = 8.0 Hz); 7.61 (s, 2H, phenyl−$C_4H$); 8.07 (s, 1H, phenyl−$C_2H$).

$C_{11}$ISA-Sty. $^{13}C$ NMR, 75 MHz, (DMSO-$d_6$): $\delta$ (ppm) = 25.5, 28.6, 28.7, 28.8, 29.1, 29.4, 30.1, 35.0, 39.7, 68.2 (alkyl); 113.2, 126.2, 128.6, 134.7, 136.7, 142.3 (styrene); 119.2, 122.3, 132.8, 158.9, 166.6 (isophthalic).

Anal. Calcd for $C_{27}H_{34}O_5$: C, 73.95; H, 7.81. Found: C, 73.89; H, 7.86.

**Emulsion Polymerization Procedure.**[19] The emulsion polymerization of different monomers (styrene, *n*-butyl acrylate, *n*-methyl acrylate) using $C_{16}$ISA as surfactant was studied and compared with the emulsion polymerization using commercial surfactants such as sodium dodecyl sulfate (SDS)

**Table 1. Cmc at 25 and 50 °C for the Potassium Salts of the Isophthalic Acid Derivatives Synthesized**

| | cmc (mol/L)[a] | |
|---|---|---|
| surfactant | 25 °C | 50 °C |
| $C_8$ISA | $8.7 \times 10^{-2}$ | $>0.1$ |
| $C_{11}$ISA | $2.2 \times 10^{-2}$ | $3.2 \times 10^{-2}$ |
| $C_{13}$ISA | $1.1 \times 10^{-2}$ | $1.9 \times 10^{-2}$ |
| $C_{16}$ISA | $2.7 \times 10^{-3}$ | $3.5 \times 10^{-3}$ |
| $C_{18}$ISA | | $1.25 \times 10^{-3}$ |
| $C_{11}$ISA-Sty | $6.6 \times 10^{-3}$ | |

[a] Determined by conductometric titration.

($\mathrm{cmc}_{35-80\ °C} = 1.1 \times 10^{-2}$ mol/L) and potassium pentadecanoate ($C_{15}$A) (cmc = $3.3 \times 10^{-3}$ mol/L).[33]

The emulsion polymerization process was carried out in a batch method. The reaction vessel was a 250 mL three-neck glass flask equipped with a mechanical stirrer (stirring speed 600 rpm), a dropping funnel, and a reflux condenser in an argon atmosphere. The flask was charged with surfactant, 1 N KOH (1.25 equiv for each acid group) solution, and 97 mL of water. The solution was heated at 50 °C, and the monomer (20 g) was added dropwise within 10 min under stirring. The emulsion was deoxygenated by bubbling argon for 30 min. Finally, a solution of potassium peroxydisulfate ($K_2S_2O_8$) (0.5 mol % relative to the monomer) in 10 mL of deoxygenated water was added rapidly via dropping funnel. The conversion was controlled for the first 5 h. To complete the polymerization of the monomers, the reactor was heated under argon for another 15 h. This gives a total reaction time of ca. 20 h. After the polymerization the pH of the reaction mixture reached a value between 8 and 9. (The high amount of KOH ensures this basic pH and the stability during polymerization.)

## Results and Discussion

**Surfactants.** The 5-alkoxyisopthalic acid derivatives prepared and studied as surfactants in this publication are $C_8$ISA, $C_{11}$ISA, $C_{13}$ISA, $C_{16}$ISA, and $C_{18}$ISA **(2)**. The polymerizable isophthalic acid derivative prepared is the 5-(11-(4-styryl)undecyloxy)isophthalic acid ($C_{11}$ISA-Sty) **(5)**.

The surfactants have been characterized by determining their critical micellar concentration (cmc). The isophthalate derivatives solutions in water were obtained by the addition of 2.5 equiv of KOH to neutralizate the two carboxylic functionalities. We used more then 1 equiv of base for each −COOH group to avoid the formation of superstructures, like those found by Menger et al.[34] The cmc values obtained are listed in Table 1. The potassium 5-octadecylisopthalate salt ($C_{18}$ISA) **(2)** is not soluble in water at 25 °C so that the cmc could only be measured at 50 °C. The empirically found equation $\log \mathrm{cmc} = A - Bn$,[35] with $A$ and $B$ being two constants for a homologous serie of surfactants and $n$ the number of C atoms in the alkyl chain, could be verified for the five potassium 5-alkoxyisophthalate salts ($C_n$ISA) **(2)** synthesized in this work. The value of $B$ (0.185) is comparable and in good agreement with the value observed for another dipotassium carboxylate salt, the potassium $n$-alkyl malonates ($B = 0.219$, $A = 1.3$).[36] However the value of $A$ (0.42) is lower. This can be attributed to the presence of the phenyl ring in the chemical composition of these isophthalic acid derivatives.[37] Comparing the cmc of $C_{11}$ISA-Sty with the cmc of $C_n$ISA, it appears that the cmc of $C_{11}$ISA-Sty is lower than that of $C_{13}$ISA but higher than that for $C_{16}$ISA (Table 1). This is in relatively good agreement with the literature, considering a phenyl group to be roughly equivalent in its effect on the cmc to three and a half methylene groups.[38]

$C_{16}$ISA was used as nonpolymerizable surfactant in emulsion polymerization because its solubility at 25 °C is very good, and it has at this temperature the lowest cmc among the homologue series. The latices obtained were compared with the polymer dispersions made with $C_{15}$A and SDS as surfactants. $C_{15}$A was chosen because it appeared appropriate to compare the effect of a monocarboxylate surfactant with a dicarboxylate surfactant, whose cmc is almost equal (cmc $C_{16}$ISA = $3.5 \times 10^{-3}$ mol/L, cmc $C_{15}$A = $3.3 \times 10^{-3}$ mol/L) in the emulsion polymerization process. SDS was used because it is one of the most used surfactants in the industrial emulsion polymerization process.

**Emulsion Polymerization with Nonpolymerizable Surfactant.**[9] A first set of experiments was carried out with ca. 16% solid content in the polymerization mixture with styrene as monomer and different amounts of surfactant ($C_{16}$ISA, $C_{15}$A, or SDS). The experimental data obtained and the recipes for the corresponding experiments are reported in Table 2. The conversion curves (Figure 2) show a very rapid polymerization of styrene with $C_{16}$ISA as surfactant. The conversion of styrene is a little faster when the amount of surfactant ($C_{16}$ISA) is increased. In the concentration range we used (above the cmc), the conversion kinetics is essentially independent of the surfactant concentration. After 40 min of polymerization, quasi-total conversion is observed even if the amount of surfactant is quite low.

It can be seen that after 5 h the conversion of the monomer in the system with SDS or in that with $C_{16}$ISA is practically 100%, but in the case of $C_{15}$A it is only 50%. In all cases, the particle size increased when the amount of surfactant decreased. The values of the particle size given by TEM are smaller than those measured by dynamic light scattering. This fact is mentioned in the literature[39] as an effect of the absorbed surfactants and the electrical double layers, which may become significant for small particle sizes because of the shrinkage of the dried particles in the electron beam.[40]

Comparing the particle sizes in the resulting latex made with $C_{16}$ISA with the sizes of the polymer latices obtained with SDS, it appears that the particles stabilized by $C_{16}$ISA are smaller (at the same concentration of surfactant utilized). One possible explanation for the smaller particles and for the rapid polymerization is the structure of $C_{16}$ISA with the two carboxylic functionalities on the hydrophilic head that allow a strong electrostatic stabilization of the latex particles (higher surface charge) so that less surfactant molecules are necessary to stabilize one particle. Another explanation of this phenomenon might be the larger hydrophobic group of $C_{16}$ISA compared to those of SDS or $C_{15}$A which could cause a more efficient adsorption. These observations could also be explained by the strong ionic repulsion occurring at the surface of the particle with $C_{16}$ISA as surfactant.[40] This would lead to a system in which an increased number of smaller particles are formed so that the nucleation is very rapid and the polymerization takes place in a shorter time than for the system with $C_{15}$A or SDS.

Using the recipe of run 2 but adding different amounts of initiator, we were able to change the particle size of the polymer latices. The diameter of the particles increases with the reduction of the quantity of initiator. We obtained particles with 57 nm (0.5 mol % initiator vs monomer), 65 nm (0.25 mol %), and 72 nm (0.15 mol %).

**Table 2. Results of the Polymerization Experiments**[a]

| | $C_{16}$ISA | | | | SDS | | | C15A | | |
|---|---|---|---|---|---|---|---|---|---|---|
| run | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| surfactant[b] | 2.5 | 2 | 1.25 | 0.625 | 2.5 | 1.25 | 0.625 | 2.5 | 1.25 | 0.5 |
| conv (%)[c] | 100 | 100 | 99 | 100 | 100 | 99 | 98 | 82* | 60* | 50* |
| final size (nm)[d] | 46 | 54 | 57 | 60 | 75 | 93 | 102 | 80 | 86 | 97 |
| final size (nm)[e] | | | 38 | 43 | 67 | 76 | 86 | 58 | 72 | 85 |

[a] Data for styrene polymerization at 50 °C with 16% weight of styrene/water and $K_2S_2O_8$ (0.5 mol % relative to styrene). [b] Concentration in mol % relative to monomer. [c] Determined gravimetrically after 5 h polymerization, *: anyway 24 h after initiation we achieved 100% conversion. [d] By dynamic light scattering. [e] By transmission electron microscopy (TEM).

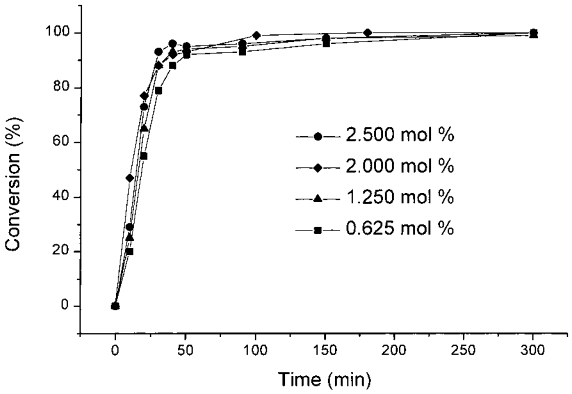


**Figure 2.** Conversion (determined gravimetrically) of styrene by using $C_{16}$ISA as surfactant at different concentrations (mol % relative to monomer).

**Table 3. Emulsion Polymerization of BA and BMA Using $C_{16}$ISA as Surfactant**[a]

| run | 11 | 12 |
|---|---|---|
| monomer | BA | BMA |
| surfactant[b] | 2 | 2 |
| fina conv (%)[c] | 95 | 100 |
| final size (nm)[d] | 79 | 80 |

[a] Data for polymerization at 50 °C with 16 wt % of monomer/water and $K_2S_2O_8$ (0.5 mol % relative to monomer). [b] Concentration in mol % relative to monomer. [c] Determined gravimetrically after 5 h polymerization. [d] By dynamic light scattering.

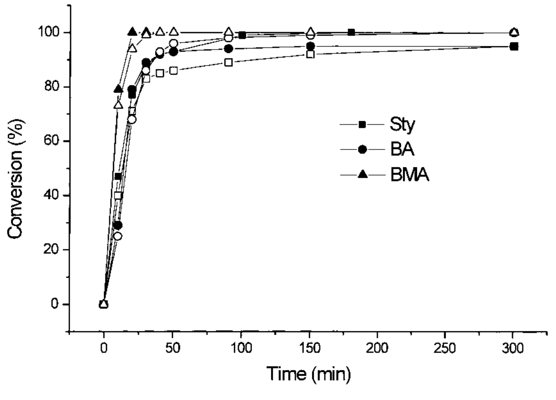


**Figure 3.** Conversion (determined gravimetrically) of the monomers using 2 mol % (vs monomer) $C_{16}$ISA (solid symbols) and $C_{11}$ISA-Sty (open symbols) as surfactant.

Using $C_{16}$ISA as surfactant, other monomers such as *n*-butyl acrylate (BA) and *n*-butyl methacrylate (BMA) were also polymerized. The results of these processes are listed in Table 3, and the conversion curves are shown in Figure 3. The conversion curve of BA is similar to that of styrene, but the polymerization of BMA takes less time (after 20 min practically 100% conversion is observed).

**Emulsion Polymerization with Polymerizable Surfactant.** A second sequence of emulsion polymerization experiments has been carried out with the polymerizable surfactant $C_{11}$ISA-Sty. Styrene (S), *n*-butyl acrylate (BA), and *n*-butyl methacrylate (BMA) were copolymerized with the surfactant ($C_{11}$ISA-Sty) The recipes for the processes are presented in Table 4.

**Table 4. Emulsion Copolymerization of $C_{11}$ISA-Sty Surfactant with Monomers**[a]

| run | 13 | 14 | 15 |
|---|---|---|---|
| monomer | S | BA | BMA |
| surfactant[b] | 2 | 2 | 2 |
| fina conv (%)[c] | 95 | 100 | 100 |
| final size (nm)[d] | 62 | 78 | 76 |
| final size (nm)[e] | 58 | | |
| surface tension (mN/M) | 70 | 67.8 | 68.8 |

[a] Data for polymerization at 50 °C with 16 wt % of monomer/water and $K_2S_2O_8$ (0.5 mol % relative to monomer). [b] Concentration in mol % relative to monomer. [c] Determined gravimetrically after 5 h polymerization. [d] By dynamic light scattering. [e] By TEM.

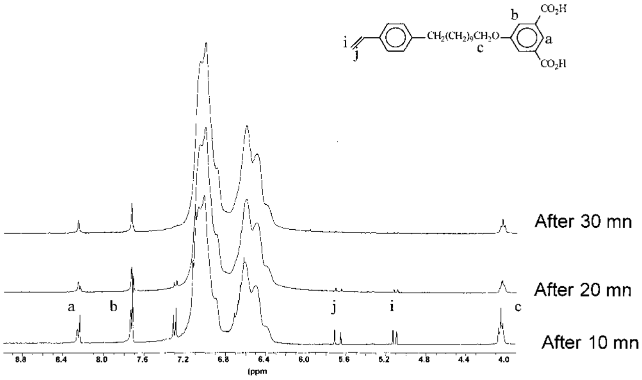


**Figure 4.** $^1$H NMR data of the styrene−$C_{11}$ISA-Sty copolymerization (300 MHz).

A complete or quasi-complete conversion of the monomer was observed for all runs, but the polymerization kinetics of BMA with the polymerizable surfactant were faster (as it was also for the $C_{16}$ISA surfactant too) than that of BA or S (Figure 3).

With $C_{11}$ISA-Sty the particle sizes were smaller than in the case of $C_{16}$ISA. The size distribution measured by dynamic light scattering indicates a monomodal and narrow size distribution for all latices and small particles with diameters below 80 nm.

The $C_{11}$ISA-Sty conversion vs time during the copolymerization process was established by $^1$H NMR measurements (Figure 4). The comparison of the $^1$H NMR spectra (Figure 1 with Figure 4) shows that each singlet, at $\delta = 8.25$ and 7.70 ppm (corresponding to the hydrogen on the isophthalic phenyl ring, $H_a$ and $H_b$ in Figure 1), is split into two distinct peaks (Figure 4). These signals correspond to a mixture of polymerized and nonpolymerized surfactant. During the emulsion polymerization process, the intensity of the nonpolymerized surfactant signal decreased. Thus, it was possible to follow the

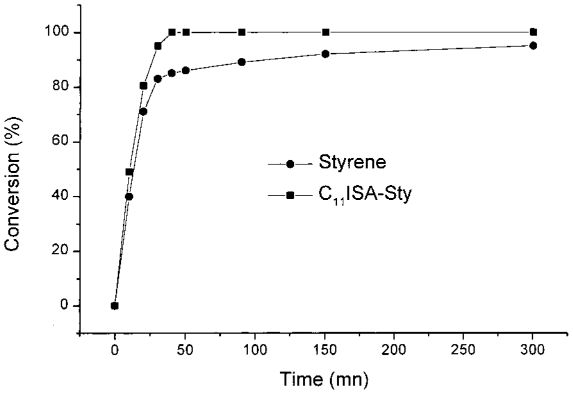


**Figure 5.** Conversion (determined gravimetrically) of the styrene and $C_{11}$ISA-Sty during the copolymerization.

copolymerization of the surfactant with styrene as illustrated in Figure 5. As can be seen, the polymerization of the $C_{11}$ISA-Sty derivative is faster than that of styrene.

The same procedure was used for the study of the $C_{11}$ISA-Sty copolymerization with BA and BMA. The surfactant was completely polymerized after 10 min. This suggests for $C_{11}$ISA-Sty that an high amount of it is buried in the polymeric particle. In the case of the BA copolymerization a conversion of 25% of BA was observed after 10 min with a 100% conversion of surfactant at the same time. For the BMA, the same observations were made with higher conversion rates (in the same time) for the monomer as well as for the surfactant. However, the surfactant conversion after 10 min was also 100%. One could conclude that some amount of surfactant homopolymerizes and forms water-soluble polyelectrolytes in accordance with findings made in the literature.[41] But the surface tension of the system after the polymerization reaches values up to 70 mN/m. According to the literature,[19,33] that means that all of the surfmer is incorporated in the latex particles, but some of it is buried inside the particle and does not contribute to the stabilization of the final particle.

**Latex Stability.** Under ambient conditions stable latices were obtained for the majority of runs. The polystyrene latices with $C_{16}$ISA were stable for at least 6 months, except the latex from run 1, where there could be separated aggregated polymer after a few days. The latices from runs 11 and 12 where unstable, and the polymer started to precipitate within a few hours.

Exposure to stress by freezing and thawing is followed by a complete precipitation of the latices prepared with the nonpolymerizable surfactant. In contrast, poly(*n*-butyl acrylate) and poly(*n*-butyl methacrylate) latices made with the surfmer $C_{11}$ISA-Sty could be partially redispersed after thawing. A surprising result was the total redispersion after thawing of the polystyrene latex made with $C_{11}$ISA-Sty. The absence of solids after the filtration of the latex confirms this total redispersion, thus demonstrating an improved stability of the latices when the polymerizable surfactant is used. The total redispersion of the poly(styrene-$C_{11}$ISA-sty) copolymer suggests that the surfmer is distributed statistically on the surface of the latex particle, and this implies that the copolymerization (styrene/surfmer) occurs statistically.

In contact with $CaCl_2$ solutions of different concentrations the latices made with $C_{15}$A, SDS, and ISA derivatives (polymerizable and nonpolymerizable) started to flocculate at a concentration of $10^{-2}$ mol/L $CaCl_2$. The low stability against $CaCl_2$ solutions could be explained by the selective binding of calcium ions to the carboxyl groups at the surface of the particles. All polystyrene latices made with $C_{16}$ISA were stable against KCl solutions up to a concentration of salt of 0.4 mol/L, but less stability was observed for the latices made with $C_{15}$A and SDS that started to flocculate respectively at a concentration of 0.2 and 0.3 mol/L. Furthermore, improved stability was observed for all polymeric dispersions made with $C_{11}$ISA-Sty. For the resulting copolymers the variation of the particle size was measured using dynamic light scattering (Figure 6). The particle size increased with the increase of the concentration of KCl salt until the flocculation concentration was reached.

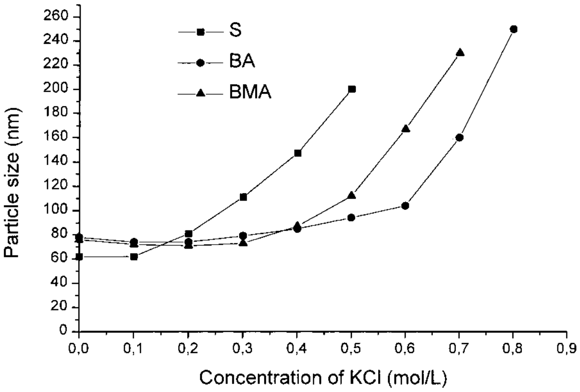


**Figure 6.** Particle size (determined by dynamic light scattering) of the latices made with $C_{11}$ISA-Sty as a function of the KCl concentration.

## Conclusion

$C_{16}$ISA and $C_{11}$ISA-Sty are efficient surfactants in emulsion polymerization. They are able to produce latices with small particle sizes (40−80 nm). The particle sizes are smaller than those obtained with conventional emulsifiers such as SDS. The presence of two potassium carboxylate functions ($C_{16}$ISA) improved the emulsion polymerization conversion and stability, compared to the monopotassium carboxylate $C_{15}$A.

The reactive surfactant, capable to copolymerize with styrene, *n*-butyl acrylate, and *n*-butyl methacrylate, produces stable latices. In the special case of the styrene copolymerization, the copolymerization process seems to be statistic between surfactant and styrene, and a complete polymerization is observed. By using the reactive surfactant, an improvement of the stability compared to that obtained with the nonpolymerizable analogue was clearly observed. Future work will investigate the copolymerization process and the surface functionalization of these latex particles.

**Acknowledgment.** Financial support by the EU-Project (TMR) FMRX-CT 97-0099 Submicron Imaging and Stimulus Induced Transformation of Organic Molecular Adsorbates at Surfaces (SISITOMAS) is gratefully acknowledged.

## References and Notes

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(41) Research Network "Reactive Surfactants in Heterophase Polymerization" and the publications therein, sponsored by the European Union (Programme: Human Capital and Mobility, CHRX CT 930159).

MA000139U