100 | *Macromol. Symp.* **2010**, 296, 100–106 DOI: 10.1002/masy.201051015

Synthesis of New Anionic and Cationic Polymerizable Surfactants for Emulsion Polymerization of Styrene

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Summary: New anionic and cationic maleic surfmers containing a benzyl or p-vinylbenzyl hydrophobic tail were prepared and characterized. The behaviour of benzyl maleate hemiester in the emulsion polymerization process of styrene has been studied in the presence of potassium persulfate as initiator. The effect of surfmer concentration on particle diameter was particularly investigated.

Keywords: emulsion polymerization; isomerization; maleic; polymerizable surfactant; styrene; surfmer

Introduction

The use of polymerizable surfactants (surfmer) in polymerization in dispersed media lead to appreciable latexes in terms of colloidal stability, size, size distribution, surface charge density and surface functionality. These properties are due to the fact that the polymerizable moiety of surfmer is able to be directly incorporated in the polymer particles such as any comonomer and thus limiting their desorption from the final particles.[1–5]

Haut du Formulaire

Therefore, there have been a number of studies on the synthesis, characterization and polymerization of new surfmers. Various potential application fields could be considered such as: paints,[6] paper coatings, inks, textile sizing, adhesives, surfactant-templated silicates,[7] polymer nanocomposites,[8,9] biomedical field (bioconjugation)[10]...

Among the structures described, maleic surfactants turn out to be the most promising ones since they do not induce homopolymerization and are easy to prepare.[11]

The aim of this work is to report on the synthesis of new cationic and anionic maleic based surfmers bearing ammonium or carboxylic function (in the polar part) respectively and the preliminary evaluation of their behaviour in radical emulsion polymerization of styrene in the presence of potassium persulfate as initiator.

Experimental Part

Techniques

^{1}H and ^{13}C NMR spectra were recorded on a Brucker 300 MHz spectrometer. Tetramethylsilane was used as internal reference for chemical shifts. Infrared spectroscopy (IR) was carried out with a Jasco-4200 Fourier transform infrared spectrometer.

The melting points were determined with a Kofler bench apparatus.

Flash chromatographies were carried out using E-Merck silica gel (Kieselgel 60, 230–400 mesh) as the stationary phase. Thin layer chromatography was carried out on aluminum plates pre-coated with Merck silica gel 60F254 and visualized by quenching of UV fluorescence or by iodine vapour.

Materials

The solvents were dried and distilled before use. Reagents were purchased from Aldrich

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and used without further purification: benzyl alcohol, triethylamine, pyridine, dicyclohexylcarbodiimide (DCC), N,N-dimethyl-4-aminopyridine (DMAP), 3-bromopropanol, sodium dodecyl sulfate (SDS), potassium persulfate (KPS), maleic anhydride. 4-vinylbenzyl maleate (3b) was prepared as described in reference [12]. Styrene was washed (in order to remove inhibitor) with an aqueous solution of NaOH 5M than three times with water and stored at −20 °C. In all polymerization procedures deionized water was used.

Synthesis of Surfactants

Synthesis of Benzyl Maleate (3a)

In a round bottom flask fitted with a condenser, were introduced (20 mmol, 2 g) of maleic anhydride and (20 mmol, 2.2 g) of benzyl alcohol. The mixture was stirred at 80 °C for 24 hours. The precipitate formed was solubilised in dichloromethane then crystallized from hexane. White bright crystals of benzyl maleate *(3a)* (2.94 g, 70%) were obtained. Mp: 59-60 °C, Rf = 0.62 (CH_2Cl_2/EtOH: 11/5).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 5.29 (s, 2H, $C_6H_5C\underline{H}_2-$), 6.41 (s, 2H, $-C\underline{H}{=}C\underline{H}-$), 7.33-7.46 (m, 5H, C_6H_5), 11.9311111 11.93 (s, 1H, $COO\underline{H}$).

^{13}C NMR (300 MHz, $CDCl_3$, δ, ppm): 66.80, 126.00, 128.38- 129.24, 135.47, 136.52, 140.63, 165.31, 167.50.

IR (KBr, ν, cm^{-1}): 2950 (ν_{O-H}), 1639 ($\nu_{C=C}$), 1731 ($\nu_{C=O}$), 1265 ($\nu_{C\text{-}O}$)

Synthesis of 4-Vinylbenzyl Maleate (3b)

3b was prepared as described in reference [12].

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 5.18 (s, 2H, $\text{-}OC\underline{H}_2\text{-}$), 5.21 (dd, 1H, $-C\underline{H}_2 = C\underline{H}-$, $J_{cis} = 10.9$ Hz, $J_{gem} = 0.8$ Hz), 5.69 (dd, 1H, $-C\underline{H}_2{=}C\underline{H}-$, $J_{trans} = 17.6$ Hz, $J_{gem} = 0.8$ Hz), 11.93116.63 (dd, 1H, $CH_2{=}C\underline{H}-$, $J_{cis} = 10.9$ Hz, $J_{trans} = 17.6$ Hz), 6.32 (dd, 2H, $-C\underline{H}{=}C\underline{H}-$, $J_{cis} = 12.6$ Hz), 7.26-7.35 (dd, 4H, $\text{-}C_6\underline{H}_4\text{-}$, $J = 8.2$Hz), 9.30 (s, 1H, $COO\underline{H}$).

^{13}C NMR (300 MHz, $CDCl_3$, δ, ppm): 68.03, 114.79, 126.52, 128.68, 129.24, 130.06, 133.66, 136.17, 138.19, 166.66, 166.52.

Synthesis of Diesters of Maleic Acid (5a-b)

A typical reaction is as follow. In a round-bottomed flask fitted with a condenser, placed in a ice bath and stirred under an atmosphere of nitrogen, were dissolved (7 mmol, 1.44 g) of benzyl maleate (3a), obtained previously, in (56 mL) of anhydrous dichloromethane. (7 mmol, 1.44 g) of (DCC), (1.4 mmol, 0.18 g) of (DMAP) and (7.3 mmol, 1.02 g) of 3-bromopropanol were then added. The mixture was stirred at room temperature for 24 hours. The resulting solution was filtered to remove the dicyclohexylurea formed. The solution obtained is washed successively with HCl 10% (2 × 60 mL) saturated solution of $NaHCO_3$ (2 × 60 mL) and finally with water (1 × 60 mL). The brown oil obtained, was purified by silica gel chromatography using CH_2Cl_2/petroleum ether (4/1) as eluent. The diester (5a) was obtained as yellow oil in (1.64 g, 48%) yield.

(5a): Rf: 0.75 (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.16 (m, 2H, $O-C\underline{H}_2-C\underline{H}_2CH_2\text{-}$), 3.43 (t, 2H, $-C\underline{H}_2\text{-}Br$, $J = 6.0$ Hz), 4.27 (t, 2H, $C\underline{H}_2O-$, $J = 6.0$ Hz), δ = 5.23 (s, 2H, $C_6H_5C\underline{H}_2\text{-}$), 6.28 (s, 2H, $-C\underline{H}{=}C\underline{H}-$), 7.34-7.39 (m, 5H, C_6H_5);

^{13}C NMR (300 MHz, $CDCl_3$, δ, ppm): 29.20, 31.45, 63.41, 64.80, 125.90, 128.32-129.20, 134.29, 135.41, 139.03, 163.27, 165.40.

(5b): Yield: 56%, Rf: 0.74 (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.26 (m, 2H, $O-C\underline{H}_2-C\underline{H}_2CH_2\text{-}$), 3.47 (t, 2H, $-C\underline{H}_2\text{-}Br$, $J = 6.5$ Hz), 4.28 (t, 2H, $C\underline{H}_2O-$, $J = 6.5$ Hz), 5.22 (s, 2H, $\text{-}OC\underline{H}_2\text{-}$), 5.28 (dd, 1H, $C\underline{H}_2{=}C\underline{H}-$, $J_{cis} = 10.8$ Hz), 5.77 (dd, 1H, $C\underline{H}_2{=}C\underline{H}-$, $J_{trans} = 17.6$ Hz), 11.9311111 6.29 (dd, 2H, $-C\underline{H}{=}C\underline{H}-$, $J_{cis} = 11.9$ Hz), 6.73 (dd, 1H, $CH_2{=}C\underline{H}-$, $J_{cis} = 10.8$ Hz, $J_{trans} = 17.6$ Hz), 7.34-7.42 (dd, 4H, $\text{-}C_6\underline{H}_4\text{-}$, $J = 8.3$ Hz),

^{13}C NMR (300 MHz, $CDCl_3$, δ, ppm): 29.12, 31.43, 63.03, 66.89, 114.57, 126.44, 128.6-128.68, 134.62, 133.53, 136.22, 137.87, 164.59, 164.62.

Synthesis of Quaternary Ammonium Salts of Maleic Acid Diesters Derivatives (6a-b)

In a typical procedure, (2.4 mmol, 1eq) of diester previously synthesized (5a or 5b), (12 mmol, 1.25 g, 5eq) of triethylamine and (20 m g) of hydroquinone were placed in a round bottom flask fitted with a condenser and stirred at 60 °C for (2- 4) days. The product was obtained after several precipitations with diethyl ether or ethyl acetate.

(6a): brown oil, yield = 49% (4 days), Maleate/Fumarate: 50/50, ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.25 (t, 9H, $-N(CH_2-C\underline{H}_3)_3$, $J = 7.2$ Hz), 2.10 (m, 2H, $O-C\underline{H}_2-C\underline{H}_2CH_2-$), 3.26-3.43 (m, 8H, $-C\underline{H}_2-N^+(C\underline{H}_2-C\underline{H}_3)_3$), 4.26 (t, 2H, $C\underline{H}_2O-$, $J = 6.0$ Hz), 5.23 (s, 2H, $C_6H_5C\underline{H}_2$), 6.27 (dd, $-C\underline{H}{=}C\underline{H}-$*(Maleate)*, $J_{cis} = 11.9$ Hz), 6.77 (dd, $-C\underline{H}{=}C\underline{H}-$ *(Fumarate)*, $J_{trans} = 15.9$ Hz), 7.23-7.32 (m, 5H, $C_6\underline{H}_5$).

(6b): brown oil, yield = 27% (3days), Maleate/Fumarate: 67/33, ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.3 (t, 9H, $-N(CH_2-C\underline{H}_3)_3$, $J = 7.1$ Hz), 2.17 (m, 2H, $O-C\underline{H}_2-C\underline{H}_2CH_2-$), 3.32-3.55 (m, 8H, $-C\underline{H}_2-N^+(C\underline{H}_2-C\underline{H}_3)_3$), 4.33 (t, 2H, $C\underline{H}_2O-$, $J = 5.8$ Hz), 5.16 (s, 2H, $-OC\underline{H}_2-$), 5.22 (d, 1H, $C\underline{H}_2{=}C\underline{H}-$, $J_{cis} = 10.9$ Hz), 5.76 (d, 1H, $C\underline{H}_2{=}C\underline{H}-$, $J_{trans} = 17.6$ Hz), 6.31 (dd, $-C\underline{H}{=}C\underline{H}-$ *(Maleate)*, $J_{cis} = 11.9$ Hz), 11.93111116.69 (dd, $CH_2 = C\underline{H}-$, $J_{cis} = 10.9$ Hz, $J_{trans} = 17.6$ Hz), 6.84 (dd, 2H, $-C\underline{H}{=}C\underline{H}-$ *(Fumarate)*, $J_{trans} = 15.8$ Hz), 7.32-7.42 (dd, 4H, $-C_6\underline{H}_4-$, $J = 8.2$ Hz),

Synthesis of Pyridinium Salts of Maleic Acid Diesters Derivatives (7a-b)

In a typical procedure, (2.4 mmol, 1eq) of diester (5a or 5b), 12 mmol, (0.98 g, 5eq) of pyridine and (20 m g) of hydroquinone were stirred at 60 °C. After 3 days the reaction was stopped and the mixture was precipitated several times with ethyl acetate.

(7a): brown oil, yield = 39% (3days), Maleate/Fumarate: 81/19, ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.53 (tt, 2H, $O-C\underline{H}_2-C\underline{H}_2CH_2-$, $J = 5.8$ Hz, $J = 7.0$ Hz), 4.29 (t, 2H, $C\underline{H}_2O-$, $J = 5.8$ Hz), 5.08 (t, 2H, $-C\underline{H}_2-N^+-$, $J = 7.0$ Hz), 5.24 (s, 2H, $C_6H_5C\underline{H}_2$), 6.36 (dd, $-C\underline{H}{=}C\underline{H}-$ *(Maleate)*, $J_{cis} = 11.9$ Hz), 6.77 (dd, $-C\underline{H}{=}C\underline{H}-$ *(Fumarate)*, $J_{trans} = 15.8$ Hz), 7.33-7.38 (m, 5H, $C_6\underline{H}_5$), 8.06 (m, 2H, pyr-H_3/H_5), 8.49 (t, 1H, pyr-H_4, $J = 7.9$ Hz), 9.54 (d, 2H, pyr-H_2/H_6, $J = 5.7$ Hz).

(7b): brown oil, yield = 21% (3days), Maleate/Fumarate: 89/11, ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.51 (tt, 2H, $O-C\underline{H}_2-C\underline{H}_2CH_2-$, $J = 5.5$ Hz, $J = 7.1$ Hz), 4.29 (t, 2H, $C\underline{H}_2O-$, $J = 5.5$ Hz), 5.09 (t, 2H, $-C\underline{H}_2-N^+-$, $J = 7.1$ Hz), 5.20 (s, 2H, $-OC\underline{H}_2-$), 5.29 (d, 1H, $C\underline{H}_2 = C\underline{H}-$, $J_{cis} = 10.9$ Hz), 5.75 (d, 1H, $C\underline{H}_2 = C\underline{H}-$, $J_{trans} = 17.6$ Hz), 6.34 (dd, $-C\underline{H}{=}C\underline{H}-$ *(Maleate)*, $J_{cis} = 11.9$ Hz), 11.93111116.68 (dd, 1H, $CH_2 = C\underline{H}-$, $J_{cis} = 10.9$ Hz, $J_{trans} = 17.6$ Hz), 6.75 (dd, $-C\underline{H}{=}C\underline{H}-$ *(Fumarate)*, $J_{trans} = 15.8$ Hz), 7.32-7.39 (dd, 4H, $-C_6\underline{H}_4-$, $J = 8.2$ Hz), 8.07 (m, 2H, pyr-H_3/H_5), 8.50 (t, 1H, pyr-H_4, $J = 7.8$ Hz), 9.52 (d, 2H, pyr-H_2/H_6, $J = 5.6$ Hz).

Emulsion Polymerization

In a typical experiment, the polymerization was performed at 70 °C in a batch reactor at a constant stirring rotation. The reactor was charged with water (50 g), styrene (2.5 g) and surfactant (0.25g of 3a and 0.07 g of soda) then stirred for 15mn. The polymerization was started by introducing 500 μl of a KPS solution (0.83g of KPS dissolved in 10ml water). The polymerization reaction was conducted during 12 hours. Polymerization conversions were determined gravimetrically.

Particle Characterization

The hydrodynamic particle size (radius and diameter Rh and Dp respectively) and the polydispersity index (PDI) characterizing the width of the particle size distribution of the latexes were obtained by quasi-elastic light scattering using Zetasizer Nano-ZS from Malvern Instruments. The samples were highly diluted in deionised water and the temperature was well controlled during measurements.

Results and Discussion

Synthesis of Surfactants

Two series of surface-active monomers derivatives were prepared containing a benzyl or 4-vinylbenzyl hydrophobic tails and a hydrophilic part being the maleic carboxylic group or ammonium salts of triethylamine or pyridine (Scheme 1). One can expect that the introduction of the benzene ring into surfactant structure will increase the compatibility of surfmers with styrene monomer during the emulsion polymerization process.

The anionic surfmer (3a) has been prepared by acylation of equimolar quantity of alcohols (2a) with dicarboxylic acid anhydride at 80 °C during 24 hours. In the case of surfmer (3b), catalytic amount of N,N-dimethyl-4-aminopyridine was necessary in order to conduct the reaction at lower temperature (60 °C) and avoid the polymerization of styrene double bound.[12] Pure products were obtained, after recrystallization, and the yields were found to be in the range of 53–70%.

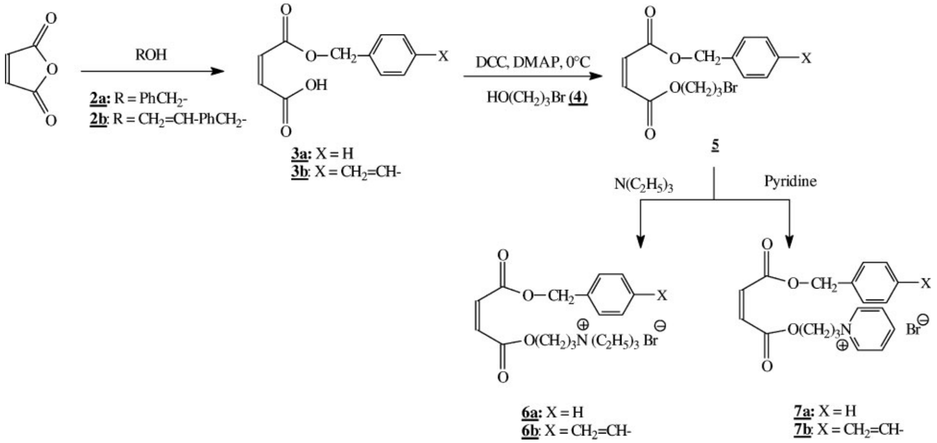
The purity of the hemiesters was examined by ^1H and ^{13}C-NMR. Special attention was focused on the isomeric purity preparation. The *cis* structure of the products was established by the resonance signal of CH=CH double bond of maleate at 6.41 ppm which is lower than that of fumarate homologous at 6.9 ppm. The proton coupling constant of the hydrogen in the maleate function $^3J = 12.6$ Hz is also typical of the cis-isomer, J of the trans-isomer being higher > 16 Hz.

Further O-alkylation of hemiesters (3a-3b) with 3-bromoprapan-1-ol using the Steglich method[13] led to the diesters of maleic acid (5a-b) after purification by chromatography on silica gel. In the same manner as previously discussed, ^1H-NMR demonstrates that no isomerisation of the double bond of maleate function occurred.

At last, these diesters were quaternized by triethylamine or pyridine at 60 °C during 3 days to give quaternary ammoniums salts. ^1H-NMR analysis showed in this case, the presence of two signals at 6.27–6.36 ppm with $^3J_{cis} = 11.9$ Hz corresponding to $C\underline{H}=C\underline{H}$ of maleic derivatives and at 6.75–6.84 ppm with $^3J_{trans} = 15.8$ Hz corresponding to the products resulting from its isomerization (fumaric derivatives).

Firstly, the purification process was considered as the origin of this isomerization (isomerisation after silica gel chromatography), but ^1H-NMR analysis of the obtained crude products showed that the percentage of two isomers is the same as after purification step.

The second parameter, which was examined, was the reaction time. When the time of quaternization reaction time was decreased to 2 days, the reaction yields are highly decreased but with low isomerisation of maleic double bond as reported in (Table 1). However, Even if the quantity of fumaric derivative is decreased, it still exists



Scheme 1.
Synthesis of anionic and cationic surfmers.

Table 1.
Characterization of quaternary ammonium derivatives of maleic acid.

Surfmer	R	Reaction time (days)	Yield (%)	M/F[a)]
6a	$PhCH_2$-	2	27	75/25
		3	41	60/40
		4	49	50/50
6b	$p-C\underline{H}_2=CHC_6H_4CH_2$-	3	27	67/33
7a	$PhCH_2$-	3	39	81/19
7b	$p-C\underline{H}_2=CHC_6H_4CH_2$	3	21	89/11

[a)] M/F: Maleate /Fumarate ratio determined with ^1H NMR.

and non-negligible. The opposite behaviour was observed when the reaction time was increased to 4 days. A maleic/fumaric ratio of 50/50 was obtained for surfmer (6a).

These results are unexpected; knowing that isomerization of the double bonds to fumarate takes place only under heating or in the presence of strong acids. Cationic surfmers homologous bearing alkyl hydrophobic tails (methyl, hexyl, decyl and dodecyl) and pyridiniums polar parts were prepared via the same process as reported by Sherrington and al. without any isomerisation of maleate double bond.[14]

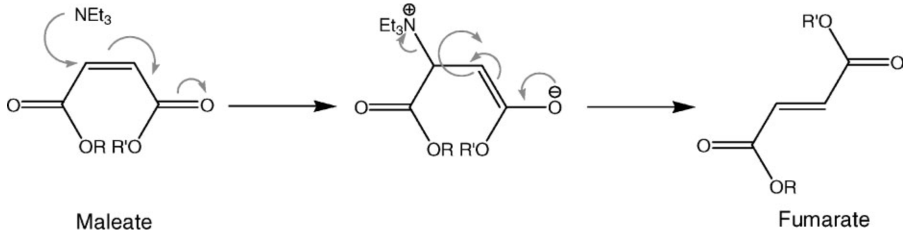
We presume that the rearrangement of Bayliss- Hillman [15] is probably responsible of such isomerisation: the amine used for the quaternization led to an opening of the maleic double bond, its rotation then its closing according to Scheme 2.

When pyridine was used as the quaternizing agent instead of triethylamine, a strong decreasing was observed in the percentage of fumarate isomer. Pyridine having a nucleophilic capacity less important than triethylamine and being more encumbered, the reaction of isomerization is limited.

Emulsion Polymerization

The critical micelle concentration of surfmer (3a) previously neutralized with NaOH, was determined by conductimetry (Figure 1). The CMC shown to be about 1.54 g/l, i.e., 7.5 mmol/l which correspond to a dissociation degree $\alpha=98\%$ and micellization free energy $\Delta G^\circ{}_m=-13.4$ Kj/mol. This measurement confirms that this monomer is a potential candidate for emulsion polymerization reactions.

Thus, preliminary experiments in batch emulsion polymerization of maleate hemiester (3a), previously neutralized with NaOH, with styrene have been carried out at 70 °C in order to appreciate it further potential. Potassium persulfate was chosen as a radical initiator. The concentration of surfactant introduced into the reaction media was varied from 3.39 to 24.27 mmol/l and the influence of surfactant



Scheme 2.
Rearrangement of Bayliss-Hillman.

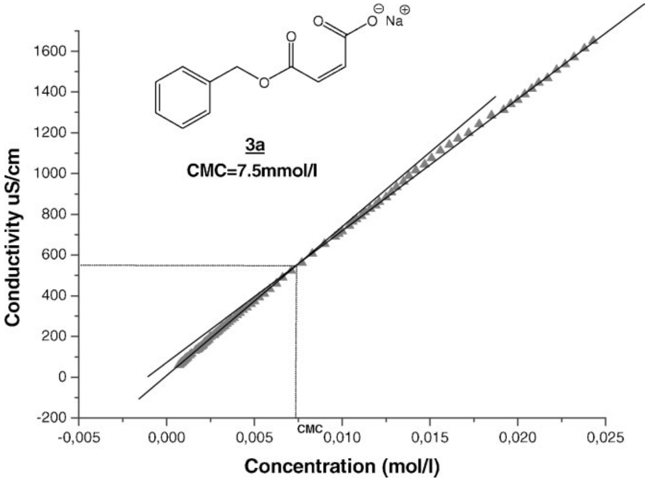


Figure 1.
Critical micelle concentration curve for surfmer 3a.

Table 2.
Results of batch polymerization.

Latex	Surfmer Concentration (mmol/l)	Solids %	D_p (nm)	PDI	Conversion (%)	$Np \times 10^{-11}$
1	3.39	5.09	660	0.013	69	2.18
2	9.70	5.25	464	0.047	77	7.00
3	24.27	5.64	345	0.103	60	13.23

N_p: Particle number in 50 ml, Dp: diameter, PDI: polydispersity index.

on particle size and solid content of the final latex was studied. Data are reported in Table 2.

One can see that the amount of surfmer introduced in the polymerization reaction has a pronounced effect on the process of emulsion polymerization styrene as well as the properties of the latexes. Increasing the surfmer concentration causes the decrease of particles diameters. In the case of low surfactant amount (3.37 mmol/l i.e. 0.07% w/w), particles with a diameter of 660 nm were obtained, whereas after surfmer concentration increase up to 24.27 mmol/l i.e. 0.5% w/w, the particles size of 345 nm were reached. The particle size distribution remained narrow all along the process (Table 2). The styrene conversion still however low (60–77%).

The particle number (Np) calculated from the hydrodynamic particle diameter (Dp), the polymerization conversion and the polystyrene density ($\rho = 1.05\,g/cm^3$) was observed to be higher for Latex 3 prepared with the highest surfmer quantity.

The polymerization rate was also dependent on the surfmer concentration. In fact, the increase in the amount of surfmer employed results in an increase of polymerization rate. This may be caused mainly by two reasons. First, increasing surfactant concentration leads to smaller particles but larger particle numbers and hence, to increase the rate of polymerization. Second, the increase in the reactive surfactant concentration may decrease the duration of nucleation period especially for surfactant concentration below the CMC value.

Conclusion

Novel maleic surfmers were synthesized and characterized using a simple synthetic pathway from maleic anhydride as starting material.

For cationic surfactants, an isomerization of maleic double bond was noted during the quaternization step which is strongly influenced by the reaction time.

It was shown that the use of one of the prepared anionic surfmer for emulsion polymerization of styrene allows obtaining stables latex particles with narrow size distributions without using other surfactants. The concentration of surfmer incorporated during polymerization allows controlling the particles sizes.

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