

ORIGINAL ARTICLE

Novel polymerizable surfactants: synthesis and application in the emulsion polymerization of styrene

Sofiane Mekki¹, Salima Saïdi-Besbes¹, Abdelhamid Elaïssari², Jean-Pierre Valour² and Aïcha Derdour¹

A series of anionic maleic surfactants were synthesized, and their chemical structures were characterized by NMR. The synthesized surfmers were then used in emulsion polymerization of styrene in the presence of potassium persulfate as an initiator. The polymerization kinetics were investigated, and the obtained latex particles were characterized in terms of particle size and size distribution. The results obtained were compared with the emulsion polymerization of styrene in the presence of an SDS surfactant. The influences of the nature and concentration of surfmers on polymerization conversion and particle size in particular were investigated and discussed.

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INTRODUCTION

A significant number of studies have been undertaken on the polymerization of surfmers.^{1–3} These molecules present the advantage of combining the physical behavior of surfactants with the reactivity of monomers. The polymerizable moiety of these surfmers can be covalently anchored onto the surface of polymer particles, limiting their migration to the surface of latex coatings or desorption from the final particles.^{4,5} Thus, appreciable latex particles in terms of colloidal stability, size, size distribution, surface charge density and surface functionality can be produced.

These latexes are interesting in various fields such as paints,⁶ paper coatings, inks, textile sizing, adhesives, the preparation of surfactant-templated silicates,⁷ polymer nanocomposites^{8,9} and biomedical applications.¹⁰

A wide variety of surfmer structures that differ with respect to polar functional groups (that is, hydrophilic and lipophilic balance) and the location of the polymerizable moiety have been reported. Examples include anionic,¹¹ cationic,¹² zwitterionic¹³ and nonionic¹⁴ surfactants. The conventional polymerizable groups that have been used include styrene,¹¹ acrylic,¹⁵ methacrylic¹⁶ and acrylamides.¹⁷

It has been established that for a surfmer to work well in the emulsion polymerization process, it must have limited solubility in water, moderate reactivity at the beginning of the process of polymerization to avoid burring the inner polymer particles and substantial reactivity at the end of polymerization so as to be anchored onto particle surfaces.¹⁸

Among the described structures, maleic surfactants are the most promising because they are easy to prepare and do not enter homo-

polymerization.¹⁹ The formation of polyelectrolytes in the water phase is thus avoided.

In this study, the synthesis of new maleic anionic surfmers containing different hydrophobic chain lengths is described. They were used for the evaluation of radical emulsion polymerization of styrene in the presence of potassium persulfate (KPS) as an initiator. Special attention was focused on the effects of surfmer concentration on the polymerization process and final particle size, size distribution and polymerization conversion.

EXPERIMENTAL PROCEDURE

Methods

¹H and ¹³C-NMR spectra were recorded on a Bruker 300 MHz spectrometer (Bruker, Wissembourg, France). Tetramethylsilane was used as an internal reference for chemical shifts. Infrared spectroscopy was carried out with a Jasco-4200 Fourier transform infrared spectrometer (Jasco, Tokyo, Japan).

Melting points were determined with a Kofler bench apparatus from Leica VM HB (Leica, Wien, Austria; temperature range: 50–264 °C).

Flash chromatography was 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 precoated with Merck silica gel 60F254 and visualized by means of ultraviolet fluorescence quenching or iodine vapor.

Materials

The solvents were dried and distilled before use. The following reagents were purchased from Aldrich (Taufkirchen, Germany) and used without further purification: benzyl alcohol, SDS, KPS and maleic anhydride. 4-phenyl-1-butanol and 7-phenyl-1-heptanol were purchased from Lancaster (Karlsruhe, Germany). Benzyl maleate (C1M) was prepared as described in our previous

¹Laboratoire de Synthèse Organique Appliquée, Département de Chimie, Université d'Oran Es-Senia, Oran, Algeria and ²Laboratoire d'Automatique et de Génie des Procédés, CNRS, UMR 5007, Université Lyon 1, Villeurbanne, France

Correspondence: Dr S Saïdi-Besbes, Laboratoire de Synthèse Organique Appliquée, Département de Chimie, Oran Es-Senia University, Bp 1412 El M'Naouer, Oran 31000, Algeria.

E-mail: salima_saïdi@yahoo.fr

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study.²⁰ Styrene was washed (to remove inhibitors) with an aqueous solution of 5 M NaOH and three times with deionized water and stored at -20°C . In all polymerization procedures, deionized water was used.

Synthesis of surfactant monomers

Synthesis of 4-phenylbutyl maleate (C4M). 4-phenylbutyl maleate (C4M) was obtained in a manner similar to that used for benzyl maleate (C1M), as described in reference,²⁰ in the form of oil. It was purified by silica gel chromatography using CH_2Cl_2 and then EtOH as eluants, yielding 74% maleate hemiester. $R_f=0.65$ ($\text{CH}_2\text{Cl}_2/\text{EtOH}$: 11/5).

^1H NMR (300 MHz, CDCl_3 , δ , p.p.m.): 1.76 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 2.68 (t, 2H, $\text{C}_6\text{H}_5\text{CH}_2-$, $^3J=6.9$ Hz), 4.3 (t, 2H, $-\text{CH}_2\text{CH}_2\text{O}-$, $^3J=6.2$ Hz), 6.41 (dd, 2H, $-\text{CH}=\text{CH}-$, $^3J_{\text{cis}}=12.6$ Hz), 7.19–7.33 (m, 5H, C_6H_5), 9.5 (s, 1H, COOH). (Underlining denotes the corresponding proton.)

^{13}C NMR (400 MHz, CDCl_3 , δ , p.p.m.): 27.48 ($\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$), 27.75 ($\text{C}_6\text{H}_5(\text{CH}_2)_2\text{CH}_2$), 35.29 ($\text{C}_6\text{H}_5\text{CH}_2$), 66.85 (CH_2O), 125.99 (1C, C_6H_5), 128.38 (1C, C_6H_5), 128.43 (1C, C_6H_5), 129.73 (2C, C_6H_5), 135.47 (CHCOOH), 135.52 ($\text{CH}=\text{CHCOOH}$), 141.63 (1C, C_6H_5), 165.37 ($\text{C}=\text{O}$), 167.56 (COOH).

Infrared (KBr, ν , cm^{-1}): 3060 ($\nu_{\text{O-H}}$), 1633 ($\nu_{\text{C}=\text{O}}$), 1729 ($\nu_{\text{C}=\text{O}}$), 1257 ($\nu_{\text{C-O}}$).

Synthesis of 7-phenylheptyl maleate (C7M). 7-phenylheptyl maleate (C7M) surfmer was obtained in a manner similar to that used for C1M and was purified by chromatography using CH_2Cl_2 and then EtOH as eluants. The corresponding maleate hemiester was obtained as a clear oil (70%).

^1H NMR (300 MHz, CDCl_3 , δ , p.p.m.): 1.35 (m, 6H, $\text{CH}_2(\text{CH}_2)_3\text{CH}_2-$), 2.6 (m, 2H, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2-$), 1.6 (m, 4H, $\text{CH}_2(\text{CH}_2)_3\text{CH}_2-$), 4.23 (m, 2H, $-\text{CH}_2\text{CH}_2\text{O}-$), 6.34 (s, 2H, $-\text{CH}=\text{CH}-$), 7.17–7.26 (m, 5H, C_6H_5), 9.1 (s, 1H, COOH).

^{13}C NMR (300 MHz, CDCl_3 , δ , p.p.m.): 27.65 ($\text{C}_6\text{H}_5(\text{CH}_2)_4\text{CH}_2$), 29.01 ($\text{C}_6\text{H}_5(\text{CH}_2)_2\text{CH}_2$), 29.07 (CH_2), 31.35 (CH_2), 33.15 ($\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$), 35.88 ($\text{C}_6\text{H}_5\text{CH}_2$), 66.61 (CH_2O), 125.62 (1C, C_6H_5), 128.24 (1C, C_6H_5), 128.37 (1C, C_6H_5), 130.10 (2C, C_6H_5), 135.40 (CHCOOH), 136.52 ($\text{CH}=\text{CHCOOH}$), 141.7 (1C, C_6H_5), 166.34 ($\text{C}=\text{O}$), 167.01 (COOH).

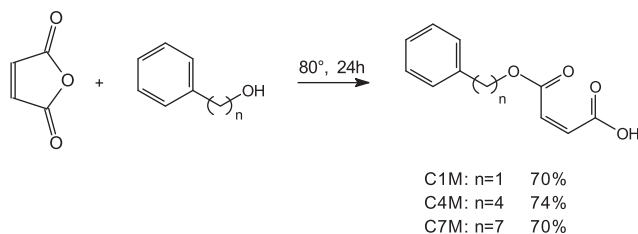
Emulsion polymerization. Emulsion polymerization of styrene was performed at 70°C in a batch reactor at a constant stirring rotation. The reactor was charged with water (50 g), styrene (2.5 g) and surfactant (0.25 g of C1M and 0.07 g of sodium hydroxide) and then stirred for 15 min. Polymerization was initiated by introducing 500 μl of a KPS solution (0.83 g of KPS dissolved in 10 ml water). The polymerization reaction was allowed to proceed for 12 h. Polymerization conversions were determined gravimetrically and used to investigate the polymerization kinetics.

Particle characterization. The hydrodynamic particle size (D_p) and the polydispersity index characterizing the width of the particle size distribution of the latexes were obtained by quasi-elastic light scattering using a Zetasizer Nano-ZS apparatus from Malvern Instruments (Malvern, UK). The latex particles were highly diluted in deionized water, and the temperature was well controlled at 20°C during measurements.

RESULTS AND DISCUSSION

Synthesis of surfactants

Novel surface-active maleic monomer derivatives (CnM $n=1, 4$ and 7) with hydrophobic alkyl benzene fragments were prepared according to Scheme 1.



Scheme 1 Synthesis of CnM surfmers.

Only a one-step synthesis strategy was required to attach the polymerizable maleic compound to the hydrophobic part, which consists of the acylation of equimolar quantities of alcohols and dicarboxylic acid anhydride at 80°C for 24 h. Well-purified products were obtained after a recrystallization step or by silica gel chromatography as solids or viscous liquids, depending on the chemical nature and length of the spacer arm between the benzene ring and the maleic function. The chemical yields are in the range of 70–74%, as gravimetrically obtained.

The prepared surfmers can be easily dissolved in water after carboxylic group ionization using sodium hydroxide to obtain the corresponding anionic surfactants.

^1H -NMR and ^{13}C -NMR were used to characterize these surfmers and particularly to examine their isomeric purity. The ^1H -NMR spectrum of the C4M surfmer is presented in Figure 1. Only the resonance signal characteristic of the *cis*-isomer was observed at 6.34–6.41 p.p.m. (signal of the $\text{CH}=\text{CH}$ double bond of the maleate function), with a proton coupling constant of the hydrogen in the maleate moiety of $^3J=12.6$ Hz.

The critical micelle concentrations (CMCs) of C1M, C4M and C7M surfmers were determined by conductivity measurements at 25.5°C after neutralization with 1 equiv of NaOH and were found to be 7.5, 3.47 and 1.61 mmol l^{-1} , respectively. These CMCs are lower than that of the SDS surfactant (8.1 mmol l^{-1}) and show the expected trend to lower values as the length of the hydrocarbon tail increases (higher hydrophobicity).

Emulsion polymerization

Batch emulsion polymerizations of styrene were performed at 70°C in the presence of maleic surfactant solubilized in water as described above or with conventional surfactant SDS. KPS was chosen as a radical initiator. The concentration of surfactant in the reaction medium was varied from 1.2 to 24.27 mmol l^{-1} to investigate the influence of surfactant (concentration and nature) on particle size, size distribution and polymerization conversion. The data obtained are reported in Table 1.

One can see that the length of the alkyl spacer arm between the benzene moiety and the maleic function has a pronounced effect on the process of emulsion polymerization of styrene, as well as on the colloidal properties of the synthesized latexes. High conversion was reached when surfmer C7M, bearing a 7-phenylheptyl spacer arm, was used, whereas only 60 to 78% polymerization conversions were obtained when the surfmer C1M, with a shorter spacer (benzyl chain), was used.

The size of the final latex particles was also dependent on the nature of the surfactant. In fact, the increase in the hydrophobic chain length results in a decrease in particle diameters. For comparable concentrations, surfactant C7M leads to smaller particles with a diameter of 73 nm. In brief, the increase in the number of carbons in the surfmer chain enhances the surfactant properties. Consequently, C7M has more active surfactant properties, compared with C4M and C1M for comparable concentrations under the investigated polymerization conditions (lower CMC). The results obtained from the investigation of the effect of C1M on polymerization kinetics are not surprising. In fact, this small surfmer is closely identical in terms of its chemical structure to a classical functional comonomer. In this case, the influence of a small amount of C1M on the final particle size is almost negligible, which explains why C1M functions as a comonomer rather than as an active surfactant molecule.

The effect of C7M surfmer on the polymerization kinetics of styrene was investigated by gravimetry-based methods. The obtained results

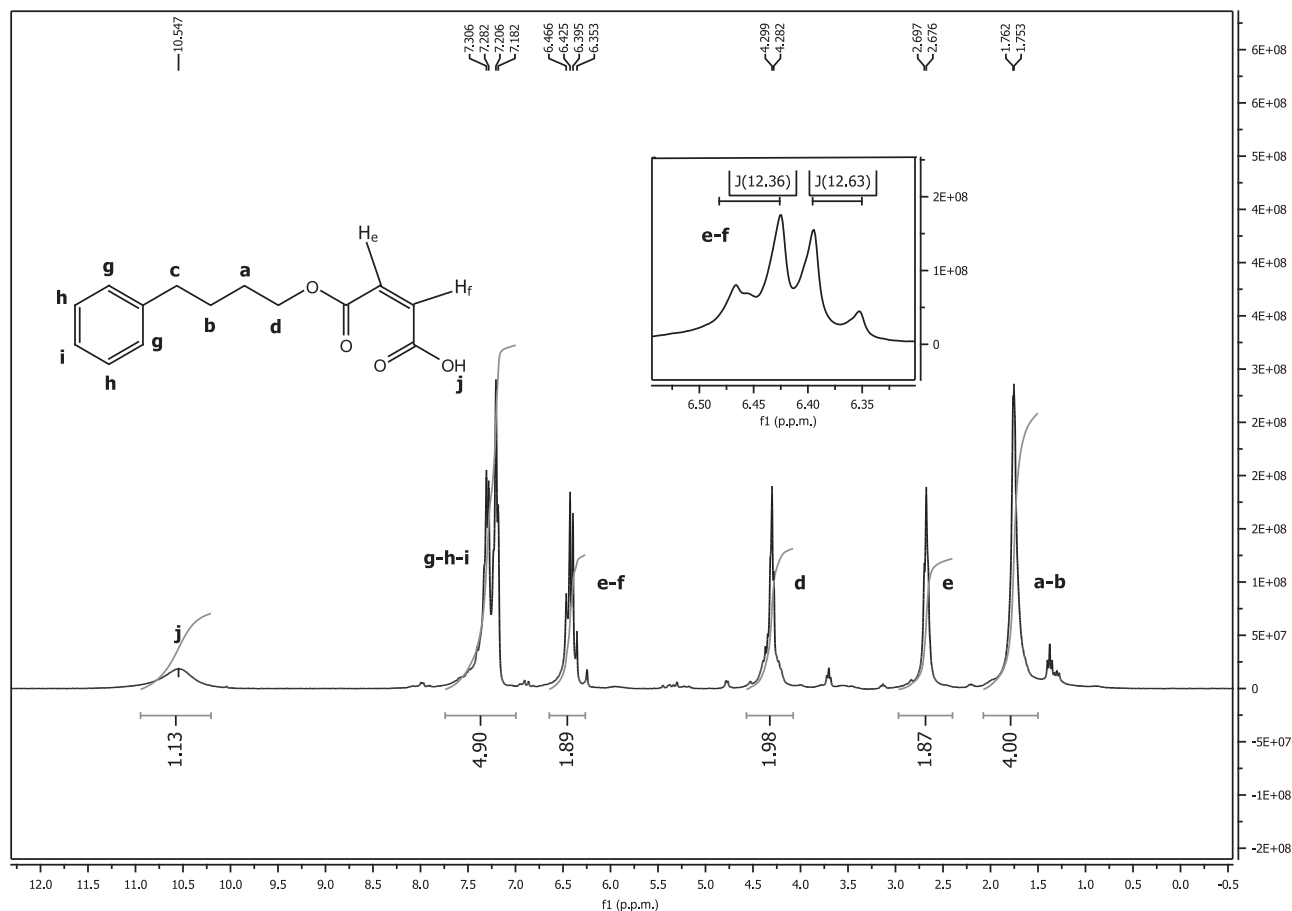


Figure 1 ^1H -NMR of surfmer C4M.

Table 1 The influence of each surfmer concentration on particle size, PDI and polymerization conversion of styrene in batch polymerization

Compound	Concentration (mol l^{-1})	Solids, %	D_p (nm)	PDI	Conversion (%C)	$N_p \times 10^{-11}$
C1M	0	5	776	0.273	78	1.51
	0.001213	5.03	692	0.055	83	2.28
	0.002427	5.06	—	—	74	—
	0.00339	5.09	660	0.013	69	2.18
	0.00485	5.13	627	0.224	70	2.57
	0.00728	5.14	596	0.056	64	2.75
	0.0097	5.25	464	0.047	77	7.00
	0.02427	5.64	345	0.103	60	13.23
	0.001213	5.03	470	0.063	89	7.78
C4M	0.002427	5.07	362	0.022	88	16.78
	0.00339	5.11	317	0.057	88	25.06
	0.00485	5.16	281	0.002	90	36.83
	0.00728	5.23	251	0.002	89	51.09
	0.0097	5.31	208	0.007	86	86.91
	0.001213	5.04	136	0.006	93	333.58
C7M	0.002427	5.09	113	0.004	97	605.26
	0.00339	5.12	107	0.002	96	709.50
	0.00485	5.17	97	0.005	97	958.55
	0.00728	5.27	90	0.008	92	1121.37
	0.0097	5.35	80	0.004	98	1688.31
	0.02427	5.89	73	0.098	96	2172.12

Abbreviations: D_p , diameter; N_p , particle number in 50ml; PDI, polydispersity index from Malvern Instrument (The PDI is a dimensionless quantity describing the width of the particle size).

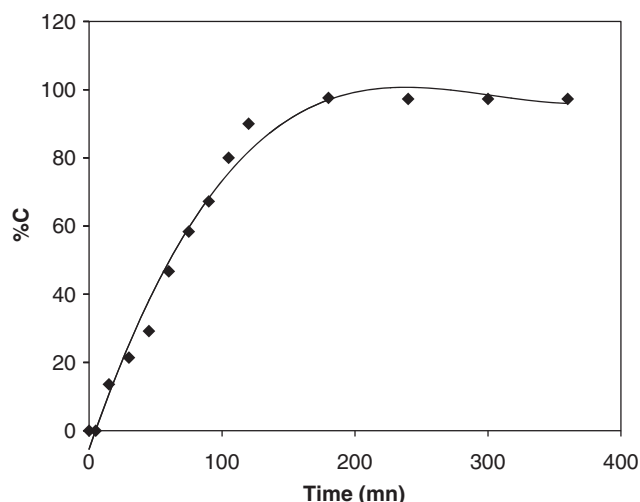


Figure 2 Polymerization conversion versus time for the C7M surfmer.

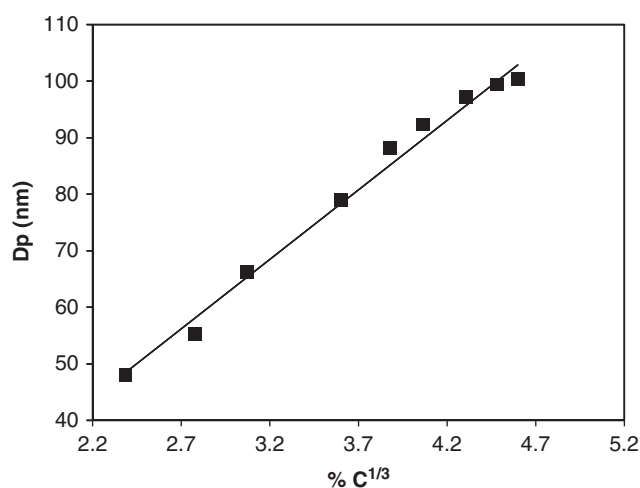


Figure 3 Variation of D_p vs $\% C^{1/3}$ (that is, $\sqrt[3]{\text{polymerization conversion}}$) for the C7M surfmer.

are reported in Figure 2, in which the polymerization conversion is plotted as a function of polymerization time. High polymerization conversion was obtained with limited amounts of aggregated particles (that is, coagulum). The particle size distribution remained narrow throughout the process, and the particle number (N_p) calculated from the hydrodynamic particle diameter (D_p) was observed to be constant above 29% polymerization conversion, as can be deduced from Figure 3, in which the hydrodynamic particle size (D_p) variation is plotted as a function of $\% C^{1/3}$ (that is, $\sqrt[3]{\text{polymerization conversion}}$). The particle number (N_p) is proportional to the slope of $C^{1/3}$ vs $\sqrt[3]{\text{polymerization conversion}}$.

The surfmer concentration in the polymerization process seems to have a small effect on the final styrene conversion, but the latex particle size decreased significantly when the surfmer concentration increased (Table 1). This can be attributed mainly to two reasons: (i) an increased anionic surfmer concentration leads to a high colloidal stability of polymer particles by means of adsorption phenomena; and (ii) an increase in the surfactant concentration reduces the duration of the nucleation period compared with the particle growth step.

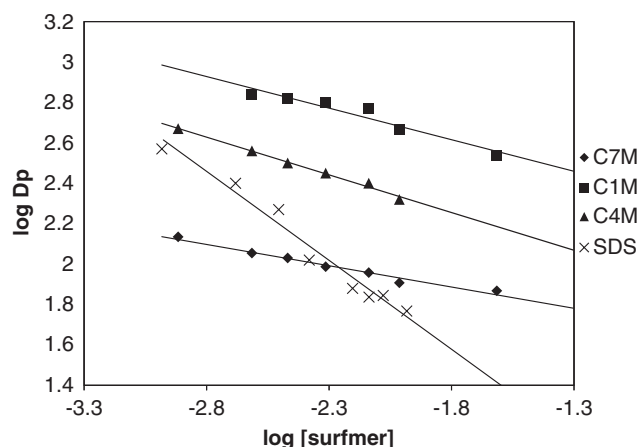


Figure 4 Log-log plot of particle size versus surfmer concentration in the polymerization medium.

In addition to the above reasons, the use of higher surfactant concentrations in the polymerization procedure induces a drastic increase in particle number N_p which can be directly attributed to an increase in the number of micelles and consequently an increase in the rate of nucleation.

The final latex particles have a narrow size distribution, irrespective of surfmer nature or concentration.

Figure 4 shows a log-log plot of the particle diameter (D_p) versus the surfactant concentration (surfmers or SDS) in the polymerization medium and reveals an almost linear relationship. Such a behavior implies a power law relation ($D_p \propto [\text{Surfactant}]^{-\alpha}$) between the particle size and the surfactant concentration in the polymerization recipe, and the obtained scaling laws are $D_p \propto [\text{C1M}]^{-0.31}$, $D_p \propto [\text{C4M}]^{-0.37}$, $D_p \propto [\text{C7M}]^{-0.21}$ and $D_p \propto [\text{SDS}]^{-0.87}$.

The number of particles can be expressed as a function of surfactant concentration by the equation ($N_p \propto [\text{surfactant}]^{\beta}$), in which the exponent $\beta = 3\alpha$. The exponent values obtained are 0.93, 1.11, 0.63 and 2.61 for C1M, C4M, C7M and SDS surfactants, respectively, and are found to be higher than the exponent expected (0.6) from Smith-Ewart's theory for hydrophobic monomers such as styrene. The exponents determined for C1M, C4M and C7M cannot be compared or discussed in comparison with the exponent $\alpha = 0.6$ for SDS, as SDS is not in a surfmer in nature.

The exponent β for the prepared surfmers can be considered to be in the same range, which may reflect an insignificant influence of the spacer arm on the emulsion polymerization of styrene. A larger value of β corresponds to a greater influence of the surfactant in terms of the polymerization reaction and particle number formation. Thus, the synthesized surfmers have a small effect on the radical emulsion polymerization of styrene, compared with SDS. Such behavior can be attributed to the ability of the prepared surfmers to enhance the colloidal stability of the formed immature particles during the growth period, as well as to the low reactivity of the polymerizable part.

CONCLUSIONS

Novel anionic maleic surfactants (that is, surfmers) were synthesized and chemically characterized by NMR. The purified surfmers were then used in batch emulsion polymerization of styrene in the presence of KPS as an initiator. It has been pointed out that the final particle size and particle size distribution of polystyrene can be controlled by

using a well-defined surfmer concentration in the polymerization reaction mixture.

The influence of the length of the hydrophobic moiety of the surfmer on the preparation of polystyrene particles was also investigated. As a general tendency, for the same molar concentrations of surfmers, the final polymerization conversions were found to increase with the increasing chain length of the hydrophobic alkyl part, whereas the average hydrodynamic particle size decreases with increasing hydrophobic chain length and surfmer concentration. It is interesting to note that the surfactants bearing the longest hydrophobic tail, that is, the 7-phenylheptyl spacer, allow for the formation of smaller particles with diameters between 73 and 136 nm with high polymerization conversion. Consequently, C1M and C4M function mainly as classical comonomers rather than as real surfactants.

- 1 Soula, O., Guyot, A., Williams, N., Grade, J. & Blease, T. Styrenic surfmer in emulsion copolymerization of acrylic monomers. II. Copolymerization and film properties. *J. Polym. Sci. Part A: Polym. Chem.* **37**, 4205–4217 (1999).
- 2 Mingyue, Z., Weihong, Q., Hongzhu, L. & Yingli, S. Synthesis of a novel polymerizable surfactant and its application in the emulsion polymerization of vinyl acetate, butyl acrylate, Veova 10, and hexafluorobutyl methacrylate. *J. Appl. Polym. Sci.* **107**, 624–628 (2008).
- 3 Summers, M. & Eastoe, J. Applications of polymerizable surfactants. *Adv. Colloid Interface Sci.* **100–102**, 137–152 (2003).
- 4 Schoonbrood, H. A. S. & Asua, J. M. Reactive surfactants in heterophase polymerization. 9. Optimum surfmer behaviour in emulsion polymerization. *Macromolecules* **30**, 6034–6041 (1997).
- 5 Guyot, A. Advances in reactive surfactants. *Adv. Colloid Interface Sci.* **108–109**, 3–22 (2004).
- 6 Aramendia, E., Barandiaran, M. J., Grade, J., Blease, T. & Asua, J. M. Polymerization of high solids content acrylic latexes using a non-ionic polymerizable surfactant. *J. Polym. Sci. Part A: Polym. Chem.* **40**, 1552–1559 (2002).
- 7 Khulashalani, D., Kuperman, A., Coombs, N. & Ozin, G. A. Mixed surfactant assemblies in the synthesis of mesoporous silicates. *Chem. Mater.* **8**, 2188–2193 (1996).
- 8 Smith, R. C., Fischer, W. M. & Gin, D. L. Ordered Poly(P-Phenylenevinylene) Matrix Nanocomposites via Lyotropic Liquid-Crystalline Monomers. *J. Am. Chem. Soc.* **119**, 4092–4093 (1997).
- 9 Pavel, F. M. & Mackay, R. A. Reverse micellar synthesis of a nanoparticle/polymer composite. *Langmuir* **16**, 8568–8574 (2000).
- 10 Herold, M., Brunner, H. & Tovar, G. E. M. Polymer nanoparticles with activated ester surface by using functional surfmer. *Macromol. Chem. Phys.* **204**, 770–778 (2003).
- 11 Wu, H., Kawaguchi, S. & Ito, K. Synthesis and polymerization of tail-type cationic polymerizable surfactants and hydrophobic counter-anion induced association of polyelectrolytes. *Colloid. Polym. Sci.* **282**, 1365–1373 (2004).
- 12 Guyot, A., Graillat, C. & Favero, C. Anionic surfmers in mini-emulsion polymerization. *C. R. Chimie.* **6**, 1319–1327 (2003).
- 13 Abele, S., Gauthier, C., Graillat, C. & Guyot, A. Films from styrene-butyl acrylate lattices using maleic or succinic surfactants: mechanical properties, water rebound and grafting of the surfactants. *Polymer* **41**, 1147–1155 (2000).
- 14 Uzulina, I., Zicmanis, A., Graillat, C., Claverie, J. & Guyot, A. Nonionic maleic surfmers. *J. Dispersion. Sci. Tech.* **23**, 799–808 (2002).
- 15 Morizur, J. F., Irvine, D. J., Rawlins, J. J. & Mathias, L. J. Synthesis of new acrylate-based nonionic surfmers and their use in heterophase polymerization. *Macromolecules* **40**, 8938–8946 (2007).
- 16 Cao, N., Wang, X., Song, L. Y. & Zhang, Z. C. Nanopore microspheres prepared by a cationic surfmer in the miniemulsion polymerization of styrene. *J. Polym. Sci. Part A: Polym. Chem.* **45**, 5800–5810 (2007).
- 17 Baumgartner, E., Besecke, S., Gänzler, W., Schröder, G., Siol, W. & Sutterlin, N. (1984) (West German Offenlegungsschrift (Laid-Open Patent Application) No. DE 3239527, laid open on 26 April 1984).
- 18 Asua, J. M. & Schoonbrood, H. A. S. Reactive surfactants in heterophase polymerization. *Acta. Polym.* **49**, 671–686 (1998).
- 19 Unuzé, M. J., Schoonbrood, H. A. S., Asua, J. M., Montoya-Gon, A., Sherrington, D. C., Stähler, K., Goebel, K.-H., Tauer, K., Sjöberg, M. & Holmberg, K. Reactive surfactants in heterophase polymerization. VI. Synthesis and screening of polymerizable surfactants (surfmers) with varying reactivity in high solids styrene–butyl acrylate–acrylic acid emulsion polymerization. *J. Appl. Polym. Sci.* **66**, 1803–1820 (1997).
- 20 Mekki, S., Saïdi-Besbes, S., Elaissari, A., Valour, J.-P. & Derdour, A. Synthesis of new anionic and cationic polymerizable surfactants for emulsion polymerization of styrene. *Macromol. Symp.* (submitted 2009).